

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

Transfer Reactions Involving Boron. IV. Dihydroboration of Acetylenes. Proposed Product Formation Involving Participation by Neighboring Boron during Hydrolysis<sup>1</sup>

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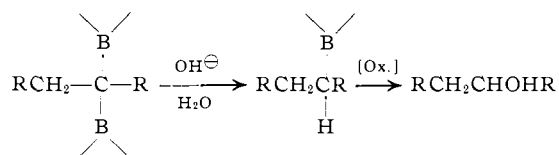
Several mechanisms have been proposed in the literature to explain the formation of the many products formed in the dihydroboration of acetylenes followed by basic hydrolysis and peroxide oxidation. Deuterium labeling studies have now shown that many of the previously suggested mechanisms are not operative and that the vicinal diboro derivative is the precursor for monoalcohol, glycol, and olefinic products. The deuterium studies indicate that the original vicinal diboro derivative undergoes an exceedingly rapid base-catalyzed hydrolysis indicating participation by the neighboring boron during the hydrolysis step. The proposed bridged boron anion may undergo deuterolysis to give a monoboro derivative, which on oxidation gives a  $\beta$ -deuterioalcohol or elimination to give olefin in certain cases. Carbon-carbon bond cleavage has also been observed in substantial yield. The mechanisms operative in the formation of the products appear to be dependent on the state of oxidation of the boron atoms involved and on the solvent system employed. Analysis of the present results shows that in many cases of dihydroboration of acetylenes with diborane the vicinal derivative may be formed in excess of the geminal derivative.

## Introduction

The dihydroboration of acetylenes, followed by basic hydrolysis and peroxide oxidation, has been reported by several authors to yield a mixture of products.

Logan and Flautt<sup>2</sup> isolated 2,2,5,5-tetramethyl-3-hexanol and 2,2,5,5-tetramethyl-3,4-hexanediol from the dihydroboration of di-*t*-butylacetylene. These authors rationalized the formation of the monoalcohol as possibly occurring by reduction of the corresponding carbonyl compound, formed by hydrolysis and oxidation, by some reducing species (B-H) present in the mixture.

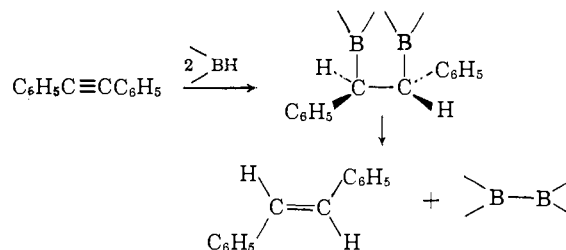
Brown and Zweifel<sup>3</sup> have isolated hexanal, 1-hexanol, and 1,2-hexanediol from the dihydroboration of 1-hexyne and 3-hexanone, 3-hexanol and 3,4-hexanediol from 3-hexyne. From evidence gathered from the dihydroboration of 1-hexyne, Brown visualized the formation of the monoalcohol as occurring *via* a base-catalyzed hydrolysis of a geminal diboro derivative to a monoboro derivative followed by oxidation as



This appeared to be a seemingly reasonable explanation.

Hassner and Braun<sup>4</sup> recently isolated *trans*-stilbene along with deoxybenzoin, 1,2-diphenylethanol, and *dl*-hydrobenzoin from the dihydroboration of diphenylacetylene. The formation of *trans*-stilbene was postulated as occurring by the elimination of a boron-boron bonded species from the vicinal diboro derivative as illustrated below.<sup>5</sup> Such an elimination did not seem

reasonable in view of the known chemistry of  $\beta$ -substituted organoboranes derived by hydroboration of



substituted olefins in other laboratories<sup>3</sup> and from results obtained in these laboratories.<sup>1,6</sup> It had been suggested that instability would occur in  $\beta$ -substituted organoboranes,<sup>1</sup> leading to either elimination or transfer reactions, only if the  $\beta$ -heteroatom possessed a pair of nonbonded electrons capable of complexing with boron to initiate the reaction relieving the instability, and if the stereochemistry was such as to allow intramolecular complexing to occur. In this particular case the  $\beta$ -boron has no nonbonded pair of electrons and would have been expected to be stable with respect to elimination. In addition, the reverse of this postulated elimination reaction is known to occur. The addition of diboron tetrachloride and tetrafluoride to olefins to give 1,2-diboro derivatives has been reported.<sup>7</sup> Tetramethyldiboron does not undergo such addition reactions, but it is doubtful that complete reversal of reactions would occur to lead to elimination when alkyl groups are bonded to the vicinal boron atoms.

Hassner and Braun<sup>4</sup> also suggested a possible mechanism for the formation of the monoalcohol *via* hydroboration of a postulated intermediate II in the scheme illustrated below. Brown<sup>3</sup> has previously suggested the possibility of formation of intermediates similar to II by an intermolecular hydroboration of I.<sup>8</sup>

depending on the rate of mixing reactants and the concentrations. In such cases a simple bond from boron will represent a bond to some group of unknown structure.

(6) D. J. Pasto and J. L. Miesel, *J. Am. Chem. Soc.*, **84**, 4991 (1962).

(7) (a) G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *ibid.*, **76**, 5299 (1954); (b) P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 6368 (1959); (c) W. B. Fox and T. Wartik, *ibid.*, **83**, 498 (1961).

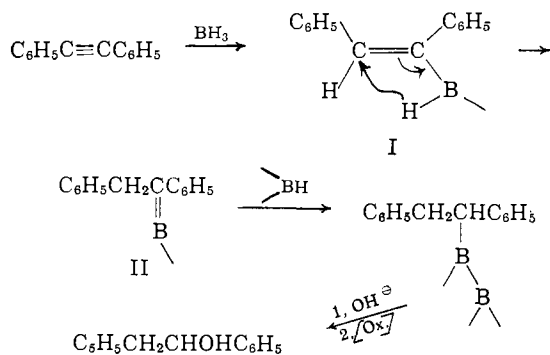
(1) Part III: D. J. Pasto and J. L. Miesel, *J. Am. Chem. Soc.*, **85**, 2118 (1963). Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) T. J. Logan and T. J. Flautt, *ibid.*, **82**, 3446 (1960).

(3) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961). See also H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(4) A. Hassner and B. H. Braun, *J. Org. Chem.*, **28**, 261 (1963).

