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Hydroboration. XIII. The Hydroboration of Dienes with Disiamylborane. A Convenient Procedure for the Conversion of Selected Dienes into Unsaturated Alcohols

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RECEIVED SEPTEMBER 1, 1961

Whereas the dihydroboration of 1,3-butadiene with diborane results in major amounts of addition of the boron at the internal position, producing after oxidation 24–35% of the 1,3-butanediol, dihydroboration with disiamylborane achieves a more selective conversion of the diene into the terminal derivative, 10% 1,3- and 90% 1,4-butanediol. Dihydroboration of 1,4-pentadiene yields a 15:85 distribution of 1,4- and 1,5-pentanediol, whereas the reaction with diborane results in the formation of 62% of the 1,4- and 38% of the 1,5-diol. Similarly, 1,5-hexadiene yields 93% of 1,6-hexanediol, with only 7% of isomeric derivatives, as compared to the 69:31 distribution realized with diborane. Disiamylborane offers no significant advantage over diborane in the monohydroboration of acyclic conjugated dienes, such as 1,3-butadiene, where the two double bonds are identical. However, in cases where one of the two double bonds possesses structural features which decrease its rate of hydroboration by disiamylborane, good yields of the monohydroboration product can be achieved. Thus, 1,3-pentadiene is readily converted into 3-pentene-1-ol in a yield of 74%. The monohydroboration of non-conjugated aliphatic dienes proceeds readily. Thus, 1,5-hexadiene was converted into 5-hexene-1-ol in 64% yield and 2-methyl-1,5-hexadiene was converted into 5-methyl-5-hexene-1-ol in 71% yield. Cyclic dienes offer some unexpected characteristics. Thus, 1,4-cyclohexadiene was readily converted into 3-cyclohexene-1-ol in 90% yield, whereas, under the same conditions, the related diene, 1,5-cyclooöctadiene, underwent dihydroboration preferentially. In the case of 1,3-cyclohexadiene, an 84% yield of alcohol was realized. However, it was predominantly (90%) 2-cyclohexene-1-ol and not the 3-derivative. Finally, bicycloheptadiene is converted into dehydronorborneol (45% yield) which exhibits the same isomeric distribution (87% *exo*, 13% *endo*) realized with diborane.

The dihydroboration of terminal dienes, such as 1,3-butadiene and 1,5-hexadiene, with diborane provides a convenient route to the α,ω-diols.[2] However, it was noted that the reaction was frequently accompanied by the formation of undesirably large amounts of isomeric diols, resulting from the addition of the boron atom at a non-terminal carbon atom of the diene. Moreover, difficulties were encountered in many cases in achieving the monohydroboration of these dienes as a synthetic route to the corresponding unsaturated alcohols.[2]

We had previously observed that disiamylborane (bis-3-methyl-2-butylborane) possesses a significantly greater selectivity over diborane for the terminal carbon atom of the double bond.[3] It also is a highly selective hydroborating agent which distinguishes sharply between double bonds of different structures.[3] For these reasons, it appeared that the application of this reagent to the diene problem might overcome some of the difficulties we had previously encountered with diborane. Indeed, in an earlier study, we had been successful in utilizing disiamylborane to achieve the monohydroboration of 4-vinylcyclohexene and *d*-limonene.[3] Accordingly, we decided to undertake a detailed study of the hydroboration of a number of representative dienes with disiamylborane in order to explore its full utility for the mono- and dihydroboration of these derivatives.[4]

Results and Discussion

Dihydroboration of Dienes.—To explore the possible advantages of disiamylborane over diborane for converting terminal dienes into the corresponding α,ω-diols, we selected 1,3-butadiene and 1,5-hexadiene as representative derivatives. Both compounds had yielded major amounts of undesired side-products in the hydroboration–oxidation procedure based upon diborane.[2]

Accordingly, a slight excess of disiamylborane, 0.22 mole, prepared from the reaction of 2-methyl-2-butene and diborane in tetrahydrofuran, was added to the 1,3-butadiene, 0.10 mole, in the same solvent. After 3 hours at 0°, the reaction product was oxidized. Gas chromatographic analysis of the product indicated the formation of the 1,3- and 1,4-butanediol in a molar ratio of 10:90, with a 78% yield of diol isolated. This compares with the presence of 24–35% of the 1,3-diol formed in the corresponding diborane reaction.[2]

The dihydroboration of 1,4-pentadiene yielded 15% of 1,4- and 85% of 1,5-pentanediol, whereas the corresponding reaction with diborane resulted in the formation of the 1,4-diol (62%) preferentially.

Similarly, 1,5-hexadiene was converted into 93% 1,6-hexanediol, with only 7% of isomeric derivatives indicated by gas chromatographic analysis. The corresponding diborane procedure had produced 69% 1,6-hexanediol with 31% of isomeric diols.

