The Addition of 4,4,6-Trimethyl-1,3,2-dioxaborinane to Allenes[1]

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Contribution from the U. S. Borax Research Corporation, Anaheim, California 92801. *Received February 19, 1968*

Abstract: The addition of 4,4,6-trimethyl-1,3,2-dioxaborinane (TMDB) to allene, 3-methyl-1,2-butadiene, 2,3-pentadiene, 2,4-dimethyl-2,3-pentadiene, and 1,2-cyclononadiene has been studied. The results indicate that attack of the boron atom on the terminal carbon atom of the allenic system is predominant when the terminal carbon atom is unsubstituted. Thus allene (>86%), 3-methyl-1,2-butadiene (78%), and 2,3-pentadiene (19%) afford decreasing amounts of boron attack at the terminal allenic position. The central carbon atom is preferentially attacked when the allenic system is substituted in the 1 and 3 positions. This is shown in 2,3-pentadiene (81%), 2,4-dimethyl-2,3-pentadiene (100%), and 1,2-cyclononadiene (100%). The only unsymmetrical allene studied, 3-methyl-1,2-butadiene, provided 22% attack of boron on the central carbon atom reflecting the effect of methyl substituents on the course of the reaction. The direction of addition and stereochemistry of these hydroboration reactions are discussed in terms of the steric and electronic effects on a four-center transition state.

Surprisingly few investigations have been reported on the hydroboration of allenes. Corsano[3] has reported that terminal boron attack (98%) is the major reaction with allene using diborane as the hydroborating agent. His results, however, with butylallene and phenylallene do not lead to a clear choice as to initial point of boron attack on the allenic system, since 1,3 and 1,2 diols were the only products isolated after oxidation of the intermediate boranes. Devaprabhakara and Gardner[4] have hydroborated 1,2-cyclononadiene and 2,3-nonadiene with diborane and have obtained ketone in both cases as the major product after oxidation. The fact that ketone was the major product indicates that central attack of the allenic system by the boron atom is predominant with the above-mentioned allenes. Lindner and Onak[5] dealt with the diborane addition to allene in the gas phase and found that the boron added to the terminal site of the allenic system.

An interesting question is raised when diborane is used as the hydroborating agent, since the addition of diborane to olefins involves at least three successive reactions. The steric effect on the transition state for each step in the reaction (eq 1–3) may have different requirements.

$$\mathrm{R} + \mathrm{BH_3} \longrightarrow \mathrm{RBH_2} \tag{1}$$

$$\mathrm{R} = \text{allene}$$

$$\mathrm{RBH_2} + \mathrm{R} \longrightarrow \mathrm{R_2BH} \tag{2}$$

$$\mathrm{R_2BH} + \mathrm{R} \longrightarrow \mathrm{R_3B} \tag{3}$$

Studies involving diborane are, therefore, subject to complications with regard to the point of initial boron attack due to different steric requirements in each stage. We feel that a monofunctional borane such as 4,4,6-trimethyl-1,3,2-dioxaborinane (TMDB), which undergoes a hydroboration reaction in one stage, creates a more unified picture of the steric effect upon changing the allene structure. The preparation and use of TMDB as a hydroborating agent have recently been reported by Woods and Strong.[6] The unusual stability of TMDB and its derivatives has permitted the isolation of the allene adducts. This eliminates the usual oxidation step, which Brown and coworkers[7] have employed to detect the point of boron attack. Although gas–liquid partition chromatography (glpc) has significantly increased the reliability of Brown's two-step method, direct isolation and characterization of the organoboron compound avoids any complications due to unexpected oxidative pathways.[8] Since some confusion exists in the hydroboration of allenes, we have undertaken a study of the reaction of five allenes with TMDB in order to correlate the direction of addition and stereochemistry of products in terms of steric and electronic effects on a four-center transition state, as a function of allene structure.

Results

The hydroboration reactions were carried out in sealed ampoules at 130° for 25–50 hr and the product ratios determined by gas–liquid partition chromatography (glpc). The products were separated by preparative gas chromatography and subjected to infrared and nuclear magnetic resonance (nmr) spectral analysis. The structures of all the products isolated are given in Chart I. Yields, product distributions, and infrared and analytical data are reported in Table I. Nmr data, including chemical shifts in τ units, are reported in Table II.

