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Ring cleavage rearrangement of methyl-substituted cyclopropylmethylboranes *

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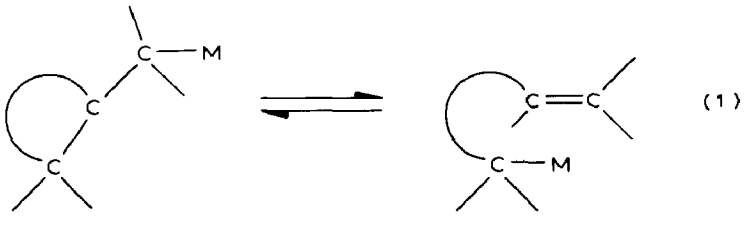
Abstract

2,2,3-Trimethyl- and 2,3-dimethylmethylenecyclopropane were prepared and hydroborated using various borane reagents. Changes in the borane solutions as a result of heating were studied by NMR and by oxidation to alcohols. Ring-cleavage rearrangement reactions were observed, analogous to rearrangements previously found for cyclopropylmethyl Grignard reagents and for unsubstituted cyclopropylmethylboranes. Methyl substitution slows the rearrangement involving cleavage of the bond to the substituted ring carbon, and has an especially large effect when *cis* to the metallomethyl group. In the 2,2,3-trimethylcyclopropylmethyl system, the ring-cleavage rearrangement does not go to completion, but instead approaches an equilibrium in which a substantial concentration of the *trans* isomer remains. Rearrangement in the 2,3-dimethylcyclopropylmethyl system occurs with retention of configuration at the ring carbon to which the boron migrates. The results of the present work suggest a mechanistic reinterpretation of the carboboration of bicyclobutane.

Introduction

Cycloalkylmethyl organometallic compounds are interconverted with open-chain unsaturated isomers in a ring-chain rearrangement equilibrium [1] (eq. 1). With cyclopropylmethyl or cyclobutylmethyl compounds, the equilibrium generally lies in the ring-opening direction, as a consequence of ring strain.



(1)

* Taken in part from the M.S. Thesis of Y.-W. Park, University of Wisconsin-Milwaukee, 1987.

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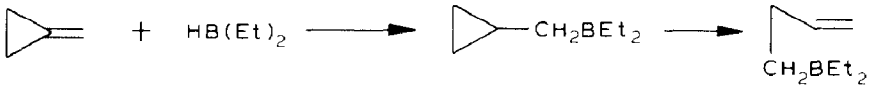
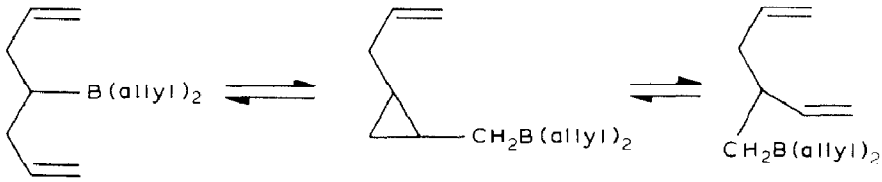
Although the most extensive studies have concerned organometallic compounds of magnesium and the more electropositive metals, there are several reports of rearrangements with boranes. Koster et al. [2] reported in 1969 that hydroboration of methylenecyclopropane with diethylborane at $-10\,^{\circ}C$ gave (cyclopropylmethyl)-diethylborane, which rearranged to (3-buten-1-yl)-diethylborane on warming to room temperature. Use of diborane gave a similar rearrangement, and addition of



(2)

pyridine was found to prevent the rearrangement. Kazanski et al. [3] have described a formal vinyl group rearrangement which most likely occurs via a cyclization-cleavage sequence (eq. 3). In several other instances, hydroboration of unsaturated cyclopropane compounds has led to products which may be explained by similar rearrangements [4–8], and cleavage of a cyclopropylmethylborane is proposed as a step in more complex reaction sequences [3,9].



(3)

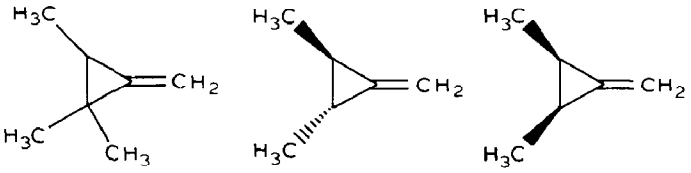
Two early reports also suggested that cyclobutylmethylboranes undergo a similar rearrangement. Brown and Zweifel [10] hydroborated methylenecyclobutane and heated the resulting solution at $160\,^{\circ}C$ with the intention of isomerizing the borane group into the ring. The yield of mono-hydroxy product obtained after oxidation was quite low, and pentanediols, obtainable from ring opening followed by a second hydroboration, were detected. Rossi and Diversi [11] detected some unsaturated product in the hydroboration of 1-methylcyclobutene, and suggested that it might arise via isomerization to a cyclobutylmethylborane, followed by ring cleavage rearrangement. On the basis of later work [12], rearrangement in the latter case seems unlikely.

