Reaction of *trans*-Piperylene with 4,4,6-Trimethyl-1,3,2-dioxaborinane (TMDB). In an ampoule was placed 2.51 g (0.0368 mol) of *trans*-piperylene and 2.36 g (0.0184 mol) of 4,4,6-trimethyl-1,3,2-dioxaborinane along with 0.5 ml of anhydrous ether. The ampoule was heated in a bomb for 25 hr at 130°. Distillation gave 1.35 g (48%), bp 49–52° (0.3 mm), of product. The infrared, nmr, and retention time in the glpc (20 ft × 3/8 in. silicone nitrile column at 100°, flow rate 100 ml/min) were identical with compound **6**.

Attempted Protodeboronation of *cis*-2-(Pent-2-en-3-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane. In a flask equipped with a magnetic stirring bar, reflux condenser, and outlet to a trap immersed in Dry Ice–acetone was placed 0.3 g (1.5×10^{-3} mol) of *cis*-2-(pent-2-en-3-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane and 0.092 g (1.5×10^{-3} mol) of glacial acetic acid. The reaction mixture was stirred for 24 hr at room temperature and then analyzed by glpc (20 ft × 3/8 in. silicon nitrile column) to show only starting material. The trap immersed in Dry Ice contained none of the expected *cis*-2-pentene. The reaction mixture was then refluxed for 24 hr and upon glpc analysis showed only starting material. Other carboxylic acids such as formic or trifluoroacetic gave similar results.

Attempted Isomerization of *cis*-2-(Pent-2-en-3-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (5). In a glass ampoule was placed a pure sample (glpc) of *cis*-2-(pent-2-en-3-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**5**). The ampoule was heated in a bomb at 130° for 25 hr and analyzed by glpc on a 20 ft × 3/8 in. silicone nitrile column at 100° to show that compound **5** remained unchanged.

Preparation of 4,4,6-Trimethyl-1,3,2-dioxaborinane (TMDB).[13] In a flask equipped with a mechanical stirrer and reflux condenser was placed 7.5 g (0.15 mol) of lithium aluminum hydride in 120 ml of tetraglyme. To this stirring suspension was added 80.25 g (0.30 mol) of 2,2′-oxybis(4,4,6-trimethyl-1,3,2-dioxaborinane) (**12**).[14] The addition was completed in 30 min, and the reaction mixture was stirred an additional 30 min at room temperature. Distillation from the reaction mixture afforded 32.2 g (85%) of 4,4,6-trimethyl-1,3,2-dioxaborinane (TMDB), bp 50–52.5° (46 mm); $n^{25}D$ 1.4036; ν_{max}^{neat} (cm^{-1}), BH 2550 (s); nmr spectrum (neat, TMS), τ 5.8 (m), 7.9–8.4 (m), 8.75 (1), 8.80 (s), in the ratio 1:2:6:3, plus a broad quartet, 6.40 (J = 172 cps).

Acknowledgments. The technical assistance of Mr. Jim Stuck is gratefully acknowledged. The author wishes to thank the chemistry faculty at California State College at Fullerton for the use of their nmr spectrometer and Dr. W. G. Woods for helpful discussions throughout this work. The author also wishes to acknowledge Professor M. C. Caserio for her helpful suggestions in preparing this manuscript.

(13) This method, which was worked out with Dr. H. C. Newsom, constitutes a facile preparation of TMDB and circumvents preparing the corresponding 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane,[6] which is quite unstable.

(14) H. S. Steinberg, "Organoboron Chemistry," Vol. 1, Interscience Publishers, New York, N. Y. 1964, p 382.

Hydroboration. XXVIII. The Hydroboration of 3-Cyclopentenyl Derivatives Containing Representative Substituents. Directive Effects and the Elimination Reaction in a Cyclic System[1]

Herbert C. Brown and Evord F. Knights[2]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907. *Received January 29, 1968*