The results are summarized in Table I.

These results clearly demonstrate the advantages of disiamylborane for the hydroboration of simple terminal dienes. Of course, in cases where the diene contains alkyl substituents in the α-position, such as 2,3-dimethyl-1,3-butadiene, there is a much more powerful influence directing the boron atom to the terminal position,[5] and hydroboration with diborane alone will provide excellent yields of an isomerically pure product.[2]

Monohydroboration of Acyclic Dienes.—A major difficulty in achieving the monohydroboration of conjugated dienes with diborane is the decreased reactivity of the diene system relative to an olefin of related structure. Thus, treatment of a mixture of 1,3-butadiene and 1-hexene with diborane leads

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[1] Visiting research associate, 1960–1961.

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

[3] H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

[4] M. F. Hawthorne, *ibid.*, **83**, 2541 (1961), has recently described the hydroboration of 1,3-butadiene, 2-methyl-1,3-butadiene and 1,4-pentadiene with trimethylamine-*t*-butylborane to produce the corresponding 1-*t*-butyl-1-boracycloalkanes.

[5] H. C. Brown and G. Zweifel, *ibid.*, **82**, 4708 (1960).

TABLE I

PREPARATION OF DIOLS BY THE DIHYDROBORATION OF DIENES WITH DISIAMYLBORANE[a]

Diene	Diol	Isomer distribution, % by G.C. analysis[b]	Yield of diol, % by isolation
1,3-Butadiene	1,3-Butanediol	10	
	1,4-Butanediol	90	78
1,4-Pentadiene	1,4-Pentanediol	15	
	1,5-Pentanediol	85	84
1,5-Hexadiene	1,5-Hexanediol 2,3-Hexanediol	7	
	1,6-Hexanediol	93	72
1,5-Cycloöctadiene	"Cycloöctanediol"		85[c]

[a] 0.1 mole of diene and 0.22 mole of disiamylborane at 0–5°. [b] G.C. analysis of crude reaction product. [c] Not identified.

TABLE II

STOICHIOMETRY OF THE REACTION OF ACYCLIC DIENES WITH DISIAMYLBORANE AT 0°[a]

Diene	Residual diene, % 0.5	1	2 hr.	Monohydroboration, % Disiamylborane[b]	Diborane[c]
1,3-Butadiene		43	46	8	4
2-Methyl-1,3-butadiene	38	38		24	4
1,3-Pentadiene	16	11	12	76	12
1,4-Pentadiene		34	35	30	10
1,5-Hexadiene	25	24		52	35
2-Methyl-1,5-hexadiene	25	17	16	68	

[a] The diene, 25 mmoles, was treated with 25 mmoles of disiamylborane in tetrahydrofuran solution at 0–5°. [b] The percentage of monohydroboration is based on the last analysis for residual diene. [c] Ref. 2.

to the preferential hydroboration of the 1-hexene. Similarly, the initial hydroboration of a conjugated diene produces an unsaturated organoborane which exhibits the higher reactivity of a simple olefin and undergoes further hydroboration in preference to the less reactive diene.

There is no apparent reason to expect disiamylborane to assist in this situation. However, in cases where the two double bonds of the diene possess structures which differ markedly in their reactivity toward disiamylborane,[3] the reagent might react preferentially at the more reactive side of the diene, the organoborane produced will have a double bond relatively inert to further attack by the reagent. In such cases disiamylborane might be expected to lead to an improvement in yield of the monohydroboration derivative.

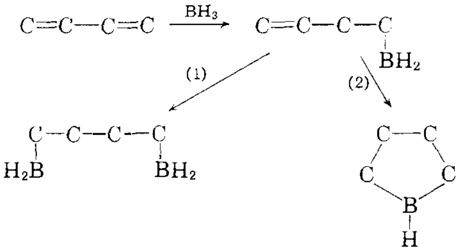
Finally, in some cases cyclization of the initially formed monoalkenylborane appears to be responsible for the poor yields realized with diborane.[2] Here also the use of disiamylborane should improve the situation.

In order to explore the influence of the structure of the diene upon the ease of achieving monohydroboration, a number of representative dienes were treated with one equivalent of disiamylborane in tetrahydrofuran at 0°. Samples were withdrawn at appropriate time intervals and analyzed by gas chromatography for residual diene.

The diene and the disiamylborane were present initially in equimolar amounts (25 mmoles each). If only monohydroboration occurred, no residual diene would be present; in the case of complete dihydroboration there would remain 12.5 mmoles of diene. Thus, the diene analysis provides an estimate of the relative importance of mono- *versus* dihydroboration in each diene structure.

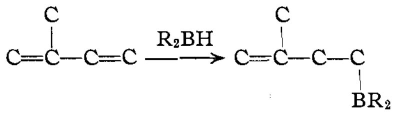
The experimental results are summarized in Table II.