(5) In this article >BH will represent any species having a boron-hydrogen bond capable of adding to an unsaturated site. In the case of addition of borane to acetylenes a highly branched polymeric addition product is formed<sup>3</sup> and the structure of the organic residues bonded to boron during the intermediate stages, and in the final product, is not known. The structure of this intermediate polymeric organoborane would be expected to vary



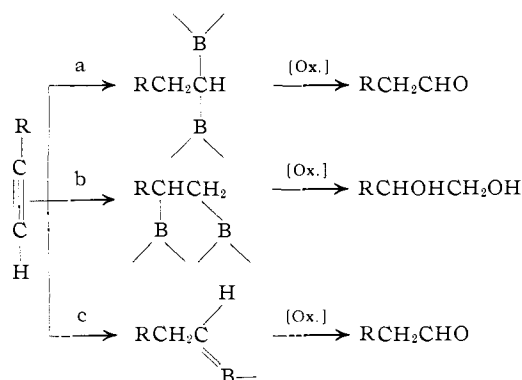
In view of the many different mechanisms proposed for the formation of the various products formed, it seemed that a careful mechanistic study of the formation of products in the dihydroboration of acetylenes followed by basic hydrolysis and oxidation was in order. The following describes the results obtained by the use of deuterium labeling and careful product analysis.

### Results

**Diphenylacetylene.**—The products formed from the dihydroboration of diphenylacetylene in diglyme, 3:2 mole ratio of acetylene:borane followed by basic deuteration and peroxide oxidation, were separated by careful column chromatography giving *cis*-stilbene, *trans*-stilbene, bibenzyl, deoxybenzoin, 1,2-diphenylethanol, and *dl*-hydrobenzoin. The yields are presented in Table I. The gas evolved during deuteration was analyzed by mass spectroscopy and shown to contain  $D_2$  in an amount roughly equal to the yield of olefin. Correction for the amount of  $D_2$  formed indicated that 1.90 hydrides were utilized per acetylene (see later discussion). The olefin fraction contained no deuterium by infrared and combustion analysis.

The 1,2-diphenylethanol contained deuterium in both the 1- and 2-positions as determined by integration of the proton magnetic resonance spectrum employing the hydroxyl proton as an internal standard (see Experimental for explanation of the methods used). The relative amounts of deuterium incorporated in the 1- and 2-positions varied with the length of deuteration time employed. These values are presented in Table II. The change in the amount of deuterium labeling in the 1,2-diphenylethanol is due to an increase in the yield of the 2-deuterioalcohol and not due primarily to

(8) Brown<sup>8</sup> has suggested that dihydroboration of an acetylene could reasonably take three paths as illustrated. To the present time, however, there is no definitive proof that a sequence *via* path c actually occurs. The



above scheme should be expanded to include an additional path to the geminal diboro derivative  $RC(B<)_2CH_3$ .

a decrease in yield of the 1-deuterioalcohol although both alcohols decrease slowly with the formation of bibenzyl (see Discussion).

It was not possible to determine directly the stereochemistry of the 2-deuterio-1,2-diphenylethanol as the infrared<sup>9</sup> and proton magnetic resonance spectra of the *dl-erythro* and *dl-threo* forms were not sufficiently different to allow an analysis of the mixture in the presence of some 1-deuterio-1,2-diphenylethanol. The stereochemistry of the 2-deuterio-1,2-diphenylethanol could, however, be inferred from the stereochemistry of the deuterated bibenzyl formed. Ozonolysis in tetrachloroethane at  $-70^\circ$  followed by formic acid-hydrogen peroxide oxidation<sup>10</sup> gave the corresponding deuterated succinic acids. Analysis of the deuterated succinic acid mixture by infrared spectroscopy<sup>11</sup> showed the presence of only a small amount of *meso*-dideuterio-succinic acid (approximately 5%) along with the 1,1- and *dl*-dideuteriosuccinic acids. As the base-catalyzed hydrolysis of a monoboro derivative in a related system has been shown to proceed with retention,<sup>12</sup> the stereochemistry of the 2-deuterio-1,2-diphenylethanol must have been predominantly *dl-threo*.

Dihydroboration of diphenylacetylene in tetrahydrofuran produced an insoluble precipitate, with the utilization of only 1.59 hydrides per acetylene. Deuteration and oxidation produced a product mixture which contained very low yields of olefin and higher yields of deoxybenzoin and *dl*-hydrobenzoin (see Table I). The 1,2-diphenylethanol fraction contained 0.43

TABLE I  
DIHYDROBORATION OF DIPHENYLACETYLENE

	Diglyme			Tetrahydrofuran
	2 min.	14 hr.	7 days	15 min.
Stilbene <sup>b</sup>	15%	17%	11%	2.8%
Bibenzyl	Trace	6	26	..
1,2-Diphenylethanol	14	11	5	11
Deoxybenzoin	12	13	24	37
<i>dl</i> -Hydrobenzoin	.. <sup>c</sup>	18	15	31
Hydrides utilized	1.90	..	..	1.59

<sup>a</sup> The time elapsed from the addition of a 25% excess of sodium deuteroxide in deuterium oxide to the addition of hydrogen peroxide. <sup>b</sup> The stilbene fraction contained approximately 2-3% of the *cis* isomer (yield 0.4%). <sup>c</sup> Not determined.

deuterium atom at carbon 1 and 0.55 deuterium atom at carbon 2. Mass spectral analysis of the gas evolved during deuteration showed the presence of only a small amount of  $D_2$ . Gas-liquid chromatographic analysis of the crude product showed the presence of small amounts of benzaldehyde and benzyl alcohol.

TABLE II  
DEUTERIUM INCORPORATION IN 1,2-DIPHENYLETHANOL IN DIGLYME

Length of deuteration time	$C_6H_5CH_2CDOHC_6H_5$	$C_6H_5CHDCHOHC_6H_5$
	%	%
2 min.	60 ± 3	35 ± 4
2 hr.	44 ± 2	57 ± 4
14 hr.	37 ± 4	60 ± 1

**Phenylacetylene.**—Dihydroboration of phenylacetylene in diglyme produced the products shown in Table

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

(10) E. J. Corey, D. J. Pasto, and W. L. Mock, *ibid.*, **83**, 2937 (1961).

(11) C. R. Childs and K. Bloch, *J. Org. Chem.*, **26**, 1630 (1961).

(12) A. J. Weinheimer and W. E. Marsico, *ibid.*, **27**, 1926 (1962).

TABLE III  
 DIHYDROBORATION OF PHENYLACETYLENE

Ratio acetylene: BH <sub>3</sub>	Diglyme	—Tetrahydrofuran—	
Benzaldehyde	4.4%	1.7%	3.1%
Benzyl alcohol	1.9	1.1	2.4
Acetophenone plus phenylacetaldehyde	4.6	2.9	5.8
1-Phenylethanol	11	10	10
2-Phenylethanol	29	39	36
Phenylethanediol	15 <sup>a</sup>	21	18
Styrene	12	0.7	..
Hydrides utilized	1.95	1.85	..

<sup>a</sup> Value is only approximate as the solvent interfered with the accurate determination of yield.