Abstract: A series of representative 3-substituted cyclopentenes was subjected to hydroboration by diborane and by disiamylborane under standardized conditions in order to extend the previous study of acyclic crotyl derivatives to a cyclic system. Both the stoichiometry of the reactions and the products formed in oxidation of the intermediate boron derivatives were utilized to deduce the relative amount of the boron which adds to the nearer β position of the double bond. With diborane in tetrahydrofuran at 0° the per cent β addition decreases in the order: chloride, 100; acetate, 100; ethyl ether, 83; alcohol (converted *in situ* to the dialkoxyborane), 78; disiamylborinate ester, 76. With disiamylborane in tetrahydrofuran at 0° the per cent β is: chloride, 100; alcohol (converted *in situ* to the disiamylborinate ester), 99; acetate, 90; ethyl ether, 82. There was a marked preference for the boron to add in the β position *trans* to the substituent. In the case of the chloride, the elimination was too rapid to be controlled. In the case of the alcohol and the ether, the elimination of the *cis*-bora intermediate was also fast. However, the elimination reactions of the *trans* derivatives were much slower, so that the reactions can be utilized as a synthetic route to *trans*-1,2-cyclopentane derivatives. In particular, the hydroboration–oxidation of the alcohol by disiamylborane provides *trans*-1,2-cyclopentanediol, essentially free of isomeric products.

In the hydroboration of simple allylic derivatives it was observed that the electronegativity of the substituent exerts a marked influence on the direction of the addition.[3,4] Thus in the reaction of allyl chloride with diborane, 40% of the boron appears at the 2 position, as compared to only 6% in the parent compound I. In simple allyl derivatives the amount of boron adding to the 2 position increases from 19% for the ethyl ether to 45% for the tosylate I, suggesting that the direction of addition is influenced by the inductive effect of the substituent.

$$CH_2{=}CHCH_2X$$
I

X = H, 6%
X = OC_2H_5, 19%
X = Cl, 40%
X = OTs, 45%

(1) Based upon a thesis submitted by E. F. Knights to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Graduate research assistant, 1965–1968, on Grant No. GM-10937 of the National Institutes of Health.

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

(4) H. C. Brown and O. J. Cope, *ibid.*, **86**, 1801 (1964).

In the allyl system, the effect of the substituent in directing the boron toward itself is offset by the marked preference for boron to become attached to the terminal carbon atom. Indeed, when disiamylborane is used as the hydroborating agent, a reagent with an enhanced tendency to add to the terminal carbon atom, essentially exclusive addition to the terminal carbon atom is achieved in spite of the counter directive influence of the substituent.

The 2-butenyl (crotyl) system affords a carbon skeleton with a balanced directive effect, so that the substituent can exert its full effect.[5] Here essentially exclusive addition to the 2 position occurs with the chloride and 84% with the ethyl ether II.

$$CH_3CH_2{=}CH_2CH_2X$$
II

X = H, 50%
X = OC_2H_5, 84%
X = Cl, 100%

The β-substituted organoboranes thus produced may undergo spontaneous elimination at 0°.[3-6] A major emphasis of previous studies has been directed to developing means of circumventing the elimination, so as to provide the β-substituted organoboranes as intermediates for synthesis.

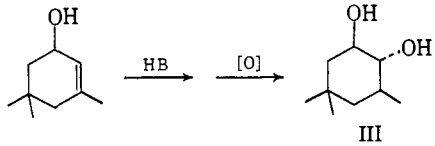
Hydroboration of crotyl alcohol produces 90% of the β-hydroxyborane. (It should be emphasized that the hydroxy group is not free, but is converted by the diborane into a borate derivative.) However, approximately one-half of this undergoes spontaneous elimination resulting in a yield of only 38.5% 1,2-diol upon oxidation. By converting the alcohol group to the disiamylborinate ester *in situ*, prior to hydroboration–oxidation, the elimination can be circumvented and an 81% yield of the 1,2-diol realized.[5]

As part of our systematic exploration of the hydroboration reaction, it was of interest to ascertain whether the hydroboration of a cyclic system related to the crotyl structure would exhibit the same or different characteristics. Such a system introduces the added feature that the boron atom becoming attached to the β position may be directed either *cis* or *trans* to the original substituent. Moreover, the elimination reaction should obviously be greatly influenced by such geometrical considerations.[6c,7] Accordingly, we undertook a systematic study of the hydroboration of a number of 3-substituted cyclopentene derivatives by diborane and by disiamylborane in tetrahydrofuran at 0° in order to obtain information on these questions. After this study had been completed, we learned from D. J. Pasto that a related study involving 3-substituted cyclohexenes was under way in his laboratories.[8,9] Fortunately, the two studies complement each other and contribute to a fuller understanding of the hydroboration of cyclic olefins containing substituents in the allylic position.

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

(6) (a) P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961); (b) L. Cagliotti and G. Cainelli, *Atti Acad. Nazl. Linei*, [8] 30, 225 (1961); (c) D. J. Pasto and R. Snyder, *J. Org. Chem.*, 31, 2777 (1966); (d) H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, 90, 2915 (1968).