We had previously considered two possible explanations for the low yields realized in the monohydroboration of 1,3-butadiene: (a) the inertness of the conjugated diene relative to the unsaturated organoborane formed in the monohydroboration stage (path 1), and (b) the incursion of a cyclization reaction (path 2).

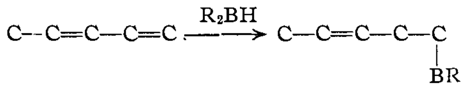


The results reveal no significant increase in the monohydroboration of 1,3-butadiene with disiamylborane (8%) over that realized in the corresponding reaction with diborane (4%). Since disiamylborane cannot participate under our conditions in the cyclization path (2), we must conclude that the low yields of monohydroboration in both hydroboration reactions must arise primarily from the increase in reactivity accompanying the conversion of the relatively inert conjugated diene into the more reactive unsaturated organoborane in the initial hydroboration stage.

2-Methyl-1-alkenes are significantly less reactive than the corresponding 1-alkenes toward disiamylborane.[3] The increase in monohydroboration (24 %) observed in the reaction of disiamylborane with 2-methyl-1,3-butadiene must be due to this influence. The disiamylborane must attack the diene preferentially at the less substituted position (3). The second hydroboration stage then involves a competition between the less hindered position of the diene and the more hindered 2-methyl-1-alkene structure of the organoborane.

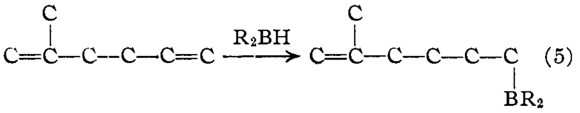

$$\text{C=}\overset{\text{C}}{\overset{|}{\text{C}}}\text{—C=C} \xrightarrow{\text{R}_2\text{BH}} \text{C=}\overset{\text{C}}{\overset{|}{\text{C}}}\text{—C—}\underset{\text{BR}_2}{\underset{|}{\text{C}}} \quad (3)$$

The difference in reactivity between internal olefins, such as 2-pentene, and terminal olefins, such as 1-pentene, is far greater than the effect of the 2-methyl substituent. On this basis, the increase in the yield of the monohydroboration product from 1,3-pentadiene is explicable in terms of the decreased reactivity of the initial hydroboration product toward the reagent (4).


$$\text{C—C=C—C=C} \xrightarrow{\text{R}_2\text{BH}} \text{C—C=C—C—}\underset{\text{BR}_2}{\underset{|}{\text{C}}} \quad (4)$$

The yields of monohydroboration realized are considerably higher for non-conjugated dienes of related structures. Thus the 8% yield realized for 1,3-butadiene increases to 30% for 1,4-pentadiene and to 52% for 1,5-hexadiene. The latter corresponds to the yield anticipated for a purely statistical reaction: 25% dihydroboration, 50% monohydroboration, 25% residual diene. The 30% yield realized for 1,4-pentadiene indicates that there must be present some influence which either deactivates the diene, or which activates the initial hydroboration product, or both.

In the case of 2-methyl-1,5-hexadiene we have both the non-conjugated system of double-bonds and the 2-methyl substituent which favor monohydroboration. A yield of 68% of monohydroboration is indicated by the experimental results (5).



$$C{=}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}C{-}C{=}C \xrightarrow{R_2BH} C{=}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}C{-}C{-}\underset{\displaystyle BR_2}{\underset{|}{C}} \quad (5)$$

It should be pointed out that the yields indicated were realized in a system containing the diene and disiamylborane reagent in equimolar amounts. The use of an excess of the diene should make it possible to reduce greatly the amount of material diverted to the dihydroboration product.

Monohydroboration of Cyclic Dienes.—A study of the monohydroboration reaction with diborane had indicated that the cyclic dienes exhibit considerably different behavior from the acyclic derivatives. Thus, 1,3-cyclohexadiene had provided a reasonable yield of monohydroborated product, in contrast to the very poor yields realized with the conjugated acyclic dienes. Accordingly, the study of the reaction of disiamylborane with an equimolar quantity of diene in tetrahydrofuran at 0°, previously described for acyclic dienes (Table II), was extended to a number of cyclic and bicyclic dienes: 1,3- and 1,4-cyclohexadiene, 1,5-cycloöctadiene and bicycloheptadiene. In the course of this study, it became of interest to compare the reactivity of cyclohexene and cycloöctene toward disiamylborane under the same experimental conditions utilized for the dienes.

The results of this study are summarized in Table III.