Allene. Allene provided, in 25% yield, a mixture containing 86.5% 2-allyl-4,4,6-trimethyl-1,3,2-dioxaborinane (**1**) and 13.5% 2-isopropenyl-4,4,6-trimethyl-1,3,2-dioxaborinane (**2**). Compound **1** was characterized by infrared bands at 3090, 1640, 993, and 892 cm^{-1} typical of allyl compounds and an nmr spectrum with a vinyl proton multiplet, τ 4.15, coupled to a terminal methylene group, τ 5.05 (m) (J_{trans} = 16 cps), 5.29 (m) (J_{cis} = 9.0 cps), and an allylic methylene group at τ 8.39 (2) (J = 6.5 cps). The characteristic 4,4,6-trimethyl-1,3,2-dioxaborinane absorptions were also present in the correct ratios. Compound **2** had infrared bands at 1623 and 930 cm^{-1} characteristic of vinylboron com-

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[1] Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract 156S.

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[3] S. Corsano, *Atti Acad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, 34, 430 (1963).

[4] D. Devaprabhakara and P. D. Gardner, *J Am. Chem. Soc.*, **85**, 1458 (1963).

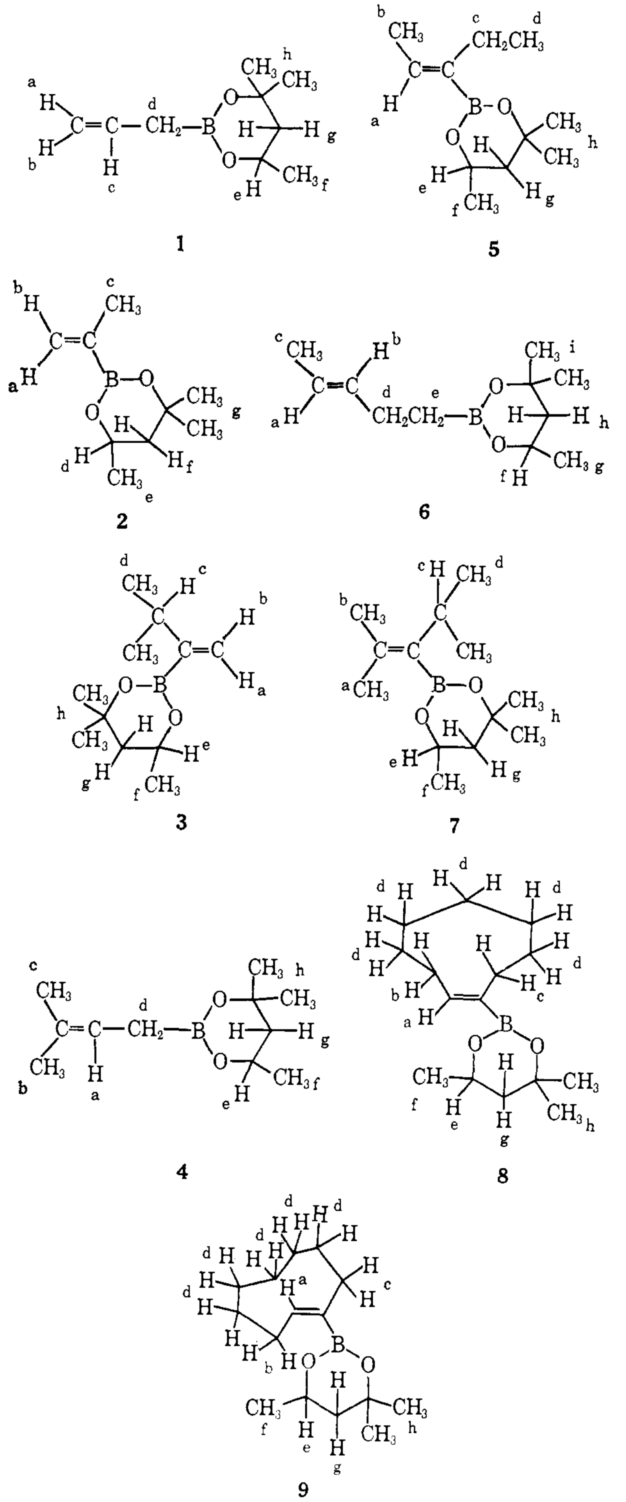
[5] H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966).

[6] W. G. Woods and P. L. Strong, *ibid.*, **88**, 4667 (1966).

[7] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[8] Reference 7, Chapter 16.