III. No styrene could be detected *before* deuterolysis by gas-liquid chromatography.

The gas evolved during deuterolysis (12% based on acetylene used) when diglyme was used as solvent contained approximately 60% D<sub>2</sub> indicating 1.95 hydrides were utilized per acetylene. However, when tetrahydrofuran was used as solvent, only a trace of D<sub>2</sub> was found in the deuterolysis gas with 1.93 hydrides utilized per acetylene.

The position of deuterium labeling in the 1- and 2-phenylethanols is given in Table IV.

 TABLE IV  
 DEUTERIUM INCORPORATION IN 1- AND 2-PHENYLETHANOL

Solvent	Length of deuterolysis time	—2-Phenylethanol—	
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHD-OH, %	C <sub>6</sub> H <sub>5</sub> CHD-CH <sub>2</sub> OH, %
Diglyme	15 sec.	66 ± 2	29 ± 4
Diglyme	2 min.	70 ± 2	29 ± 2
Diglyme	5 min.	70 ± 2	28 ± 2
Tetrahydrofuran	5 min.	85 ± 2	17 ± 1
		—1-Phenylethanol—	
		C <sub>6</sub> H <sub>5</sub> CD <sub>2</sub> OH-CH <sub>3</sub> , %	C <sub>6</sub> H <sub>5</sub> CHOH-CH <sub>2</sub> D, %
Diglyme	15 sec.	42 ± 1	58 ± 3
Diglyme	2 min.	45 ± 2	55 ± 2
Diglyme	5 min.	36 ± 1	62 ± 3
Tetrahydrofuran	5 min.	8	92 ± 4

**1-Hexyne.**—The dihydroboration of 1-hexyne in diglyme followed by hydrolysis and oxidation resulted in the formation of the products shown in Table V.

 TABLE V  
 DIHYDROBORATION OF 1-HEXYNE

	—Solvent—	
	Diglyme	Tetrahydrofuran
1-Pentanol	1.0%	2.0%
Hexanal	5.7	6.4
1-Hexanol	59	50
2-Hexanol	4.3	1.8
1,2-Hexanediol	6.3	15
Hydrides utilized	1.95	1.88

Deuterolysis of the hydroboration mixture, produced from a mole ratio of acetylene to diborane of 3:1, gave 0.10 mole of gas per mole of acetylene which contained 10% D<sub>2</sub> by mass analysis. Correction for the D<sub>2</sub> present indicated the utilization of 1.91 hydrides per acetylene. The 1- and 2-hexanols, isolated from the deuterolyzed mixture in a ratio 83:17 (65% total yield), contained 0.88 and 1.00 deuterium atom in position 1, respectively.

The dihydroboration of 1-hexyne in tetrahydrofuran resulted in the utilization of 1.88 hydrides per acetylene.

Only a trace of D<sub>2</sub> was formed during deuterolysis. The deuterium labeling in the 1- and 2-hexanol was the same as that observed above using diglyme as solvent.

**3-Hexyne.**—Dihydroboration of 3-hexyne in diglyme, mole ratio of acetylene to diborane of 3:1, resulted in the utilization of 1.87 hydrides per acetylene. Mass analysis of the gases evolved during deuterolysis revealed the presence of D<sub>2</sub> (1.3% yield). A complete analysis of the products proved difficult due to interference from diglyme. The 3-hexanol (34%) contained 0.71 ± 0.02 hydrogen atom at carbon atom 3.

The dihydroboration of 3-hexyne in tetrahydrofuran resulted in the utilization of 1.74 hydrides per acetylene and produced 1-propanol (1.5%), 3-hexene (approximately 1%), 3-hexanone (43%), 3-hexanol (23%), and 3,4-hexanediol (11%). The gases evolved on deuterolysis contained a small amount of D<sub>2</sub> (1.5% based on 3-hexyne used). Integration of the n.m.r. spectrum of the 3-hexanol allowed determination of the deuterium content at carbon atom 3 (0.29 ± 0.02 deuterium atom) but determination of the deuterium at position 4 was not possible due to an apparent facile saturation. The 3-hexanol was oxidized to 3-hexanone, the n.m.r. spectrum of which showed 0.60 ± 0.04 deuterium atom at position 4.

### Discussion

**Monoalcohol and Olefin Formation.**—Several facts are readily apparent on inspection of the foregoing results. The olefin is not formed by the elimination of a boron-boron bonded species from a vicinal diboro derivative. The inability to detect olefin prior to deuterolysis and the detection of the *cis* isomer are not compatible with an elimination of a boron-boron bonded species. The stereochemistry of the intermediate vicinal diboro derivative, formed by two *cis* additions of BH to the carbon-carbon triple bond, would require the formation of only *trans*-olefin. The olefins are stable to isomerization under the work-up and separation procedure. The possibility for olefin formation by the hydrolysis of a vinyl carbon-boron bond is eliminated by the lack of deuterium incorporation in the olefin during deuterolysis.

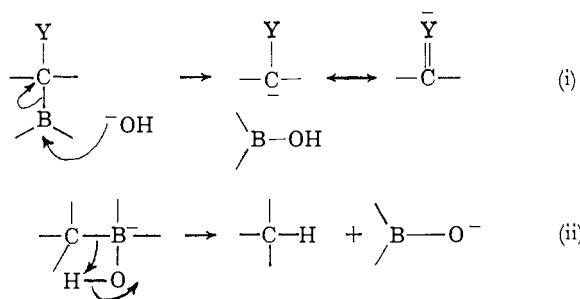
The monoalcohol is not formed (1) exclusively by hydrolysis of a geminal diboro derivative followed by oxidation, (2) by hydroboration of an intermediate having a carbon-boron double bond similar to structure II, or (3) by reduction of an intermediate carbonyl compound during work-up. The first is evidenced by the incorporation of deuterium in the 2-position of the monoalcohols. In fact, in many of the cases the monoalcohol is formed predominately by deuterolysis of a vicinal diboro derivative. Evidence against 2 and 3 above is provided by the incorporation of 1.00 ± 0.03 deuterium atom in the monoalcohols. The operation of either 2 or 3 would lead to a lesser amount of deuterium incorporation by the introduction of hydrogen at the 1-position of the alcohol, in 2 the hydrogen would originate from the diborane, and in 3 from a borohydride species formed during basic hydrolysis the hydrogen of which would also be derived from the diborane.<sup>13</sup>

(13) Exchange of hydrogen for deuterium during deuterolysis does not appreciably occur. In a control experiment *trans*-stilbene was hydroborated with an excess of diborane and then subjected to deuterolysis. The gas evolved showed the presence of only 2.5% D<sub>2</sub>. R. E. Davis (R. E. Davis, A. E. Brown, R. Hopmann, and C. L. Kibby, *J. Am. Chem. Soc.*, **85**, 487 (1963)) has observed the exchange of deuterium for hydrogen in trimethylaminoborane in acidic deuterium oxide.

These facts clearly demonstrate that the mechanisms previously suggested for the formation of the various products, except Brown's suggestion of the hydrolysis of a geminal diboro derivative which contributes in part to the over-all mechanism, are not operative.