(7) For example, recently J. Klein and E. Dunkelblum, *Tetrahedron Letters*, 6049 (1966), reported that the hydroboration–oxidation of isophorone (and related ketones) affords a 65% yield of a single diol (III), without the use of a protective group to avoid elimination.



III

Clearly the boron atom must add preferentially to the β position, *trans* to the hydroxyl group, to provide such a high yield of a single isomer. Presumably, the smaller amount of *cis*-boron intermediate is destroyed by a much faster elimination reaction, whereas the *trans* isomer is relatively stable and provides the diol.

Results and Discussion

Stoichiometry Studies with Diborane. The following 3-substituted cyclopentenes were selected for study: chloride, acetate, alcohol, disiamylborinate ester, and ethyl ether.

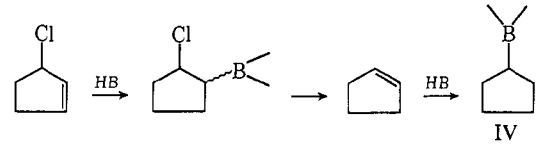
For the stoichiometry studies 12.5 mmol of each compound in 5 ml of tetrahydrofuran was added over 2 min to 16.7 mmol of borane (50 mequiv of "hydride") in 45 ml of tetrahydrofuran solution at 0°. In the case of the alcohol and acetate, additional borane was used to compensate for that used in hydrogen evolution with the alcohol and reduction of the ester grouping in the case of the acetate. At appropriate intervals of time 5-ml aliquots were removed and analyzed for residual hydride by hydrolysis. The results of these experiments are summarized in Table I.

Table I. Stoichiometries of the Reactions of Representative 3-Substituted Cyclopentenes with Borane–Tetrahydrofuran at 0°

	Hydride utilized[a] — Time, min				
	5	30	60	240	48 (hr)
Cyclopentene	1.00	1.00	1.00	1.00	
Chloride	1.96	1.96	1.94	1.96	
Acetate	1.72	2.33	2.48	2.93	3.80
Alcohol	2.19	2.23	2.28	2.30	
Disiamyl borinate ester	0.98	0.99	1.00	0.99	
Ethyl ether	1.11	1.12	1.14	1.14	1.21

[a] Equivalent of hydrides utilized per mole of olefin.

Cyclopentene utilizes 1 equiv of hydride very rapidly, with no further uptake of hydride with time indicated. In contrast, 3-chlorocyclopentene utilizes 1.96 equiv of hydride corresponding to a rapid β addition of borane followed by elimination and rehydroboration (IV).



IV

The acetate utilizes 3.80 equiv of hydride per mole, corresponding to utilization of 2 hydrides for hydroboration, placing the boron in the β position, followed

(8) D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, 90, 4445 (1968).

(9) Attention should be called to a number of related, highly interesting individual studies of the hydroboration of cyclic, bicyclic, and steroidal derivatives of this type which have appeared in the literature: (a) myrtenal and verbenone, Y. Chrétien-Bessière, *Bull. Soc. Chim. France*, 9, 2182 (1964); (b) α,β-unsaturated steroid ketones, L. Caglioti and G. Cainelli, *Atti Accad. Nazl. Lincei*, [8] 29, 555 (1960); L. Caglioti, G. Cainelli, G. Maina, and A. Selva, *Gazz. Chim. Ital.*, 92, 309 (1962); L. Caglioti, G. Cainelli, G. Maina, and A. Selva, *Tetrahedron*, 20, 957 (1964); (c) substituted 2-cyclohexen-1-ols, A. Uzarewicz, I. Uzarewicz, and W. Zacharewicz, *Roczniki Chem.*, 34, 19 (1965); (d) 3-methyl-2,5-dihydrothiophene 1,1-dioxide, R. C. Krug and D. E. Boswell, *J. Org. Chem.*, 27, 45 (1962); (e) methyl esters of N-carbobenzyloxy-3,4-dehydro-DL-proline and -4,5-dehydro-DL-pipecolic acid, Y. Fukita, F. Irreverre, and B. Witkop, *J. Am. Chem. Soc.*, 86, 1795 (1964).

by elimination and rehydroboration. The other 2 hydrides are utilized to reduce the acetoxy group to the alcohol.

It should be noted that the hydride utilization, 1.96 and 3.80, is slightly less than the 2.00 and 4.00 values that should have been required had the reactions proceeded quantitatively as indicated. It is probable that small amounts of addition to the 3 position occur. However, we were interested in defining the major course of the reaction and did not attempt to explore the nature of minor contributions.