Chart I. 4,4,6-Trimethyl-1,3,2-dioxaborinane–Allene Adducts



pounds. The nmr spectrum had vinyl proton multiplets at τ 4.30 and 4.45 ($J = 1.2$ cps), while the methyl group on a vinyl carbon atom, τ 8.25, was a singlet. There was also formed 25% of a product which was not completely characterized but is probably the diadduct of compound **1**. In that case the ratio **1**:**2** is probably closer to 97:3.

3-Methyl-1,2-butadiene. 3-Methyl-1,2-butadiene provided, in 71.5% yield, two products in the ratio 22:78. The product of 22%, 2-(3-methylbut-1-en-2-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**3**), had infrared bands at 1610 (C=C) and 934 (=CH$_2$) cm^{-1} and an nmr spectrum with vinyl proton multiplets of unit area at τ 3.70 and 3.93 ($J = 3.0$ cps), while the tertiary allylic proton consisted of a seven-line multiplet, τ 7.26, coupled to the geminal methyls at τ 8.92 ($J = 8.5$ cps). Compound **4** (78%) had an infrared band at 1642 cm^{-1} (C=C) and an nmr spectrum which consisted of one vinyl proton triplet, τ 4.77, coupled with an unresolved allylic methylene group, τ 8.35 ($J = 7.0$ cps), while the methyl groups on the double bond consisted of singlets at τ 8.30 and 8.40.

2,3-Pentadiene. The reaction products were *cis*-2-(pent-2-en-3-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**5**) (73%), *trans*-2-(pent-2-en-5-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**6**) (17%), and two other unidentified (glpc) products (10%) which are possibly the *trans* isomer of **5** and the *cis* isomer of **6**. The ratio of **5**:**6** is thus 81:19. Compound **5** had an infrared band at 1632 cm^{-1} (C=C). The nmr spectrum consisted of a vinyl proton quartet, τ 3.82, coupled to a methyl doublet, τ 8.37 ($J = 7.0$ cps), and a methylene quartet, τ 7.93, coupled with a methyl triplet, τ 9.15 ($J = 8.0$ cps). The assignment of the *cis* configuration of **5** (vinyl proton *cis* to boron) is based on some work of Matteson and Liedtke.[9] They prepared the corresponding *cis*- and *trans*-dibutyl-2-butene-2-boronates. The *cis* isomer has a vinyl proton quartet at τ 3.73 and an infrared double-bond stretch at 1633 cm^{-1} which is completely consistent with the results obtained for **5**. Unfortunately, attempts to protodeboronate **5** with several carboxylic acids to the *cis* olefin were unsuccessful. Compound **6** had infrared bands at 1650 (C=C) and the characteristic *trans* out-of-plane deformation at 960 cm^{-1}. The nmr spectrum had a complex vinyl multiplet τ 4.67 (two protons), the methyl group as a partially resolved doublet at τ 8.40 (*ca.* $J = 5.0$ cps), and the allylic methylene a multiplet at τ 8.05. The homoallylic methylene group was a triplet, τ 9.35 ($J = 9.0$ cps). Compound **6** also had an infrared and nmr spectra as well as a glpc retention time which were in complete agreement with those of the hydroboration product of *trans*-piperylene.

2,4-Dimethyl-2,3-pentadiene. The only product that was isolated in 38% yield was from exclusive attack of boron at the central carbon atom of the allenic system. Thus 2-(2,4-dimethylpent-2-en-3-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**7**) had infrared bands at 1634, 888, and 815 cm^{-1} and an nmr spectrum with vinyl methyl singlets at τ 8.30 and 8.37 as well as a tertiary allylic multiplet, τ 7.44, coupled with two methyl groups at τ 9.03 ($J = 7.5$ cps).

1,2-Cyclononadiene. The only products formed were from boron attack at the central carbon atom. *cis*-2-(Cyclonon-1-en-2-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**8**) and its *trans* isomer **9**, which could not be separated by glpc, were present in the ratio 85:15 (nmr). The infrared spectrum of **8** and **9** had a band (C=C) at 1634 cm^{-1}, while the nmr spectrum consisted of a triplet at τ 3.07 ($J = 10.0$ cps) assigned to **8** and a triplet at τ 3.97 ($J = 9.0$ cps) assigned to **9** in the ratio 85:15. The remaining spectrum consisted of the methylene groups α to the double bond as a broad singlet at τ 7.6 and the other methylene groups of the cyclononene ring at τ 8.1–8.5. The dioxaborinane pro-

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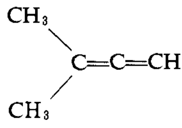
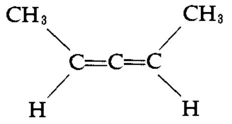
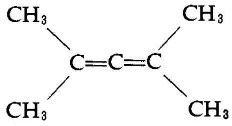
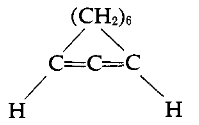
[9] D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, **87**, 1526 (1965).