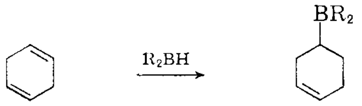
TABLE III

STOICHIOMETRY OF THE REACTION OF CYCLIC DIENES WITH DISIAMYLBORANE AT 0°[a]

Diene	Residual diene, % 0.5	1	2	4	8	24 hr.	Monohydroboration, % Disiamylborane[b]	Diborane[c]
1,3-Cyclohexadiene	62	49		17	6		88	51
1,4-Cyclohexadiene	56	50	40	27	20	9	82	
1,5-Cycloöctadiene	55	47	46	47			6	10
Bicycloheptadiene	59	44	40	35	30		40	34
Cyclohexene[d]		82	77	72	61			
Cycloöctene[d]	6	5	5					

[a] The diene, 25 mmoles, was treated with 25 mmoles of disiamylborane in tetrahydrofuran solution at 0–5°. [b] The percentage of monohydroboration is based on the last analysis for residual diene. [c] Ref. 2. [d] 25 mmoles of olefin and 25 mmoles of disiamylborane.

The results reveal that both 1,3- and 1,4-cyclohexadiene undergo monohydroboration predominantly. Presumably, the high yields realized are the result of the marked inertness of the cyclohexene system toward disiamylborane.[3] For example, under the identical conditions used for the hydroboration of the dienes, the reaction with cyclohexene is only 61% complete in a reaction period of 8 hours (Table III). Presumably, the initial hydroboration step yields a cyclohexene derivative (6) which resists further hydroboration

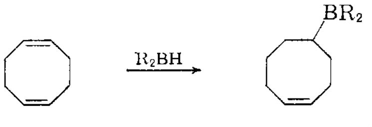


(6)

There is an unexpected feature. Simple acyclic conjugated dienes, such as 1,3-butadiene, react at a considerably slower rate than the corresponding olefins, such as 1-hexene.[2] Yet the results indicate that 1,3-cyclohexadiene reacts with disiamylborane at a rate slightly greater than the unconjugated derivative, 1,4-cyclohexadiene, with both dienes exhibiting considerably greater reactivity than the simple olefin, cyclohexene. Of course, the acyclic dienes exist primarily in the more stable s-*trans* form.[6] In the case of simple olefins, we observed that the *trans* form was much less reactive than the *cis* toward disiamylborane.[3] Consequently, the greater reactivity of 1,3-cyclohexadiene may be in part the result of the more reactive *cis* configuration enforced by the geometrical requirements of the ring.

As discussed subsequently, the enhanced rate of reaction of 1,3-cyclohexadiene with disiamylborane is accompanied by an unusual orientation taken by the entering disiamylboryl group. These observations suggest that steric influences may be important both in the enhanced rate and the unusual orientation exhibited by 1,3-cyclohexadiene.

In contrast to the cyclohexadienes, 1,5-cyclooctadiene undergoes dihydroboration preferentially. As indicated in Table III, cycloöctene is exceedingly reactive toward the reagent.[7] Since the initial product of the hydroboration of 1,5-cyclooctadiene must be a cycloöctene derivative (7), the speed of the second stage is not unexpected. Nevertheless, the failure to realize any significant yield of the monohydroboration product indicates that the diene is less reactive than the olefin, possibly the result of *trans*-annular conjugation between the two double bonds.



(7)

The dihydroboration of 1,5-cycloöctadiene by diethylborane has been reported recently.[8] Consequently, we dropped plans to explore the nature of the cycloöctanediol produced by the oxidation of the dihydroboration product.

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(6) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, 1959, pp. 21–24.

(7) For a discussion of the reactivity of medium ring olefins toward hydridic reagents, with pertinent literature references, see H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **83**, 3417 (1961).

(8) R. Köster and G. Griaznov, *Angew. Chem.*, **73**, 171 (1961).

Preparation of Unsaturated Alcohols.—A number of representative dienes were hydroborated on a preparative scale with disiamylborane under conditions conducive to the formation of the monohydroboration products. Oxidation with alkaline hydrogen peroxide converted the organoboranes into the corresponding alcohols. In this way it was possible to check both the utility of the procedure as a practical method for the conversion of selected dienes into unsaturated alcohols and our deductions as to the preferred point of attack in unsymmetrical dienes.

In order to favor the formation of the monohydroboration product, we utilized 100% excess of the diene. In the standard procedure, 0.2 mole of the diene in tetrahydrofuran was treated at 0–5° with 0.1 mole of the reagent, disiamylborane, in the same solvent. The organoborane formed was oxidized at 20–30° by alkaline hydrogen peroxide. The tetrahydrofuran layer was separated, and the aqueous phase was extracted with ether. The organic phase was analyzed by gas chromatography. The product then was isolated by distillation.

The experimental results are summarized in Table IV.