Several other pertinent facts might be pointed out before plunging into a consideration of the possible mechanistic paths involved in the formation of the various products. First, the ratio of the yield of olefin to that of monoalcohol plus hydrocarbon remains relatively constant with a given substrate under varying deuterolytic conditions. This would indicate that perhaps a common intermediate is involved in the formation of olefin and monoalcohol. Secondly, the yield of deuterium gas formed during deuterolysis parallels the yield of olefin in all cases. Thirdly, the rate of incorporation of deuterium in the 2-position of the monoalcohols occurs at a rate comparable with the rate of incorporation of deuterium at the 1-position and these rates are faster than the deuterolysis of a monoboro derivative, to give hydrocarbon, by a factor of approximately  $10^3$  to  $10^4$ .

Two mechanisms have thus far been proposed for the base-catalyzed hydrolysis of a carbon-boron bond. The first mechanism (i) involves a nucleophilic attack by base on boron<sup>3</sup> extruding a carbanion. The ease of this reaction would depend on the subsequent stabilization of the carbanion. In the case of the geminal bisdialkylboro systems this reaction is very rapid as evidenced by the rapid formation of the 1-deuterated alcohols, the intermediate carbanion being stabilized by interaction with the vacant p-orbital of the adjacent boron atom. The second mechanism (ii) involves



a four-centered concerted transfer with retention of stereochemistry about carbon.<sup>12</sup> This reaction, in the systems involved in this study (1,2-diphenylethyl), occurs at an extremely slow rate. The rate of reaction *via* mechanism ii, as represented above, should be affected mainly by the inductive effects of the functional groups in the neighborhood of the boron-carbon bond.

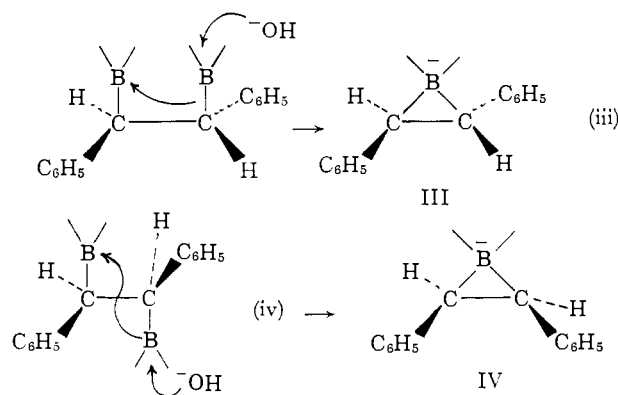
The observed rapid deuterolysis of one of the carbon-boron bonds of the vicinal diboro derivative is best explained as occurring *via* a reaction mechanism similar to i in which a carbanion is formed. An acceleration in the deuterolysis of the carbon-boron bond by a factor of approximately  $10^3$  to  $10^4$  over that for the deuterolysis of a 1,2-diphenylethyl boron derivative can hardly be explained on the basis of an inductive effect due to the neighboring boron in a mechanism similar to ii.

The enhanced rate of deuterolysis of one of the carbon-boron bonds of the vicinal diboro derivative can be explained by invoking a participation by the neighboring boron during carbanion formation. This type

of participation by an electron-deficient neighboring group with an electron-rich reaction center is electronically the exact opposite of neighboring group participation in the formation of carbonium ions.<sup>14</sup> In the latter the interaction is that of an electron-rich group with a developing positive charge, the electron-rich group approaching the back side of the developing carbonium ion from which the leaving group with its pair of electrons is departing.

The participation by a neighboring group in carbanion formation is a relatively unknown reaction. Zimmerman<sup>15</sup> has reported the interaction of an adjacent *p*-nitrophenyl group during carbanion formation with 1,1,1,2-tetra-*p*-nitrophenylethane. Owing to the limited amount of knowledge concerning such interactions,<sup>16</sup> the stereochemistries involved during the participation and in subsequent reactions of the anion are not known.

The vicinal diboro derivative formed by dihydroboration of diphenylacetylene may undergo anion formation by nucleophilic attack by base on boron in either of two ways. The first would involve an "electrophilic" type interaction in which the neighboring boron participates at the front side of the carbon at which the carbanion is being formed (retention). This is illustrated in mechanism iii. The alternative possibility is that a "nucleophilic" type of participation may occur in which the neighboring boron participates at the back side of the carbon at which the carbanion is being formed (inversion). This is illustrated in mechanism iv.



The mechanism, and thus the over-all stereochemistry, involved in the participation and ring-opening reactions of the bridged anions of type III and IV is not readily obvious. It should, however, be pointed out that mechanisms similar to i and ii, in which the reagent from which the proton is transferred coordinates with boron before the transfer, cannot be operative in III and IV in that the boron is already tetra-coordinate. Bridged ions formed in carbonium ion participations open with inversion by nucleophilic attack on carbon, but such systems are of little help

(14) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, Chapter 14, p. 561.

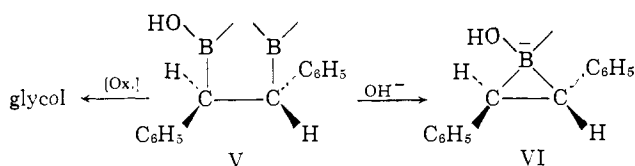
(15) H. Zimmerman, presented before the Organic Division at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1963.

(16) One might expect neighboring group participation to occur when the neighboring group possesses a vacant p-orbital, such as boron, aluminum, etc., and d-orbitals, such as sulfur, phosphorus, etc. Sulfur and phosphorus compounds are known to stabilize  $\alpha$ -carbanions and thus might be expected to stabilize a carbanion on a more distant carbon atom providing the stereochemistry is favorable for orbital overlap.



diate hydroboration product which may lead to products of differing stereochemistry. Additional work will be required to deduce clearly the stereochemistry involved in the participation during carbanion formation and in the subsequent deuterolysis and elimination steps.

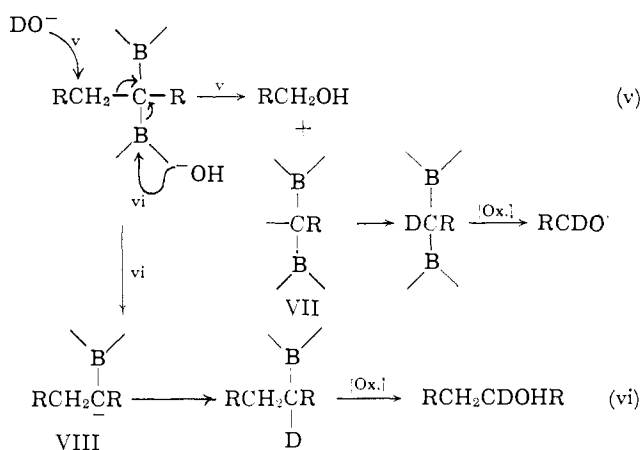
The isolation of substantial quantities of glycol indicates that a portion of the vicinal diboro derivative originally formed in the dihydroboration survives the hydrolysis step and is oxidized to the corresponding glycol. The dihydroboration product undoubtedly has a complex polymeric structure derived from a bifunctional organic molecule and the trifunctional borane.<sup>3</sup> Hydrolysis of one carbon-boron bond would produce a partial structure within the polymeric product which could be represented by V. The ability of a boron which is bonded to oxygen to participate during carbanion formation to give VI should be sub-



stantially reduced owing to interaction of the nonbonded electrons on oxygen with the vacant p-orbital on boron. Whether it requires one or two oxygens bonded to boron to completely inhibit participation cannot be clearly deduced.