Table I. Preparative, Physical, and Analytical Data on 4,4,6-Trimethyl-1,3,2-dioxaborinane–Allene Adducts

Allene	Conditions[a] Temp, °C	Time, hr	Bp, °C (mm)	Yield, %	Product distribution[b] Compd	%	nD (°C)
$CH_2{=}C{=}CH_2$	130	25	92–93 (23–25)	25	**1** **2**	86.5 13.5	1.4290 (25) 1.4298 (25)
	130	50	53 (0.12–0.15)	71.5	**3** **4**	22 78	 1.4429 (25)
	130	45	34 (0.16)	60	**5** **6**	81 19[c]	1.4412 (26) 1.4366 (25)
	130	50	67 (0.10–0.12)	38	**7**	100	1.4461 (25)
	130	36	113–116 (0.35)	42	**8** **9**	85[d] 15	1.4849 (24)

Compd	Formula	Calcd, % C	H	B	Found, % C	H	B	Prominent ir bands, cm^{-1}
1	$C_9H_{17}BO_2$	64.32	10.19	6.43	64.14	10.23	6.61	3090 (w), 1640 (m), 993 (s), 892 (s)
2	$C_9H_{17}BO_2$	64.32	10.19	6.43	64.25	10.10	6.58	1623 (m), 930 (s)
3	$C_{11}H_{21}BO_2$	67.36	10.79	5.51	67.53	10.58	...	1610 (m), 934 (s)
4	$C_{11}H_{21}BO_2$	67.36	10.79	5.51	67.13	10.89	5.31	1642 (w)
5	$C_{11}H_{21}BO_2$	67.36	10.79	5.51	67.20	10.72	5.49	1632 (m)
6	$C_{11}H_{21}BO_2$	67.36	10.79	5.51	67.13	11.05	5.87	1650 (w), 960 (s)
7	$C_{13}H_{25}BO_2$	69.65	11.24	4.82	69.43	11.24	4.92	1634 (m), 888 (m), 815 (m)
8 and **9**	$C_{15}H_{27}BO_2$	72.00	10.87	4.32	72.19	10.89	4.50	1634 (m)

[a] Catalyzed with 1 ml of anhydrous diethyl ether. [b] Separation was achieved on a 20 ft × $^3/_8$ in. silicone nitrile column, and peak areas were used to determine isomeric ratios. [c] This product possibly arises from isomerization of tertiary allylic isomer, which we believe is first formed. [d] Based on the vinyl proton triplet areas in the nmr spectrum.

Table II. Nmr Spectral Data on the 4,4,6-Trimethyl-1,3,2-dioxaborinane–Allene Adducts[a,b]