TABLE IV

PREPARATION OF UNSATURATED ALCOHOLS BY THE MONOHYDROBORATION OF DIENES WITH DISIAMYLBORANE[a]

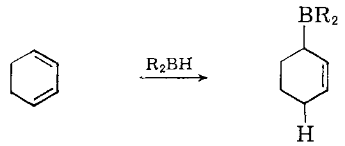
Diene	Alcohol	Yield of alcohol, % G.C. analysis	Yield of alcohol, % Isolation
1,3-Pentadiene[b]	3-Pentene-1-ol	74[c]	[d]
1,5-Hexadiene	5-Hexene-1-ol	64	51
2-Methyl-1,5-hexadiene	5-Methyl-5-hexene-1-ol	71	68
1,4-Cyclohexadiene	3-Cyclohexene-1-ol	90	75
1,3-Cyclohexadiene	2-Cyclohexene-1-ol[e]	84	70
Bicycloheptadiene	*exo*-Dehydronorborneol[f]	45	

[a] 0.2 mole of diene and 0.1 mole of disiamylborane at 0–5°. [b] *cis–trans* mixture of 1,3-pentadiene. [c] Both *cis*- and *trans*-3-pentene-1-ol indicated by the G.C. examination. [d] Pure *trans*-3-pentene-1-ol obtained by distillation in a Podbielniak Heli-Grid column. [e] G.C. analysis indicated the presence of 7–10% 3-cyclohexene-1-ol. [f] G.C. analysis indicated the presence of 13% of another product, presumably *endo*-dehydronorborneol.

It is quite clear that disiamylborane adds preferentially to the less substituted end of 1,3-pentadiene (4) and of 2-methyl-1,5-hexadiene (5). The results are in excellent agreement with the predictions based on the stoichiometry experiments for the acyclic dienes (Table II). Consequently, it appears that we possess a reasonably satisfactory understanding of the factors influencing the monohydroboration of acyclic dienes with disiamylborane.[9]

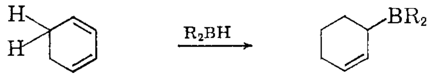
The only possible alcohol from 1,4-cyclohexadiene is 3-cyclohexene-1-ol (6), obtained in very high yield (Table IV). However, the formation of 2-cyclohexene-1-ol from 1,3-cyclohexadiene in a purity of 90–93% was quite unexpected.

One possible explanation for the predominant formation of 2-cyclohexene-1-ol would involve a 1,4-addition of the reagent (8). However, arguing against this interpretation is the fact that we have observed almost no evidence for such 1,4-addition in other systems.[10]



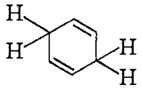
(8)

A second possible explanation is based upon the steric influence of methylene hydrogen atoms adjacent to the diene system (9).



(9)

In support of this tentative explanation is the somewhat higher reactivity of the conjugated diene, 1,3-cyclohexadiene, as compared with the unconjugated derivative, 1,4-cyclohexadiene, and the simple olefin, cyclohexene, discussed earlier. It will be noted that both 1,4-cyclohexadiene (I)



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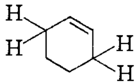

II

and cyclohexene (II) possess such a methylene group which could hinder the addition of the bulky disiamylboryl group to the adjacent carbon atom. On the other hand, the disiamylboryl group can avoid such steric interactions with the methylene group by adding to the 2-position of the 1,3-cyclohexadiene.[11]

Even though we do not have as full an understanding of the factors influencing the hydroboration of cyclic dienes with disiamylborane as compared to the acyclic derivatives, the results already available indicate that this reaction should be an exceedingly valuable one for the synthesis of cyclic unsaturated alcohols. We are continuing our exploration of this reaction.

Experimental Part

Materials.—Diglyme, tetrahydrofuran and boron trifluoride were purified as described previously.[2] Many of the dienes used in the present study were described earlier.[2] Data for hydrocarbons not described in the preceding paper are given in Table V.

TABLE V

SUMMARY OF DATA FOR THE DIENES AND OLEFINS USED

Hydrocarbon	Source	n^{20}D	n^{20}D (lit.)
2-Methyl-2-butene	Phillips	1.3890	1.3872
Cyclohexene	Phillips	1.4467	1.4468
Cyclooöctene	Cities Service	1.4703	1.4693
2-Methyl-1,5-hexadiene	Columbia	1.4185	1.4184
1,4-Cyclohexadiene	Farchan	1.4725	1.4734
1,5-Cyclooöctadiene	Cities Service	1.4943	1.4905 (25°)

Diborane in tetrahydrofuran was prepared following the procedure described previously.[2]

Preparation of Disiamylborane.—In a 3-neck flask, fitted with a side-arm covered with a rubber septum, was placed 16.8 g. of 2-methyl-2-butene (0.24 mole) in 15 ml. of tetra-

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(9) We are currently exploring the utility of the reagent in achieving the selective hydroboration of acyclic terpenes, such as myrcene; work in progress with Dr. K. P. Singh.