1,2-Diboron derivatives have been prepared and briefly described in the literature.<sup>7</sup> Ethane-1,2-diboronic acid has been prepared and is reported to be stable to hydrolysis.<sup>7b</sup> 1,2-Bisdimethylboroethane was prepared and described as a relative unstable material unless carefully purified.<sup>7a,b</sup> Unfortunately no reference to any hydrolysis experiments with this compound was reported.

**Carbon-Carbon Bond Cleavage.**—The cleavage of carbon-carbon bonds during the hydroboration process, including the hydrolysis and oxidation steps, has not been observed previously. Control experiments have shown that the cleavage products are not derived from the glycol or the cyclic borate ester of the glycol. The alcohol which is formed is not formed by a Cannizzaro reaction involving the aldehyde. These facts indicate that the cleavage occurs while boron is still bonded to carbon. The incorporation of deuterium in the aldehyde indicates that the cleavage is occurring during the deuterolysis and oxidation steps. In order to derive an aldehyde on oxidation, the intermediate organoboron compound must have been a geminal diboro derivative. The base-catalyzed cleavage is believed to proceed by mechanism v in which base attacks the methylene group of a geminal diboro derivative with the formation of anion VII. It has already been pointed out that the 1-deuterated alcohols are formed by a base-catalyzed hydrolysis of a geminal diboro derivative *via* a carbanion VIII in mechanism vi. One must then question what are the factors influencing the operation of the two mechanisms v and vi. If the boron atoms of the geminal diboro derivative have undergone partial deuterolysis and oxidation and are bonded to oxygen, cleavage of the carbon-carbon bond with formation of anion VII, which should be more



stable than VIII if boron is bonded to oxygen due to stabilization by two boron atoms instead of one, should then be favored over deuterolysis *via* mechanism vi. The cleavage must occur in part during the oxidation with hydrogen peroxide resulting in the observed isotope dilution. During the oxidation process an increasing number of oxygen-boron bonds are being formed in the geminal diboro derivative thus increasing the probability for reaction *via* mechanism v.

Despite the apparent low yields in which the carbon-carbon bond cleavage products are formed, the yields are quite significant if one considers the amount of precursor geminal diboro derivative formed. Contrary to earlier belief,<sup>3</sup> the geminal diboro derivatives in most cases are actually formed in relatively low yields during the dihydroboration. If the original diboro derivatives are formed in low yields, the amount of diboro derivative with the boron atoms in an oxidation state required for the operation of mechanism v must be much lower and in fact the cleavage reaction may then be the preferred reaction path under these conditions. For example, in the dihydroboration of phenylacetylene the 1,1-substituted diboro-1-phenylethane is formed in about 10% yield with the cleavage product benzaldehyde in 4.4% and the 1,1-substituted diboro-2-phenylethane in 30% with the cleavage product benzyl alcohol in about 2%. Obviously other factors such as steric and added stabilizations by phenyl play an important role in these reactions.

**Formation of Carbonyl Compounds.**—It would appear that the carbonyl compounds are derived by oxidation of vinylboranes and to a lesser extent by oxidation of geminal diboro derivatives. The HD evolved during deuterolysis is formed by deuterolysis of unreacted B-H. In cases where the mole ratio of acetylene to diborane was 3:2, the HD formed would be a measure of the amount of vinylborane present and, in turn, a portion of the carbonyl compound expected. The yield of HD and carbonyl compounds are reasonably comparable. The amount of carbonyl compounds formed by oxidation of geminal diboro derivatives under these conditions would appear to be small.

### Conclusions

The dihydroboration of acetylenes gives rise to a complex mixture of products, the formation of which has been rationalized in the preceding section. The mechanisms proposed involve a participation by

neighboring boron in carbanion formation and a base-catalyzed carbon-carbon bond cleavage. The chemistry observed has revealed some new and interesting chemistry associated with geminal and vicinal diboro derivatives which will require a great deal of further study. However, owing to the complexity of the reaction mixtures described above, substantiation or revision of the proposed mechanisms must await the results of studies with monomeric geminal and vicinal diboro compounds. This work is under progress.

Analysis of the products and their mode of formation reveals that in most of the cases presently studied, except 1-hexyne, the vicinal diboro derivatives are formed in greater yields than the geminal derivatives. The results of such an analysis are presented in Table VI. The difference between the hydrides utilized per

TABLE VI  
COMPOSITION OF THE DIHYDROBORATED PRODUCT FROM  
ACETYLENES<sup>a</sup>

Acetylene	Product	Solvent	
		Diglyme	Tetrahydrofuran
Diphenylacetylene	Vicinal	67	49
	Geminal	18	6
	Mono	15	45
Phenylacetylene	Vicinal	56	42
	Geminal (terminal)	28	38
	(internal)	10	3
	Mono	6	17
1-Hexyne	Vicinal	25	30
	Geminal	69	62
	Mono	6	8
3-Hexyne	Vicinal	.. <sup>b</sup>	36
	Geminal	..	32
	Mono	..	32

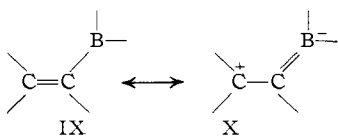
<sup>a</sup> Based on the products isolated and normalized to 100%.

<sup>b</sup> Reliable values cannot be calculated due to difficulties in obtaining accurate yield data (see Experimental).

acetylene and 2.00, the maximum possible value, was used as a measure of the monoboro derivative formed. The amounts of vicinal and geminal diboro derivatives were calculated using the isolated yields and deuterium distribution values. The values in Table VI have been normalized to 100%. Care should be exercised in the interpretation as to the mechanism of formation of products from the dihydroboration of other acetylenes.