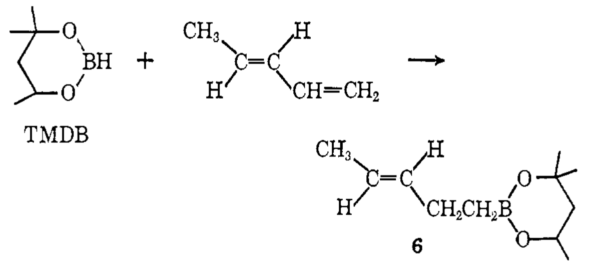
Adduct	Concn in CCl_4, %	a	b	c	d	e	f	g	h	i	J_{ab}	J_{ac}	J_{bc}	J_{cd}	J_{ad}	J_{de}
1	15	4.15(m)	5.05(m)	5.29(m)	8.39(2)	5.84(m)	8.86(2)	8.39 m)	8.72(1)		9.0	16	2.0		6.5	
2	15	4.30(m)	4.45(m)	8.25(1)	5.75(m)	8.78(2)	8.25(m)	8.71(1)			1.2					
3	50	3.70(2)	3.93(m)	7.26(7)	8.92(2)	5.30(m)	8.68(2)	8.0(m)	8.60(1)		3.0			8.5		
4	20	4.77(3)	8.30(1)	8.40(1)	8.35(?)	5.80(m)	8.82(2)	8.35(?)	8.72(1)						7.0	
5	50	3.82(4)	8.37(2)	7.93(4)	9.15(3)	5.90(m)	8.85(2)	8.37(m)	8.76(1)		7.0			8.0		
6	20	4.67(m)	4.67(m)	8.40(m)	8.05(m)	9.35(3)	5.90(m)	8.80(2)	8.40(m)	8.74(1)	5.0					9.0
7	15	8.30(1)	8.37(1)	7.44(m)	9.03(2)	5.71(m)	8.81(2)	8.35(m)	8.70(1)					7.5		
8	50	3.07(3)	7.6(m)	7.6(m)	8.1–8.5(m)	5.50(m)	8.68(2)	8.0(m)	8.60(1)		10.0					
9	50	3.97(3)	7.6(m)	7.6(m)	8.1–8.5(m)	5.50(m)	8.68(2)	8.0(m)	8.60(1)		9.0					

[a] See Chart I for structure and proton designation. [b] Values reported in τ units and measured at the center of each multiplet; J values in cps. The multiplicity is designated in parentheses.

tons at τ 8.0 (m), 8.60 (1), and 8.62 (2) were also present in the correct ratios. The assignment of the stereochemistry is consistent with Matteson and Liedtke's results[9] (*trans*-vinyl proton chemical shift at a higher field than *cis*) and with a shielding effect of the ring on a *trans*-vinyl hydrogen. The *trans*-vinyl hydrogen can be placed inside the cyclononene ring; thus the shielding effect of the ring places the vinyl proton *trans* to boron at a higher field then its corresponding *cis* isomer **8**.

Discussion

Steric Effect. Steric effects in the hydroboration of olefins have been thoroughly discussed by Brown.[7] They are important in controlling the direction of addition; therefore, a discussion of their role in the hydroboration of allenes is pertinent. If we assume that a four-center transition state is in operation, then addition to one of the orthogonal double bonds of the allenic system must occur in a plane parallel with substituents attached to that double bond. In view of this fact, our results show that terminally unsubstituted allenic positions are sterically the most favorable site for boron atom attack. Thus allene (>86%), 3-methyl-1,2-butadiene (78%) and 2,3-pentadiene (19%) afford decreasing amounts of boron atom attack at the terminal allenic positions. The product from terminal attack of 2,3-pentadiene was not isolated; however, its homallylic isomer **6** was isolated. The isomerization of a boron atom on a tertiary or secondary position to a terminal position is well documented.[7] We confirmed by experiment, however, that **5** was not isomerized to **6** under our reaction conditions. Compound **6** was also prepared by the hydroboration of *trans*-piperylene (eq 4).

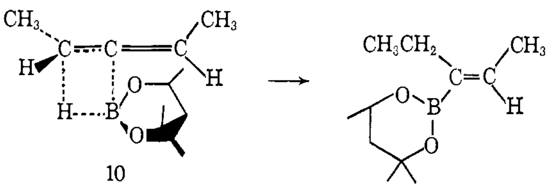


TMDB

6

(4)

In the case where the boron atom attacks the central carbon atom of the allenic system considerable nonbonded interaction of the incoming dioxaborinane ring system can exist with groups attached to the other orthogonal double bond. An example of this is shown in transition-state **10** for addition of TMDB to 2,3-pentadiene leading to compound **5**. The dioxaborinane ring is shown as entering in the preferred orientation, *i.e.*, it approaches on the same side as the hydrogen of the orthogonal double bond, leading to the *cis* product **5**.

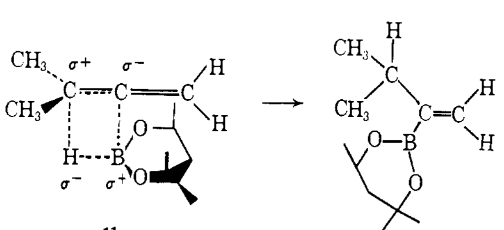


10

5

Thus, the steric requirements of the transition state have a pronounced influence on the stereochemistry of products derived from attack of the boron atom on the central carbon atom of 1,3-substituted allenes. This is evident with 2,3-pentadiene (transition-state **10**) and 1,2-cyclononadiene where the *cis* isomer predominates. This is also consistent with the result obtained by Devaprabhakara and Gardner,[4] who isolated *cis*-cyclononene upon protonolysis of their intermediate borane. It is also noteworthy to point out that the nonbonded interactions between the dioxaborinane ring and the hydrogen or alkyl group can be alleviated to some extent as the boron atom becomes tetrahedral in the transition state.