(10) In the dihydroboration of 1,3-butadienene we have observed a minor amount of 1,2-butanediol (4%), indicating a 1,4-addition; Ref. 2.

(11) It should be possible to distinguish between these two alternative explanations by studying the hydroboration of a 1,3-cyclohexadiene containing a tagged position. We hope to undertake such a study.

hydrofuran. The flask was immersed in an ice-bath. Then 60 ml. of an approximately 1.0 *M* solution of diborane (0.12 mole of borane) in tetrahydrofuran was added, maintaining the temperature at 0–5°. The reaction mixture was permitted to remain for 6 hours at this temperature to complete the reaction. To standardize the solution precisely, several ml. was withdrawn and analyzed for hydride by treatment with ethylene glycol and measuring the evolved gas. The solution obtained was approximately 1.2 *M* in disiamylborane. The standard solution was maintained under nitrogen and stored in a cold room (0–5°). No changes in the hydride content of such solutions have been observed over periods of several days.

Stoichiometry of the Monohydroboration of Dienes.—In a 100-ml. flask was placed 25 ml. of a 1 *M* solution of the diene in tetrahydrofuran. The flask was immersed in an ice-bath. Then 25 ml. of a 1 *M* solution of disiamylborane in tetrahydrofuran was added to the diene over a period of 10–15 minutes.

The rate of disappearance of the diene was followed by withdrawing samples at various time intervals and quenching them with 1-pentene or 1-decene. The solution was then analyzed by gas chromatography on an adiponitrile or Ucon Polar column for unreacted diene, using the internal standard as a reference. The results of these experiments are reported in Tables II and III.

The experiments designed to reveal the rate of reaction of cyclohexene and cyclooctene under these conditions were carried out in an identical manner, replacing the 25 mmoles of the diene by 25 mmoles of the olefin.

1,4-Butanediol.—In a 500-ml. flask was placed 5.4 g. of 1,3-butadiene (0.10 mole) in 50 ml. of tetrahydrofuran. The flask was immersed in an ice-bath and 0.22 mole of disiamylborane in tetrahydrofuran was added to the diene over 1 hour. The flask was maintained at 0–5° for 3 hours. Then 10 ml. of water was added to decompose residual hydride. The organoborane was oxidized *in situ* at 30° by adding 80 ml. of 3 *N* sodium hydroxide, followed by the dropwise addition of 67 ml. of 30% hydrogen peroxide. The aqueous phase was saturated with solid potassium carbonate. The tetrahydrofuran layer was separated. The aqueous phase was extracted twice with 25 ml. of tetrahydrofuran, and the combined extracts were dried over anhydrous magnesium sulfate. Distillation yielded 7.0 g. of 1,4-butanediol (78% yield), b.p. 80–82° at 0.3 to 0.4 mm., n^{20}D 1.4463; reported[12] b.p. at 106° at 0.7 mm., n^{20}D 1.4461. Gas chromatographic analysis of the product on a silicon-sorbitol column indicated that the product was at least 90% 1,4-butanediol, with approximately 10% of 1,3-butanediol indicated.

Preparation of 1,5-Pentanediol.—1,4-Pentadiene (6.8 g., 0.10 mole) was hydroborated with 0.22 mole of disiamylborane in tetrahydrofuran. Gas chromatographic analysis of the tetrahydrofuran extract on a sorbitol–silicone column revealed 85% of 1,5- and 15% of 1,4-pentanediol. Distillation yielded 8.5 g. of 1,5-pentanediol (82% yield), b.p. 137–139° at 15 mm., n^{20}D 1.4490; reported[13] b.p. 103–105° at 3–4 mm., n^{20}D 1.4498.

1,6-Hexanediol.—By the precise procedure described above, 8.2 g. of 1,5-hexadiene (0.10 mole) was converted into the diol. Gas chromatographic analysis of the tetrahydrofuran extract on a silicone–sorbitol column indicated 93% 1,6-hexanediol and 7% of 1,5- and/or 2,5-hexanediol.[14] The product obtained after removal of the tetrahydrofuran and the 3-methyl-2-butanol crystallized. Recrystallization from ethanol–ether gave 8.5 g. of 1,6-hexanediol (72% yield), m.p. 42–44°, reported,[15] m.p. 42.8°.

Cyclooctanediol.—The above procedure was utilized to convert 10.5 g. of 1,5-cyclooctadiene (0.10 mole) into 12.3 g. of cyclooctanediol (85% yield), b.p. 110–118° at 0.3 mm.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.13; H, 11.19. Found: C, 66.38; H, 11.08.