The alcohol utilizes 2.30 equiv of hydride, 1 in reaction with the hydroxyl hydrogen resulting in the evolution of 1 equiv of hydrogen, 1 in hydroboration of the double bond, and the remainder in hydroboration of olefin produced in a partial elimination. The stoichiometry corresponds to 30% elimination. The elimination was completely avoided when the alcohol was converted *in situ* to the disiamylborinic ester, as indicated by the utilization of only 1 equiv of hydride.

The ethyl ether utilizes 1.12 equiv of hydride in 0.5 hr, rising to 1.21 equiv in 48 hr. This corresponds to 1 equiv for hydroboration and 12–21% elimination followed by rehydroboration.

Product Studies for the Diborane Hydroborations. In order to determine the direction of addition of borane–tetrahydrofuran, the derivatives were hydroborated at 0° and the resulting organoboranes oxidized with alkaline hydrogen peroxide to form the corresponding alcohols. There is now available thoroughly convincing evidence that oxidation of organoboranes by alkaline hydrogen peroxide proceeds with retention of configuration.[10,11] Therefore, the stereochemistry of the organoborane could be deduced from that of the oxidation product and the direction of addition of the boron–hydrogen moiety could be established.

In the case of 3-chlorocyclopentene, the only product observed was cyclopentanol, detected in 88% yield. The elimination is very rapid and is complete in less than 5 min after hydroboration. It was impossible to establish whether hydroboration had involved a *cis* or *trans* addition preferentially, followed by a *cis* or *trans* elimination. However, it is quite clear from the results that the addition proceeds practically exclusively β in this derivative.[12]

Hydroboration–oxidation of 3-hydroxycyclopentene[13] yielded 40% *trans*-1,2-diol, but no *cis*-1,2-diol. A 28% yield of cyclopentanol was also observed, presumably the result of rehydroboration after elimination of a 2-bora derivative. This product distribution correlates well with the stoichiometry of 2.30, which indicates 30% elimination. The complete absence of *cis*-1,2-cyclopentanediol must either be the result of exclusive *trans* addition to the β carbon or the result of a very fast *cis* elimination of the *cis*-2-bora isomer. The product also contained 11% each of *cis*- and *trans*-1,3-cyclopentanediols. This indicates that the substituent exerts little or no control on the direction of addition of boron to the γ-carbon atom. However, it is evident from the results that hydroboration at the 2 position must occur preferentially, if not predominantly or exclusively, *trans*.

Hydroboration–oxidation of the disiamylborinate ester of 3-hydroxycyclopentene yielded only 5% elimination–rehydroboration product. Once again the major product was the *trans*-1,2-diol, and equal amounts of 1,3-diols were formed.

3-Acetoxycyclopentene afforded an unusual case in that its rate of hydride consumption was much slower than the earlier results with crotyl acetate[5] would have predicted. Moreover, a significant percentage of the *cis*-1,2-cyclopentane derivative was noted after oxidation of the intermediate organoboranes. The powerful directive influence of the acetoxy substituent is indicated by the absence of any 1,3-cyclopentane derivatives in the products.

Since the rate of uptake of hydride was slow, it was of interest to determine the change of product distribution with time. Accordingly samples of the acetate were oxidized at 3 hr after hydroboration and at 48 hr after hydroboration. The yield of *trans*-1,2-diol[14] dropped faster than that of the *cis*, indicating that the *trans*-β-organoborane eliminated faster than the *cis*, although elimination was relatively slow over-all.

The presence of 2% cyclopentene in the product indicates that some elimination occurred upon addition of aqueous base for the oxidation, since excess of hydroborating agent was present up to the moment the excess was destroyed by the aqueous base.

In the case of 3-ethoxycyclopentene, it was again observed that no *cis*-1,2 product was formed. The predominant product (66%) was *trans*-2-ethoxycyclopentanol. As in the case of the alcohol, equal amounts of *cis*- and *trans*-1,3 products were formed. Significantly, a much larger percentage of cyclopentanol (18%) was formed from elimination to cyclopentene than was anticipated from previous experience with crotyl ether where a 98% yield of hydroxy ethers was realized.[5] This may be evidence that a small per cent of *cis*-1,2-organoborane was formed and that a rapid *cis* elimination occurred, or it may indicate that elimination of a β-bora derivative is more facile in this cyclopentane system than in the analogous acyclic system.

The products of the hydroboration–oxidation of the representative 3-substituted cyclopentenes are tabulated in Table II. Product distribution correlates well with the observed hydride consumption in each case.