Electronic Effect. Steric effects alone, as Gardner[4] pointed out, cannot accommodate all the results. The electronic effect, which may not be as important as the steric effect, recently has been shown by Brown and Sharp[10] to be quite influential in the hydroboration of substituted styrenes. The electronic effect is shown in the reaction of TMDB with 3-methyl-1,2-butadiene, where 22% attack by the boron atom on the central carbon atom was found.



11

3

This can be attributed to the hyperconjugative effect of both methyl groups which tends to make the central carbon atom more susceptible to electrophilic attack. We would also point out that transition-state **11** is sterically more favorable, since reversing the mode of central attack by the boron atom places the dioxaborinane ring in steric conflict with the methyl groups on the orthogonal double bond. The electronic effect becomes more pronounced with 1,3-substituted allenes, as evidenced by the fact that central carbon attack is predominant in 2,3-pentadiene (81%), 2,4-dimethyl-2,3-pentadiene (100%), and 1,2-cyclononadiene (100%).

In conclusion, the interpretation of the results of the hydroboration of allenes, using TMDB as the hydroborating agent, are complicated by the necessity to consider both the steric and electronic effect as a function of allene structure; more work is needed to help define the importance of each effect.

Experimental Section

Boiling points are uncorrected. Elemental analysis were carried out by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Model 137 (sodium chloride optics). The nmr spectra were recorded on a Varian A-60A instrument with tetramethylsilane as an internal standard. The glpc analysis were performed on a Varian Aerograph 1520-1B instrument. Peak areas were used to calculate percentages of the isomeric products.

Materials. Allene (Matheson Co.) was found to be free of methylacetylene (glpc on a 10 ft × 0.25 in. dimethylsulfolane column on C-22 Firebrick at room temperature). 1,2-Butadiene and 2,4-dimethyl-2,3-pentadiene were purchased from Aldrich Chemical Co. and found to be of greater than 98% purity (glpc). 2,3-Pentadiene and 1,2-cyclononadiene were prepared by a previously described method.[11,12]

A Typical 4,4,6-Trimethyl-1,3,2-dioxaborinane–Allene Reaction. In a glass ampoule was placed 4.23 g (0.105 mol) of allene and 6.7 g (0.052 mol) of 4,4,6-trimethyl-1,3,2-dioxaborinane along with 2 ml of anhydrous ether as a catalyst. The ampoule was sealed at −78° and placed in a bomb for 25.5 hr at 130°. The contents of the ampoule was distilled to give 2.05 g (25%), bp 82-84° (22 mm), o-monoadducts and 1.7 g (22%), bp 96-99° (0.15 mm), of an unf identified but presumed diadduct. The lower boiling material was examined by glpc on a 5 ft × 25 in. silicone nitrile (XF 1150) column on Chromosorb W (60–80 mesh) isothermally at 75° with a flow rate of 40 ml/min to give two products in the ratio 86.5:13.5. Another experiment without ether present as a catalyst gave a 33% yield of monoadducts in the same ratio. Preparative glpc was performed using a 20 ft × $^3/_8$ in. silicone nitrile column at 100° with a flow rate of *ca.* 150 ml/min. Samples of 100 μl allowed separation of two pure adducts. The 86.5% product, 2-allyl-4,4,6-trimethyl-1,3,2-dioxaborinane (**1**), and that of 13.5%, 2-isopropenyl-4,4,6-trimethyl-1,3,2-dioxaborinane (**2**), were determined by infrared, nmr, and elemental analysis. See Tables I and II for pertinent physical and spectroscopic data on all the allene adducts. The excess allene gas was found (glpc) to contain no methylacetylene. Thus no isomerization of allene to methylacetylene was found under our reaction conditions.

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(10) H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, **88**, 5851 (1966).

(11) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(12) L. Skatteböl, *Tetrahedron Letters*, 167 (1961).

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^{26}D 1.4036; $\nu_{\max}^{\text{neat}}$ (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]

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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%

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(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).