3-Pentene-1-ol.—In a 300-ml. flask was placed 50 ml. of a 4 *M* solution of 1,3-pentadiene (*cis–trans* mixture, 13.6 g., 0.20 mole). The flask was immersed in an ice-bath and 50 ml. of a 2 *M* solution of disiamylborane in tetrahydrofuran (100 mmoles) was added to the diene over a period of 30 minutes. The reaction mixture was permitted to remain for 2 hours at 0–5°, then 10 ml. of water was added to decompose residual hydride.

The organoborane was oxidized at 20–30° by adding 45 ml. of 3 *N* sodium hydroxide, followed by the dropwise addition of 32 ml. of 30% hydrogen peroxide. The reaction mixture was stirred for an additional hour. The tetrahydrofuran phase was separated and the aqueous phase was extracted with ether. The tetrahydrofuran and ether extracts were combined, washed with aqueous sodium chloride, and dried. Gas chromatographic analysis of the extract indicated a 74% yield of *cis*- and *trans*-3-pentene-1-ol. Distillation in a Podbielniak Heli-Grid column yielded *trans*-3-pentene-1-ol, b.p. 136–137° at 749 mm., n^{20}D 1.4335, m.p. α-naphthylurethan 91–92°; reported,[16] b.p. 136–137°, n^{20}D 1.4340, m.p. α-naphthylurethan 93°.

5-Hexene-1-ol.—1,5-Hexadiene (0.20 mole) was hydroborated and oxidized by the standard procedure described above. Gas chromatographic analysis of the extract on a Carbowax-1500 column indicated a 64% yield of 5-hexene-1-ol. Distillation gave 5.1 g. of 5-hexene-1-ol (51% yield), b.p. 67–70° at 20 mm., n^{20}D 1.4352, m.p. α-naphthylurethan 61–63°; reported[17] b.p. 152–155°, n^{20}D 1.4348, m.p. α-naphthylurethan 62°.

5-Methyl-5-hexene-1-ol.—From 19.2 g. of 2-methyl-1,5-hexadiene (0.20 mole) there was obtained a 71% yield of alcohol by gas chromatographic examination of the extract. Distillation gave 7.7 g. of 5-methyl-5-hexene-1-ol (68% yield), b.p. 80–82° at 12 mm., n^{20}D 1.4421; reported[18] b.p. 71° at 11 mm., n^{20}D 1.4415. The phenylurethan was prepared, m.p. 52–53°.

Anal. Calcd. for $C_{14}H_{19}O_2N$: C, 72.07; H, 8.31; N, 6.06. Found: C, 72.16; H, 7.89; N, 6.06.

Gas chromatographic examination of the distillate indicated a purity of at least 95%. Infrared examination revealed a strong absorption band at 890 cm.$^{-1}$, corresponding to the presence of a disubstituted double bond. The presence of two very weak bands at 910 and 990 cm.$^{-1}$ suggests the presence of a minor amount of the isomeric alcohol, 2-methyl-5-hexene-1-ol.

3-Cyclohexene-1-ol.—1,4-Cyclohexadiene (16.0 g., 0.20 mole) was hydroborated with 100 mmoles of disiamylborane at 0–5°. After 4 hours, the reaction mixture was converted to the alcohol by the usual procedure. Gas chromatographic examination of the extract revealed a 90% yield of alcohol (external standard). Distillation yielded 7.35 g. of 3-cyclohexene-1-ol (75% yield), b.p. 74–76° at 20 mm., n^{20}D 1.4865, m.p. phenylurethan 79–81°; reported[19] b.p. 162–163°, n^{21}D 1.4860, m.p. phenylurethan 81°.

2-Cyclohexene-1-ol.—To 1,3-cyclohexadiene (16.0 g., 0.20 mole) was added 0.10 mole of disiamylborane. After 4 hours at 0–5°, the product was converted to the alcohol. An 84% yield was indicated by gas chromatographic examination of the extract. Distillation yielded 6.8 g. of 2-cyclohexene-1-ol (70% yield, b.p. 78–80° at 20 mm., n^{20}D 1.4834, m.p. phenylurethan 103°; reported[17] b.p. 160–165°, n^{30}D 1.4777, m.p. phenylurethan 107°.

The infrared spectrum of this alcohol was not identical with that obtained from 3-cyclohexene-1-ol. Gas chromatographic examination of the distillate on a 2-m. Carbowax-1500 column indicated the presence of 90–93% of 2-cyclohexene-1-ol and 7–10% of 3-cyclohexene-1-ol.