Stoichiometry Studies with Disiamylborane. In general the rate of hydride consumption with disiamylborane was much slower than with borane–tetrahydrofuran. For example, 3-chlorocyclopentene hydroborated completely in less than 5 min with borane–tetrahydrofuran, whereas hydride consumption did not cease for 72 hr with disiamylborane. In each case the stoichiometry of the hydride utilization was less with

(10) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 131.

(11) Indeed the only case for which oxidation with inversion was claimed has now been disproven: S. P. Acharya and H. C. Brown, *J. Am. Chem. Soc.*, **89**, 1925 (1967); H. C. Brown and A. Suzuki, *ibid.*, **89**, 1933 (1967).

(12) The elimination reaction is much slower in ethyl ether and Pasto and Hickman noted that the hydroboration of 3-chlorocyclohexene in this solvent yields 10% *cis*-2-bora and 85% *trans*-2-bora derivative. Consequently, there appears to be little doubt, especially in view of the results with the other derivatives, that in 3-chlorocyclopentene the boron adds predominantly to the 2 position *trans* to the chloro substituent.

(13) It should be pointed out that just as in the corresponding case of crotyl alcohol[5] hydrogen is rapidly evolved when the alcohol and diborane come into contact. Consequently, it is actually a borate ester, probably a dialkoxyborane, which is undergoing hydroboration and elimination.

(14) The oxidation product in dry tetrahydrofuran was treated with lithium aluminum hydride to remove the acetoxy group prior to glpc analysis for the diols.

Table II. Oxidation Products for the Hydroboration of Representative 3-Substituted Cyclopentenes with Borane–Tetrahydrofuran at 0°

	Time, hr	Hydride[a] utilized	Products, % yield[b] 					
Chloride	1	1.96	88	...	..	..	..	..
Acetate[c]	3	3.00	60	2	15	13	..	..
	48	3.80	67	3	12	5	..	..
Alcohol	3	2.30	28	2	..	40	11	11
Disiamylborinate ester	1	1.00	5	7	..	52	10	10
Ethyl ether	3	1.14	18		..	66[d]	8[d]	7[d]

[a] The stoichiometry of the reaction is represented here as equivalents of hydride consumed per mole of compound. [b] Determined by glpc analysis. [c] Reference 14. [d] Monoethyl ether of diol.

disiamylborane than with borane–tetrahydrofuran, indicating a lower tendency for the hydroboration product to undergo elimination followed by rehydroboration.

For example, the alcohol utilized 1.98 equiv of hydride in 1 hr, rising to 2.10 equiv in 4 hr, but remaining constant at that level for 48 hr. Since 1 equiv of hydride is utilized for the liberation of hydrogen and the formation of the disiamylborinate ester, it is evident that elimination–rehydroboration is only 10%, in contrast to the 30% observed with diborane. The ethyl ether utilizes a maximum of 1.00 equiv of hydride, essentially constant at this level from 12 to 48 hr. Clearly, elimination–rehydroboration is not a significant factor here.

Reactions of disiamylborane with the chloride and the acetate are much slower than with the alcohol and the ether, presumably also a manifestation of the greater −I inductive effects of the former substituents which deactivate the double bond toward electrophilic attack by the reagent. Because of this slow rate, it proved impractical to carry the reaction on for a time adequate to establish a clearly established plateau for these derivatives. The results of these studies are summarized in Table III.

Table III. Stoichiometries for the Reactions of Representative 3-Substituted Cyclopentenes with Disiamylborane in Tetrahydrofuran at 0°

	Hydride utilized[a] Time, hr				
Compound	1	4	12	24	48
Chloride	0.64	1.17	...	1.50	1.53
Chloride[b]	1.50	1.60	1.69	1.86	1.87
Acetate	0.58	1.25	1.33	1.37	1.40
Alcohol	1.98	2.10	2.10	2.10	2.10
Ethyl ether	0.63	0.89	0.98	1.01	0.98

[a] Equivalents of hydride utilized per mole of olefin. [b] Reaction at 25°.

Product Studies for the Disiamylborane Hydroborations. Oxidation of the hydroboration product of the alcohol with disiamylborane provided an 80% yield of *trans*-1,2-cyclopentanediol, with only minor amounts (~0.5%) of the other three isomeric diols. A 5% recovery of cyclopentanol supports the indication from the stoichiometry study of a small amount of elimination–rehydroboration. It is evident that the boron atom of disiamylborane is directed by the substituent (Sia_2BO–) predominantly to the *trans*-2 position and provides a convenient route to derivatives of this kind.