In a previous study from our laboratory [12], we reported that heating of the hydroboration product from methylenecyclobutane does indeed lead to the anticipated ring-cleavage rearrangement, though quite slowly, and in competition with destructive side reactions. It was further found that the rate of rearrangement was quite similar for reaction stoichiometries corresponding to R_3B and RBH_2. Although the weak Lewis base, methyl sulfide, had little effect on the rate, an equivalent of pyridine essentially prevented reaction. Because of competing side reactions and the slow rearrangement of the cyclobutylmethyl group, we have chosen to carry out further studies with cyclopropylmethyl systems.

Results

2,2,3-Trimethylmethylenecyclopropane (**1**) and a mixture of the isomeric 2,3-dimethylmethylenecyclopropanes (**2** and **3**) were prepared by known methods [13]. Their hydroboration with a variety of reagents and the behavior of the boranes so

produced were studied by NMR and by isolation of the alcohols produced on oxidation.



(1) (2) (3)

^{13}C NMR spectra of the trialkylborane solutions were quite informative. Data from the literature [14] and spectra obtained in the present work suggest that a carbon two bonds removed from the boron appears several ppm to higher field than that in the corresponding alcohol, but down-field from the parent hydrocarbon. More remote carbons are less influenced. Olefinic carbons are shifted in the sense expected from the electronegativity of boron [15]. Carbons directly bonded to the boron are quite broadened, and were not very useful in examination of a reaction mixture. Different groups attached to the boron can produce minor variations in the shifts for a given *B*-alkyl group, leading to a fragmentation of the signal into a cluster of peaks when the same alkyl group may be present in several different borane species. This complication is absent in samples using 9-BBN (9-borabicyclo[3.3.1]nonane) for the hydroboration, since the remaining two bonds to boron are uniform. A published study of the ^{13}C NMR spectra of 9-BBN and its derivatives indicates characteristic shifts for the C(2,4,6,8) and C(3,7) positions, which are only slightly influenced by the 9-substituent [16]. ^{13}C data from the present study are summarized in Table 1, along with some relevant literature data for comparison.

The hydroboration-oxidation of **1** using 9-BBN yielded a mixture of two alcohols, in a ratio of about 93/7. These were identified as **4-OH** and **5-OH** on the basis of their proton [7] and ^{13}C NMR spectra and mass spectra [18]. As expected, the hydroboration occurred preferentially from the less hindered side, forming **4-OH** as the major product.

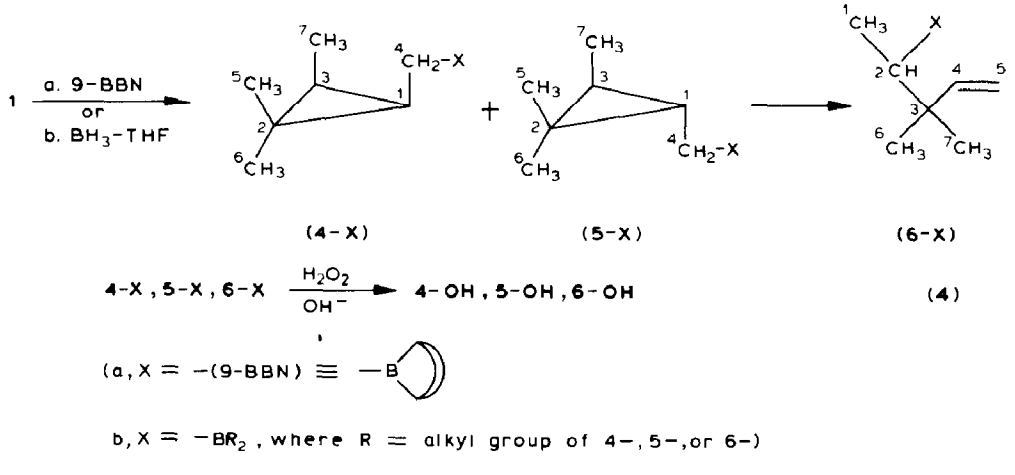


Table 1

^{13}C NMR spectra [a]