The preference for the formation of vicinal over geminal diboro derivatives is rather surprising. The direction of addition of B-H to an unsaturated center is highly dependent on the steric environment and the electron distribution within the double bond with the electronic effect apparently more important.<sup>20</sup>

The electronic structure of vinylboranes may be represented by the resonance contribution forms IX and X. Evidence has been presented for such contri-



(20) For example, the hydroboration of 4-substituted styrenes leads to 9% addition to the  $\alpha$ -carbon when the substituent is methoxy and 35% when chlorine (H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960)). The hydroboration of 1-phenyl-1-phenylmercapto-1-propene proceeds by the preferential addition of boron to the 1-carbon (approximately 80-85%). In this case the inductive effects of the phenyl and phenylmer-

captions<sup>21</sup> based on oxidation with oxygen and boron 11 magnetic resonance spectra.<sup>22</sup> Contribution by structure X to the vinylborane would lead one to predict that hydroboration of a vinylborane would result in the formation of the geminal diboro derivative. The factors leading to the direction of addition with the vinylboranes in this investigation is not readily apparent, although it may in part be due to the complex polymeric nature of the intermediate hydroboration product.

### Experimental

Deuterium analyses were obtained by integration, electronic and manual integration of peak areas, of the proton magnetic resonance spectra. The hydroxyl proton was employed as an internal standard in the analysis of 1,2-diphenylethanol and 1- and 2-phenylethanol after first demonstrating the accuracy of the method with pure samples of the alcohols. The methyl protons were used as the internal standard for analysis of the hexanols. The values cited for deuterium content are the averages of several scans (3 to 5) of the same sample. The precision of the determinations is given as the standard deviation.

**Dihydroboration of Diphenylacetylene in Diglyme.**—Diphenylacetylene (0.0225 mole) in diglyme (50 ml.) was subjected to hydroboration at 0° with 0.0075 of diborane, generated *in situ* from stoichiometric amounts of sodium borohydride and boron trifluoride etherate, and allowed to stir at room temperature for 2 hr. The reaction mixture was cooled to 0° and subjected to deuterolysis with a 25% excess of sodium deuterioxide, based on the deuterolysis of all B-H and B-F bonds, in deuterium oxide for varying lengths of time. Measurement of the gases evolved during deuterolysis indicated that an average of 0.0051 mole of gas was evolved which on mass spectral analysis was shown to be approximately 55-60% D<sub>2</sub>. The hydrolyzed mixture was then oxidized by the addition of a 25% excess of 30% hydrogen peroxide. After stirring at room temperature for 0.5 hr. the mixture was poured into 300 ml. of water and extracted with three 100-ml. portions of ether. The extract was washed with water and saturated sodium chloride solution and finally dried over magnesium sulfate. The solvent was removed under reduced pressure giving 80-90% of a crude mixture.

Trituration of the crude mixture with petroleum ether produced a crystalline precipitate which was removed by filtration. Recrystallization from petroleum ether-benzene gave colorless needles, m.p. 98.5-99.0°. A mixture m.p. with authentic *dl*-hydrobenzoin, m.p. 98.5-99.0°, prepared from *meso*-dibromostilbene with silver acetate in wet acetic acid, was undepressed.<sup>23</sup>

The filtrate from above was evaporated and the residue was chromatographed<sup>4</sup> on Woelm Neutral Activity 1 alumina giving *cis*-stilbene (10.82 and 12.8  $\mu$  in carbon disulfide), traces of starting material (9.22 and 10.92  $\mu$  in carbon disulfide), bibenzyl, *trans*-stilbene, deoxybenzoin, and 1,2-diphenylethanol. The yields obtained after varying deuterolysis times are listed in Table I.

The stilbene fractions showed no C-D absorption in the infrared and gave 0.08 mole per cent deuterium on combustion analysis; theoretical for the presence of one deuterium, 8.3 mole per cent.

The bibenzyl displayed strong C-D absorption in the infrared at 4.6-4.7  $\mu$ . Conversion to the corresponding deuteriosuccinic acids<sup>10</sup> followed by infrared analysis<sup>11</sup> showed only a small amount of *meso*-dideuteriosuccinic acid (approximately 5%) present with unsymmetrical and *dl*-dideuteriosuccinic acid.

capto groups outweigh the steric effects. Similar observations have been made in the hydroboration of enol ethers in the presence of boron trifluoride (D. J. Pasto and C. C. Cumbo, manuscript in preparation).

(21) T. D. Parsons, M. B. Silverman, and D. M. Miller, *ibid.*, **79**, 5091 (1957).

(22) C. D. Good and D. M. Ritter, *ibid.*, **84**, 1162 (1962).

(23) The melting point recorded for *dl*-hydrobenzoin is 120°. Several attempts were made to obtain this value, the best being partial melting at 99-100° with the remainder melting at 118-122°. E. Ott (*Z. anorg. allgem. Chem.*, **188**, 49 (1930)) has recorded melting points of 95 and 103°. The solution infrared spectra of both samples were identical. The n.m.r. spectrum showed the sample to be pure *dl*-hydrobenzoin (CHOH- at -279 c.p.s. relative to tetramethylsilane in deuteriochloroform with *meso*-absorbing at -288 c.p.s. Authentic *dl*-hydrobenzoin was prepared as described by L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 188.

The 1,2-diphenylethanol displayed C-D stretching bands at 4.6 to 4.75  $\mu$ . The position and extent of deuterium labeling was determined by integration of the proton magnetic resonance spectrum. The results are listed in Table II.

#### Dihydroboration of Diphenylacetylene in Tetrahydrofuran.

A solution of 2.84 g. (0.016 mole) of diphenylacetylene in 10 ml. of tetrahydrofuran was added at 0° to 10 ml. of 1.07 M borane in tetrahydrofuran diluted to 25 ml. with tetrahydrofuran. A white precipitate formed after a short period of time. The reaction mixture was stirred for 12 hr. at room temperature. The mixture was deuterolyzed for 15 min. with a 50% excess of 30% sodium deuterioxide in deuterium oxide giving 0.00655 mole of gas. Mass spectrographic analysis showed only a trace of D<sub>2</sub>. The reaction mixture was cooled to 0° and oxidized by the addition of 30% hydrogen peroxide (50% excess). The oxidized mixture was allowed to come to room temperature and was stirred for 1 hr. The mixture was poured into 300 ml. of water and extracted with two 150-ml. portions of ether. The ether extract was washed twice with water and dried over magnesium sulfate. The solvent was removed under reduced pressure giving 2.95 g. of material which quickly crystallized.

The residue was triturated with petroleum ether and filtered giving 1.07 g. (31%) of *dl*-hydrobenzoin. The filtrate was evaporated and the residue chromatographed on Woelm Neutral Activity 1 alumina giving 0.08 g. of *trans*-stilbene (2.8%), 1.15 g. of deoxybenzoin (37%), and 0.35 g. of 1,2-diphenylethanol (11%).

Analysis of the 1,2-diphenylethanol by proton magnetic resonance showed 0.57 H at position 1 and 1.45 H at position 2.