In the case of the ethyl ether, the product was predominantly (66%) the monoethyl ether of *trans*-1,2-cyclopentanediol. None of the *cis* isomer was identified. There is also formed 8% *cis*-1,3 and 9% *trans*-1,3. Consequently, the directive influence of the ethoxy substituent is far less effective than that of the disiamylborinoxy group. A puzzling feature is the observation that the product contained 2% cyclopentene and 6% cyclopentanol, whereas the stoichiometry results indicated no excess hydride utilized and consequently no elimination.

The chloride indicated an approach to the utilization of 2.0 hydrides (actually 1.87 in 24 hr). Oxidation produced 84% cyclopentanol and 3% cyclopentene. Consequently, here also hydroboration must take place predominantly to place the boron atom at the 2 position, followed by an elimination–rehydroboration.

In the case of 3-acetoxycyclopentene, the rate of hydride consumption was very slow after 3 hr, when a stoichiometry of 1.25 was reached. After 120 hr a stoichiometry of 1.47 was indicated. In contrast to borane, the reactions of disiamylborane with esters and with carboxylic acids are very slow at 0°.[15] Hence the over-all hydride consumption was smaller for disiamylborane. However, a 10% yield of ethanol along with a 13% yield of cyclopentanol was observed upon oxidation. The cyclopentanol was the product of elimination to cyclopentene. The ethanol was assumed to be the product of reduction of eliminated acetate. A 13% elimination along with a 13% reduction of acetate would produce a stoichiometry of 1.39, which correlates reasonably well with the observed stoichiometry of 1.47. The 13% yield of cyclopentanol was in marked contrast to the 67% yield obtained with borane–tetrahydrofuran. A 13% yield of cyclopentene indicated considerable elimination occurred upon addition of aqueous base. The direction of addition of boron was not as specifically β as was the case with borane–tetrahydrofuran, since 8% *cis*- and *trans*-1,3-diols was produced. The results of product studies are summarized in Table IV.

Implications. The stoichiometries and per cent β addition of the reactions of 3-substituted cyclopentenes are quite similar to that observed in the

(15) H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, 83, 486 (1961).

Table IV. Oxidation Products for the Hydroboration of Representative 3-Substituted Cyclopentenes with Disiamylborane in Tetrahydrofuran at 0°

Compound	Time, hr	Hydride[a] utilized	Products, % yield[b]					
								
Chloride	24	1.87	3	84	...	..	...	...
Acetate[c]	120	1.47	13	13	...	50	4	4
Alcohol	24	2.10	2	5	...	80	...	...
Ethyl ether	24	1.01	2	6	...	66[d]	8[d]	9[d]

[a] The stoichiometry of the reaction is represented here as equivalents of hydride consumed per mole of compound. [b] Determined by glpc analysis. [c] Reference 14. [d] Monoethyl ether of diol.

2-butenyl (crotyl) system. A comparison of these results appears in Table V.

It is apparent that the predominant mode of addition of boron to the 3-substituted cyclopentenes affords the *trans*-β-organoborane. This is consistent with the results of Klein and Dunkleblum[7] in the hydroboration of cyclohexenones and of Pasto and Hickman[8] in the hydroboration of 3-substituted cyclohexenes.

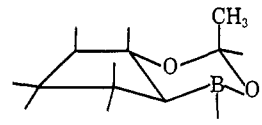
In the hydroboration of 3-chlorocyclopentene, the elimination is complete in less than 5 min. This is a much faster rate than that observed for crotyl chloride. Two factors could be influencing the faster rate. First, it has been observed that in the hydroboration of a series of allylic chlorides the products from secondary chlorides undergo elimination considerably faster than do the products from primary chlorides.[16] Secondly, it is pointed out by Pasto and Hickman[8] that the elimination of a β-boron-substituted chloride should proceed *via* a *trans* process, so that the *trans*-2-chloroborane, evidently formed predominantly in the hydroboration stage, would be in an ideal configuration to undergo elimination.

Table V. Comparison of the Stoichiometries and Per Cent β Addition for the Reactions of 2-Butenyl (Crotyl) and 3-Substituted Cyclopentenyl Compounds with Borane–Tetrahydrofuran at 0°

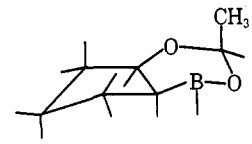
Compound	Crotyl[a] Hydride utilized[b]	Crotyl[a] % β	Cyclopentenyl Hydride utilized[b]	Cyclopentenyl % β
Chloride	1.99	100	1.96	100
Acetate	4.08	95	3.80	100
Alcohol	2.47	90	2.30	78
Disiamylborinate	1.04	86	1.00	76
Ethyl ether	1.15	84	1.14	83

[a] Data from ref 5. [b] The stoichiometry is represented here as equivalents of hydride utilized per mole of compound.