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
4-H [b]	19.71	9.96	19.71	28.98	7.86	14.13	28.98
	(19.71)	(ca. 16–22)	(19.71)	(7.86)	(14.13)	(28.98)	(7.86)
4-OH [c,d]	28.34(d)	17.94(s)	20.82(d)	60.0(t)	14.49(q)	29.01(q)	8.38(q)
4-(9-BBN) [e]	22.77(d)	16.56(s)	20.37(d)	ca. 20(b)	14.80(q)	29.23(1)	8.48(q)
4-(BR_2) [e,f]	23.72(d)	17.08(s)	20.79(d)	ca. 22.5	15.19(q)	29.65(q)	8.40(q)
	(23.52)	(17.28, 17.37)	(21.00)		(16.23, 14.26)	(29.73)	(9.39, 10.20)
5-OH [c]	33.92(d)	19.60(s)	23.22(d)	63.77(t)	[21.5, 21.6(q)] [g]		13.43(q)
5-(9-BBN) [e]	28.33	18.9(s)			[21.66, 22.02] [g]		13.86(q)
5-(BR_2) [e,f]	28.62	18.74(s)	23.0		[21.57, 21.95] [g]		13.78(q)
		(18.05, 18.90)			(22.25)		(13.00, 14.05)
10-H [h]	18.2	20.6	18.2	11.8	–	17.1	11.8
10-OH [c]	26.54	[18.15, 18.87] [f]		62.68	–	18.42	12.72
10-(BR_2) [e,f]	22.13(d)	[20.94(d), 18.36(d)] [g]			–	19.00(q)	12.96(q)
i	(22.34)	(18.48)					(13.05)
	21.98	[20.70, 18.22] [g]			–	19.07	13.05
	(22.16, 22.28)	(18.50)					(13.17)
11-H [h]	10.4	10.4	10.4	6.1	6.1	–	6.1
11-OH [c]	19.99	12.18	12.18	59.34	7.28	–	7.28
11-(Br_2) [e,f]	14.35	11.60(d)	11.60(d)		7.41(q)	–	7.41(q)
	(14.24)				(7.56)		(7.56)
i	14.2	11.50	11.50		7.48	–	7.48
		(11.60)	(11.60)		(7.64)		(7.64)
6-H [j]	8.8	35.2	36.7	148.4	110.4	26.3	26.3
6-OH [c,k]	17.56(q)	74.05(d)	41.63(s)	145.33(d)	113.28(t)	[21.63,23.22(q)] [g]	
6-(9-BBN) [e]	10.89		39.90	149.52	109.93	[26.58, 27.02] [g]	
6-(BR_2) [e,f]	10.28		39.28(s)	149.16(d)	110.02(t)	[26.58, 27.02] [g]	
	(9.85, 10.20)			(149.29)	(109.84, 110.58		
12-H [l]	11.7	29.7	39.8	144.7	112.6	19.8	–
12-OH [m]	20.16	70.85	45.95	140.66	116.18	15.98	–
12-(BR_2) [e,f]	11.74		40.80(d)	146.13(d)	111.87(t)	18.65	–
			(40.85)			(18.51)	
i	11.77		40.66	146.15	111.84	18.70	–
	(11.85)		(40.60, 40.40)	(146.36, 146.05)	(111.90, 111.98)	(18.50)	

[a] Run at 62.9 MHz; multiplicities are for SFORD spectra; values are omitted where uncertain due to overlap. See text for numbering. [b] Ref. 31e; reported shifts do not seem rational in relationship to other data; estimates based on other methylcyclopropanes [31] and on **4-OH** are more consistent with assignments in parentheses. [c] $CDCl_3$/TMS. [d] Assignments assisted by proton–carbon correlation spectrum. [e] THF (C_6D_6 = 128.0). [f] Minor peaks of cluster in parentheses; in some cases relative intensitities change on heating. [g] Assignment of close-lying peaks enclosed in brackets is uncertain. [h] Ref. 31h. [i] Same, in CH_2Cl_2 (C_6D_6 = 128.0). [j] Ref. 35, no. 19522. [k] Ref. 19 reports the following shifts: 17.58, 73.99, 41.50, 145.32, 112.91, 21.91, 22.95. [l] Ref. 35, no. 11635. [m] Ref. 20 lists the following shifts for *threo*: 20.5, 71.0, 45.6, 141.4, 114.8, 15.3; for *erythro*: 19.8, 70.8, 45.3, 141.2, 114.4, 15.9.

The ^{13}C NMR spectrum of the reaction mixture from **1** and a slight excess of 9-BBN had several strong resonances which were readily assigned to the borane **4-(9-BBN)**. These underwent little change with heating up to 6 d at 80–90 °C. Several minor peaks in the spectrum were reduced in intensity after 4 h at 52 °C and disappeared completely after 12 h at 60 °C; these may reasonably be assigned to the minor borane isomer **5-(9-BBN)**. No olefinic carbon resonances were seen, because the intitial rearrangement product **6-(9-BBN)** should react with the excess of 9-BBN. However, some minor new peaks did appear, which were subsequently assigned to products of further hydroboration (see below). Approximate compositions of the reaction mixture as estimated from the ^{13}C NMR spectra are listed in Table 2A.