***exo*-Dehydronorborneol.**—To 18.5 g. of bicycloheptadiene (0.20 mole) was added 0.10 mole of disiamylborane. After 4 hours at 0–5°, the reaction mixture was oxidized. Gas chromatographic examination of the extract indicated a 45% yield of alcohol, consisting of 87% *exo*-dehydronorborneol and 13% of another product of similar retention time, presumably *endo*-dehydronorborneol. The solvents and excess of bicycloheptadiene were removed. The product obtained was taken up in a small quantity of *n*-hexane. On cooling to about −50°, the product crystallized. The precipitate was collected, pressed on a porous plate, and sublimed: m.p. 89–90°, m.p. phenylurethan (from *n*-hexane)

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Acknowledgment.—This investigation was made possible by the award of a visiting studentship (to K. N.) from the Kao Soap Co., Ltd., Tokyo, Japan.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

Amines Derived from Dihalopropenes. I. The Mechanism of Allenimine Formation[1a,b]

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RECEIVED JULY 31, 1961

Treatment of N-(2-bromoallyl)-*n*-propylamine (Ia) with sodium amide in tritium-labeled liquid ammonia has been found to yield radioactive N-*n*-propylallenimine (IIa). No significant exchange with solvent of the hydrogens bonded to carbon of Ia and IIa occurred under the reaction conditions. Compound IIa was degraded and determination of the radioactivity of the degradation products showed that 99.8 ± 0.3% of the tritium was incorporated in IIa at the ring-methylene group. These results are consistent with the proposal that an N-alkylallenimine is formed *via* an elimination–addition mechanism involving an allenic amine intermediate (III).

When an N-(2-bromoallyl)-alkylamine (I) is treated with an alkali metal amide in liquid ammonia the principal product is the N-alkylallenimine (1-alkyl-2-methyleneaziridine, II).[2] A small amount of the corresponding N-alkylpropargylamine (IV) also is formed.

Several plausible mechanisms can be written to explain the formation of II from I.[3] Internal displacement of bromide ion can be envisaged as occurring by an SN2-type reaction (1) or an addition–elimination reaction (2). Formation of II can also be the result of an elimination–addition reaction (3) involving an allenic amine intermediate (III). The possibility of an analogous elimination–addition mechanism (4) involving IV is precluded by the high yields of N-alkylpropargylamines obtained from reactions of N-(2-chloroallyl)-alkylamines with alkali metal amides in liquid ammonia.[2b,]

From consideration of these mechanisms, it appeared likely that a choice between paths 1, 2 and 3 could be made by examination of II obtained from an appropriate N-(2-bromoallyl)-alkylamine (I) and amide ion in tritium-enriched ammonia. The absence of tritium in II would indicate that 1 is the reaction path since intermediates V in 2 and VII in 3 would be expected to abstract a proton from the solvent. However, the absence of tritium in II could not be used to rule out 2 as the reaction mechanism since it is conceivable that loss of bromide ion from V to yield unlabeled II could occur at a much faster rate than the reaction of V with ammonia to yield radioactive VI. If I and II (aside from the amine hydrogen) do not undergo exchange with the solvent under the reaction conditions, presence of tritium in II would definitely rule out 1 as the exclusive reaction mechanism. A choice between 2 and 3 could be made by degrading II and determining the location of the incorporated tritium. Path 2 would yield II labeled at the exocyclic-methylene group; path 3 would yield II labeled at the ring-methylene group.

It was decided to treat N-(2-bromoallyl)-*n*-propylamine (Ia, R = *n*-C_3H_7) with sodium amide in tritium-labeled liquid ammonia because it appeared likely that the N-*n*-propylallenimine (IIa, R = *n*-C_3H_7) obtained could be hydrogenated to di-*n*-propylamine in high yield[2a] and a convenient procedure for conversion of primary and secondary amines to the corresponding carbonyl compounds had been worked out in these laboratories.

Compound Ia was prepared in 81% yield by treatment of 2,3-dibromopropene with excess *n*-propylamine in water. Treatment of Ia with sodium amide in liquid ammonia which had been equilibrated with a small amount of tritium oxide gave IIa in 39% yield together with a small amount of N-*n*-propylpropargylamine (IVa, R = *n*-C_3H_7). Compound IIa was freed of the last traces of IVa by distillation from lithium aluminum hydride at reduced pressure. Determination of the radioactivity of purified IIa indicated that it had a specific activity equal to the calculated specific activity of the hydrogens of the ammonia, *i.e.*, one-third the specific activity of the ammonia. The hydrogens bonded to carbon of Ia and IIa did not undergo exchange with the solvent under the reaction conditions since treatment of excess Ia with sodium amide in tritium-enriched liquid ammonia and treatment of radioactive IIa with sodium amide in ordinary liquid ammonia caused no significant change in the specific activity of either compound. These results ruled out 1 as the exclusive mode of formation of IIa. The equal specific activities of the product and the hydrogens of the solvent, which is to be expected if a carbanion intermediate such as VII or, possibly, V is

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(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, Administered by the American Chemical Society, for partial support of this research. (b) Presented in part at the 140th National meeting of the American Chemical Society, Chicago, Ill., September, 1961. (c) American Chemical Society–Petroleum Research Fund Fellow, 1961.

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