Hydroboration of 3-acetoxycyclopentene likewise affords predominantly the elimination–rehydroboration products. In the hydroboration of 1-acetoxycyclopentene, where the β-bora derivative can only have the *trans* structure, 44% elimination occurred in 30 min.[17] Hence, *trans* elimination is facile with acetate derivatives. The acetate is unusual in that it is the only derivative which affords a stable *cis*-β-borane, although only in 15% yield. The incomplete elimination of the *trans*-β-borane and the stability of the *cis*-β-borane may be the result of formation of heterocycles, such as V and VI.

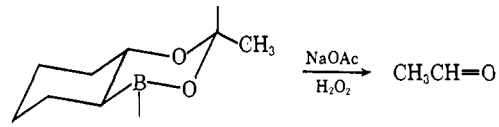


V



VI

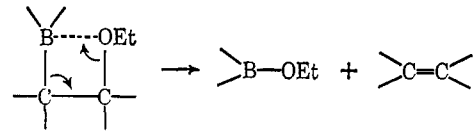
Such an intermediate was suggested to account for the slow elimination in the hydroboration product from 1-acetoxycyclohexene.[17] Oxidation of the intermediate from 1-acetoxycyclohexene, presumably VII, with sodium acetate and hydrogen peroxide, afforded acetaldehyde as one product,[16] in agreement with the structure indicated.



VII

The formation of a similar heterocycle is not possible with disiamylborane. In agreement with this explanation is the observation that, in contrast to the results with diborane, none of the *cis*-1,2-diol is obtained from disiamylborane (Table IV).

Hydroboration of the ethyl ether affords a stable *trans*-β-adduct and a *cis*-β-adduct which undergoes rapid elimination. This is consistent with the formation of a stable *trans*-β-adduct in the hydroboration of 1-ethoxycyclohexene.[17] Evidently the 18% elimination product arises exclusively from the formation of a *cis*-β-ethoxyborane. Even when disiamylborane is used a 6% yield of elimination product arises, showing the formation of 6% *cis*-β-adduct which undergoes a facile elimination. Also, ethoxy is a very poor leaving group and would not be expected to participate in a *trans* elimination.[6c]



Hydroboration of 3-hydroxycyclopentene with diborane yields 28% elimination product and 40% stable *trans*-β-adduct. No stable *cis*-β-adduct is observed, indicating the derivative undergoes a spontaneous *cis* elimination. If all of the cyclopentanol (28%) arises from a *cis*-β-adduct, this would indicate 28% *cis*-β

(16) E. F. Knights, unpublished results.
(17) See ref 6d.

Table VI. Physical Constants of the 3-Substituted Cyclopentenes and Related Hydroboration–Oxidation Products

Compound	Obsd constants		Reptd constants		Ref
	Bp, °C (mm)	n^{20}D	Bp, °C (mm)	n^{20}D	
3-Chlorocyclopentene[a]	19–24 (5)	1.4755	18–25 (5)	1.4708	*a*
3-Hydroxycyclopentene[b]	54–58 (12)	1.4728	52 (12)	1.4717	*b*
3-Ethoxycyclopentene[c]	122–124 (750)	1.4380	120–121	1.4426	*c*
3-Acetoxycyclopentene[a]	52 (12)	1.4495	48 (11)	1.4480	*a*
Cyclopentanol[d]	139	1.4534	139–140	1.4530	*l*
Cyclopentene oxide[e]	99–101	1.4350	99–101	1.4370[o]	*e*
cis-1,2-Cyclopentanediol	*f*				
trans-1,2-Cyclopentanediol[g]	121 (10) mp 46–47[n]		136 (22) 55[n]		*m*
cis-1,3-Cyclopentanediol	*h*				
trans-1,3-Cyclopentanediol[i]	126–129 (5)	1.4840	86–87 (0.5)	1.4832	*i*
trans-2-Chlorocyclopentanol[j]	78 (15)	1.4804	78 (15)	1.4808	*j*
trans-2-Ethoxycyclopentanol[k]	178–180	1.4546	182	1.4512[p]	*k*