**Dihydroboration of Phenylacetylene in Diglyme.**—A diglyme solution of phenylacetylene was subjected to hydroboration by the *in situ* generation of diborane from sodium borohydride and boron trifluoride etherate (ratio of 3 acetylenes to 1 diborane) and was allowed to stir at room temperature for 2 hr.

A portion of the hydroboration mixture, from one run, was removed and distilled under vacuum at room temperature into a flask immersed in a Dry Ice-acetone bath. Analysis of the distillate by gas-liquid chromatography on Carbowax 20-M showed no styrene present.

The hydroboration mixture was subjected to deuterolysis for varying lengths of time with a 25% excess of sodium deuterioxide in deuterium oxide giving an average of 0.11 mole of gas per mole of acetylene used (60% D<sub>2</sub>). The deuterolyzed mixture was then oxidized with a 25% excess of hydrogen peroxide and the crude product isolated as described for diphenylacetylene in diglyme.

A quantitative analysis of the mixture was carried out by gas-liquid chromatography on Carbowax 20-M at 160–180° by the addition of a known excess of 2-phenylethanol to an aliquot of the mixture. The weight ratio-area ratio of each component was determined with respect to 2-phenylethanol and the percentage yield of each component calculated. The yield of products were essentially independent of the length of deuterolysis time and are listed in Table III.

The 1- and 2-phenylethanols were collected by preparative gas-liquid chromatography and the position and extent of deuterium labeling determined by proton nuclear magnetic resonance integrations.

The benzaldehyde was similarly collected and analyzed by mass spectroscopy and shown to contain 23% of monodeuterated material. The benzyl alcohol could not be resolved sufficiently from the 1- and 2-phenylethanols under preparative conditions.

#### Dihydroboration of Phenylacetylene in Tetrahydrofuran.

A solution of 0.0321 mole of phenylacetylene in 10 ml. of tetrahydrofuran was added to 0.0214 mole of borane in 30 ml. of tetrahydrofuran at 0° and allowed to stir 12 hr. at room temperature. The mixture was cooled in an ice bath and a 25% excess of sodium deuterioxide in deuterium oxide was added producing 0.00468 mole of gas. Mass spectral analysis of the gases evolved showed only a trace of D<sub>2</sub>.

The deuterolyzed mixture was oxidized by the addition of a 25% excess of hydrogen peroxide and the crude product was isolated and analyzed as described above. The analysis of products is given in Table III.

**Dihydroboration of 1-Hexyne in Diglyme.**—1-Hexyne (0.060 mole) was subjected to hydroboration, *in situ* generation, with 0.020 mole of diborane and allowed to stand at room temperature for 14 hr. The reaction mixture was hydrolyzed with a 20% excess of sodium hydroxide giving 0.00115 mole of gas. Mass spectral analysis of the gases evolved after a similar hy-

droboration followed by deuterolysis showed it to contain 10% D<sub>2</sub>. Analysis of the crude product, after oxidation with a 20% excess of hydrogen peroxide and extraction as in above experiments, showed the presence of 1-hexene (approximately 1%), hexanal (6%), 2-hexanol (4.3%), 1-pentanol (1.0%), 1-hexanol (60%), and 1,2-hexanediol (6%).

The 1- and 2-hexanols (65% in a ratio of 83:17) isolated from a different deuterolysis experiment contained  $0.88 \pm 0.01$  and  $1.00 \pm 0.02$  deuterium atom at position 1, respectively.

**Dihydroboration of 1-Hexyne in Tetrahydrofuran.**—To a solution of 1.39 g. (0.017 mole) of 1-hexyne in 5 ml. of tetrahydrofuran was added 25 ml. of 0.64 M borane in tetrahydrofuran at 0°. The reaction mixture was stirred for 3 hr. at room temperature and deuterolyzed with 20% excess of sodium deuterioxide giving 0.00161 mole of gas which contained no D<sub>2</sub> on mass spectral analysis. The deuterolyzed mixture was oxidized with a 50% excess of hydrogen peroxide. The product was isolated by ether extraction of the crude reaction mixture and was analyzed by g.l.c. showing the presence of hexanal (6.4%), 1-pentanol (2.0%), 2-hexanol (1.8%), 1-hexanol (50%), and 1,2-hexanediol (15%). The 1-hexanol contained  $0.88 \pm 2$  deuterium atom at position 1. The 2-hexanol was not present in sufficient quantity for isolation.

**Dihydroboration of 3-Hexyne in Diglyme.**—3-Hexyne (0.0321 mole) was hydroborated, *in situ* generation, with 0.0107 mole of diborane in diglyme at 0°. Deuterolysis of the reaction mixture with a 20% excess of sodium deuterioxide in deuterium oxide produced 0.00462 mole of gas which contained 10% D<sub>2</sub>. The reaction mixture was oxidized with a 20% excess of hydrogen peroxide and the crude reaction mixture was extracted with ether. A complete analysis could not be accomplished due to interference by the diglyme. The 3-hexanol (34%) contained  $0.71 \pm 0.02$  hydrogen atom at position 3.

**Dihydroboration of 3-Hexyne in Tetrahydrofuran.**—A solution of 1.94 g. of 3-hexyne (0.0237 mole) in 5 ml. of tetrahydrofuran was slowly added to 25 ml. of 0.63 M borane (0.0158 mole) in tetrahydrofuran at 0°. The reaction mixture was stirred at 0° for 0.5 hr. and a 20% excess of sodium deuterioxide in deuterium oxide was added producing 0.0065 mole of gas. The deuterolyzed mixture was oxidized by the addition of 10% excess hydrogen peroxide. Potassium carbonate was added to saturate the aqueous phase. Ether (100 ml.) was added and the mixture shaken. The organic layer was analyzed directly by gas-liquid chromatography on a Carbowax column, using a weighed quantity of 1-hexanol as an internal standard and predetermined weight ratio-area ratio values, giving 1.5% 1-propanol, approximately 1% 3-hexene, 43% 3-hexanone, 23% 3-hexanol, and 11% 3,4-hexanediol.

The organic layer was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. The solvent was removed under reduced pressure and the 3-hexanol purified by preparative scale gas-liquid chromatography. Proton magnetic resonance analysis of the 3-hexanol gave the results: methyl (as internal standard), 6.00; methylene, 5.4 to 6.4 (the broad multiplet appeared to saturate readily); carbinol,  $0.71 \pm 0.02$ ; hydroxyl,  $0.99 \pm 0.01$  proton.

A 100-mg. portion of the 3-hexanol was dissolved in 10 ml. of acetone and 4 ml. of 30% sulfuric acid at 0°. Aqueous sodium dichromate solution was added, until an excess of oxidizing agent was present, and allowed to stand for 10 min. The reaction mixture was poured into 30 ml. of water and extracted with three 20-ml. portions of ether. The extract was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. The solvent was carefully removed and the 3-hexanone was purified by preparative scale gas-liquid chromatography. Integration of the proton magnetic resonance spectrum of the 3-hexanone gave the following proton analysis: methyl (as two overlapping triplets); 6.00;  $\beta$ -methylene,  $2.03 \pm 0.05$ ;  $\alpha$ -methylene,  $3.40 \pm 0.04$  protons.