[a] N. Rabjohn, Ed., "Organic Synthesis," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 238. [b] K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956). [c] R. Ya. Levina, T. I. Godovikova, and V. N. Vinogradova, *Vestn. Mosk. Univ. Ser. Mat., Mekh., Astron., Fiz. i Khim.*, **14**, 171 (1959). [d] Aldrich Chemical Co. [e] L. Goodman, A. Benilez, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 1680 (1958). [f] Sample from R. Gallivan. [g] S. Winstein and R. M. Roberts, *J. Am. Chem. Soc.*, **75**, 2297 (1953). [h] Sample from G. Zweifel. [i] K. A. Saegebarth, *J. Org. Chem.*, **25**, 2212 (1960). [j] L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4026 (1952). [k] M. Mousseron, R. Granger, and A. Merle, *Bull. Soc. Chim. France*, 457 (1949). [l] C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 1084 (1926). [m] P. E. Verkade, *et al.*, *Ann.*, **477**, 279 (1930). [n] Melting point. [o] Temperature 16°. [p] Temperature 25°.

addition. However, this can only be considered to be an upper limit, with a modest contribution resulting from a slow elimination of the *trans*-β-adduct. When the reaction was conducted for 24 hr at 25°, a 70% yield of elimination product was obtained, confirming that the *trans* derivative is capable of undergoing such elimination. Crotyl alcohol also exhibits this partial elimination at 0°.[5] Evidently the *cis*-β-adduct undergoes rapid elimination and the *trans*-β-adduct undergoes elimination only slowly.

Converting the alcohol to the disiamylborinate ester *in situ* before hydroboration leads to a reduction in elimination product from 28% to 5% and an increase in the stable *trans*-β-adduct, which yields the *trans*-1,2-diol, from 40% to 52%. The 5% elimination product probably arises from a rapid elimination of a small quantity of a *cis*-β-adduct formed in the hydroboration.

When the representative 3-cyclopentene derivatives were hydroborated with disiamylborane, two trends were observed. The amount of the *cis*-β-adduct which was formed decreased, and the stability of the *trans*-β-adduct was increased. The first is presumably a result of the steric effect of the bulky alkyl groups of the hydroborating agent, which favors hydroboration to occur on the less hindered side of the ring. The second may also be due to the bulkiness of the alkyl groups, which should hinder solvent coordination with the boron, believed to be an essential stage in the *trans* elimination.[6c] This is particularly evident in the case of the chloride which undergoes complete elimination in less than 5 min at 0° when borane is used, but is not completely eliminated in 3 days at 0° when disiamylborane is used.

Conclusions

The hydroboration of 3-cyclopentenyl derivatives proceeds to place the boron predominantly in the *trans*-β position. In the case of the chloride and acetate, rapid elimination follows hydroboration. The *trans*-β-adduct is only partially eliminated in the case of the alcohol, and no significant elimination of *trans*-β-adduct occurs under the reaction conditions with the disiamylborinate ester and the ethyl ether.

The use of disiamylborane as a hydroborating agent provides higher yields of *trans*-β-adducts, presumably because the bulky borane is more specific in adding to the less hindered side and the bulky alkyl groups hinder solvent attack of boron, favoring the *trans* elimination.

In those cases where 1,3 products were formed, there was no major *cis*/*trans* directive effect observed, and roughly equal amounts of *cis*- and *trans*-1,3 products were formed.

The use of disiamylborane in the hydroboration of 3-hydroxycyclopentene was by far the best method for production of the *trans*-1,2-diol.

Experimental Section

Materials. Preparations of solvents and reagent solutions and general procedures have been described previously.[3-5]

Preparation of Cyclopentene Derivatives. All derivatives were prepared by known methods. Purity of 98–99% was verified for each derivative by glpc analysis and nmr spectra. It was necessary to store the chloride in a Dry Ice bath. The others were stored in a cold room. Physical constants of derivatives are listed in Table VI.

Glpc Analysis. Two columns were used for glpc analysis. First a 21-ft 5% FFAP on Chromosorb W–DCMS treated with 0.5% Armac was used on an F & M 500 instrument. Conditions were: detector 300°, injector 275°, gas 60 cc/min, column 125° programmed to 200° at 5.6°/min. For the separation of *cis*- and *trans*-1,3-cyclopentanediols a 6-ft Hyprose SP 80 on Chromosorb W column was used at 150° on a Perkin-Elmer 154-B. An internal standard of *p*-dimethoxybenzene was used for all product analyses. Retention times and relative response ratios of the products were determined from authentic samples either available in our laboratories or synthesized by known methods. Samples of *cis*- and *trans*-3-ethoxycyclopentanols were obtained by glpc separation of the hydroboration product of 3-ethoxycyclopentene. Structure was assigned on the basis of ir and nmr spectra.