**Control Reactions. A.**—A solution of 0.5 g. of phenylethanedol in 20 ml. of tetrahydrofuran and 5 ml. of water was stirred with 7 ml. of 30% aqueous sodium hydroxide and 10 ml. of 30% hydrogen peroxide for 3 hr. at room temperature. The mixture was poured into 300 ml. of water and extracted with two 100-ml. portions of ether. The extract was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure. The residue contained no benzaldehyde or benzyl alcohol when analyzed on a Carbowax 20-M column.

**B.**—A solution of 0.5 g. (0.0036 mole) of phenylethanedol



in 20 ml. of tetrahydrofuran was treated with 0.0040 mole of borane and allowed to stand for 15 min. at room temperature. The reaction mixture was worked up as described in A above giving no benzaldehyde or benzyl alcohol.

C.—A solution of 0.5 g. of benzaldehyde in 10 ml. of tetrahydrofuran was stirred for 1 hr. at room temperature with 5 ml. of 30% sodium hydroxide and 5 ml. of 30% hydrogen peroxide.

Isolation and analysis of the material as described in A above showed that no benzyl alcohol had been formed.

**Acknowledgment.**—The author wishes to acknowledge the aid of Mr. George Hennion, Jr., of the Radiation Laboratory of the University of Notre Dame, for the mass spectral analysis.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE, DURHAM, N. H., AND FROM THE GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

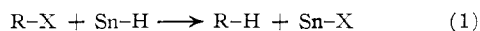
## Mechanism of Reduction of Alkyl Halides by Organotin Hydrides<sup>1,2</sup>

BY LAWRENCE W. MENAPACE AND HENRY G. KUIVILA<sup>3</sup>

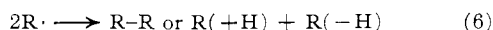
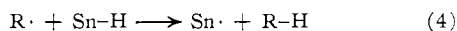
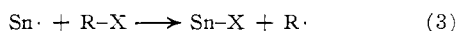
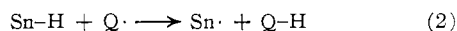
RECEIVED MARCH 18, 1964

Evidence is presented which leads to the conclusion that the reduction of alkyl halides by organotin hydrides proceeds by a free-radical mechanism. Pertinent observations are: (a) Optically active  $\alpha$ -phenylethyl chloride gives racemic  $\alpha$ -deuterioethylbenzene. (b) Allylic and propargylic halides give both rearranged and unrearranged reduction products. (c) The reaction is subject to retardation by hydroquinone. (d) Reactivities of halides follow a free-radical order. Reduction of  $\gamma$ -chlorobutyrophenone gives a mixture of butyrophenone and  $\alpha$ -phenyltetrahydrofuran.

Organotin hydrides have been found to be useful in the selective reduction of alkyl,<sup>2a,4-10</sup> cycloalkyl,<sup>2a,7,9,10</sup> acyl,<sup>5,11,12</sup> and aryl<sup>2a,6,13</sup> halides; see eq. 1 in which Sn is a trisubstituted tin group.



We have been interested in this reaction, particularly from the mechanistic standpoint, and we report in this paper results which point convincingly to a free-radical chain mechanism. A reasonable scheme, in terms of which our results will be discussed, is that shown in eq. 2-6.



**Initiation.**—The initiation step of eq. 2 is brought about by the abstraction of a hydrogen atom from the tin hydride by some free radical  $Q \cdot$ . It was shown earlier<sup>10</sup> that small amounts of oxygen exert a definite catalytic effect on the reduction of *n*-butyl bromide by tri-*n*-butyltin hydride, although larger amounts

(1) This research was supported by the National Science Foundation under Grant NSF-G-10000 to the University of New Hampshire.

(2) (a) For a preliminary report on a portion of this work see H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962); (b) presented at the XIXth International Congress of Pure and Applied Chemistry, London, July, 1963.

(3) (a) Department of Chemistry, State University of New York at Albany, Albany, N. Y.; (b) National Science Foundation Senior Postdoctoral Fellow, California Institute of Technology, 1959-1960.

(4) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luitjen, *J. Appl. Chem.*, **7**, 356 (1957).

(5) J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Eng., 1956, p. 72.

(6) J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind. (London)*, 294 (1959).

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(10) H. G. Kuivila and L. W. Menapace, *ibid.*, **28**, 2165 (1963).

(11) H. G. Kuivila, *ibid.*, **25**, 284 (1960).

(12) E. J. Walsh, Jr., unpublished observations in this laboratory.

(13) (a) L. A. Rothman and E. I. Becker, *J. Org. Chem.*, **24**, 294 (1959); **25**, 2203 (1960); (b) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *ibid.*, **28**, 2332 (1963).

(20% or more) in the atmosphere over the reaction mixture have a profound inhibitory effect. Azobisisobutyronitrile has been shown to be an effective catalyst.<sup>10</sup> As an example, chlorocyclohexane is reduced to the extent of about 1% by tri-*n*-butyltin hydride in 35 min. at 80°, but in the presence of 1.5 mole per cent of the azo compound 70% reduction occurs under the same conditions. The fact that a small amount of catalyst has such a large effect on the over-all reaction rate supports the postulate of a chain reaction.

Thermal decomposition of the hydride could also lead to formation of  $Sn \cdot$ . In view of the fact that the hydride can be distilled at 135° without significant decomposition, it is unlikely that this is an important initiation step at room temperature. A further possibility concerning which no information is currently available involves a reaction between halide and hydride to form two free radicals.

**Propagation.**—Evidence for the formation of free alkyl radicals as intermediates comes from several observations. Reduction of optically active  $\alpha$ -phenylethyl chloride by triphenyltin deuteride produced racemic  $\alpha$ -deuterioethylbenzene. That this result was not due to racemization of the chloride followed by reduction is shown by the fact that the chloride did not undergo racemization in the presence of triphenyltin chloride under the conditions of the reduction reaction. Since an  $SN_2$  mechanism would lead to inversion and a four-center reaction would lead to retention, each of these can be eliminated on the basis of this observation. Reduction of propargyl bromide with tri-*n*-butyltin hydride led to the formation of a mixture of 84% propyne and 16% allene.<sup>14</sup> Such a product mixture could be formed as a result of either a combination of four-center  $SN_2$  and  $SN_2'$  reactions

(14) In connection with other work in these laboratories C. R. Warner has observed that reduction of the bromonortricyclene (**1**) with tri-*n*-butyltin hydride leads to a mixture of 55% norbornene and 45% nortricyclene. This result is consistent with the formation of radicals **2** and **3** as intermediates.