A similar solution prepared with a slight excess of alkene was heated at 85 °C with periodic observation of the ^{13}C NMR spectrum. On short heating, weak olefinic resonances of **6-(9-BBN)** appeared and resonances assigned to **5-(9-BBN)** disappeared. With longer heating both increased, in a ratio of about 2.5/1 to 3/1, at the expense of **4-(9-BBN)**. The approximate composition of the mixture at various times is listed in Table 2. The oxidation product also contained a small amount (ca. 3%) of the tertiary alcohol isomer **7-OH**; however, its significance is uncertain (see Discussion section). NMR signals of the excess **1** decreased by a factor of about 3 during the 1400-h period of heating.

Table 2

Composition of mixtures from heating of solutions from hydroboration of **1** [a]

A. Excess 9-BBN with **1**

R	0 h	4 h, 52 °C	12 h, 60 °C	12 h, 85 °C
4-	0.92, 0.93 [b]	0.88	0.9	0.91
5-	0.08, 0.07 [b]	0.05	0.0	0.00
[d]		0.07	0.1	0.09

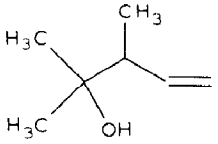
B. 9-BBN with excess **1**. Time (h) at 85 °C

R	0	28	317	480	500	790	1400
4-	0.93	0.89	0.4	0.4	0.44, 0.57 [c], 0.57 [b]	0.36	0.21, 0.28 [c], 0.29 [b]
5-	0.04	0.00	0.1	0.15	0.18, 0.10 [c], 0.09 [b]	0.17	0.21, 0.17 [c], 0.21 [b]
6-	0.03	0.10	0.5	0.45	0.38, 0.33 [c], 0.34 [b]	0.47	0.57, 0.55 [c], 0.50 [b]

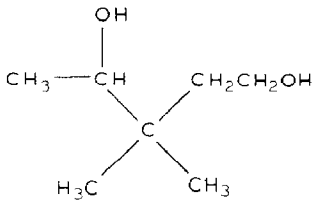
C. BH_3·THF with **1**. Time (h) at 85 °C [e]

R	0	1.2	3.4	5.5	9.9	25.3	194	434	650
4-	0.86	0.85	0.83	0.80	0.77	0.77	0.52	0.28	0.24, 0.24 [c], 0.34 [b]
5-	0.14	0.12	0.13	0.15	0.16	0.17	0.34	0.45	0.47, 0.40 [c], 0.53 [b]
6-	0.00	0.03	0.04	0.05	0.065	0.055	0.14	0.14	0.12, 0.11 [c], 0.15 [b]
[f]								0.13	0.16, 0.25 [c]

[a] From ^{13}C NMR of borane solutions, unless otherwise indicated. [b] From GC of alcohol mixture. [c] From ^{13}C NMR of alcohol mixture. [d] Probable precursors to **8** and **9** at 37.85 and 10.63 ppm and at 41.3 and 28 ppm, respectively. [e] Sums of intensities of peak clusters used to estimate relative concentrations. [f] Probable precursors to **8** and **9** at 37.19 ppm and at 40 and 28 ppm respectively.



(7-OH)



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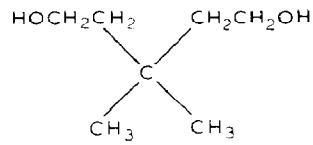
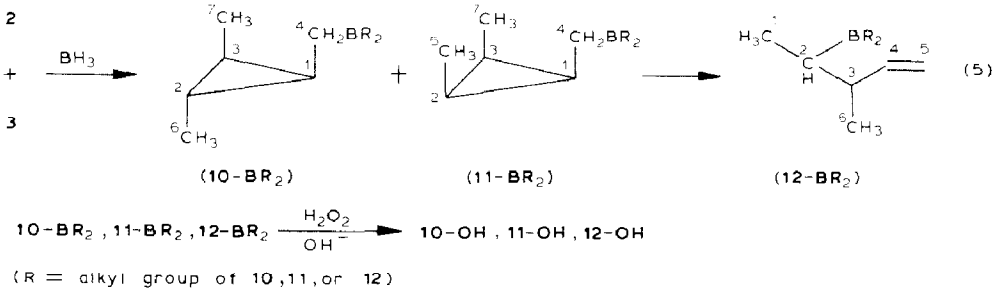


(9)

A solution prepared by hydroboration of **1** with borane-THF was also studied by ^{13}C NMR. The spectra were complicated by multiple resonances for each carbon, most probably as a consequence of the presence of mixed trialkylborane molecules. In addition to the different alkyl group structures (**4**-, **5**-, and **6**-), all of the alkyl groups are chiral, so that the environment of a given alkyl group on boron depends upon the configurations of the other attached groups. Again, olefinic resonances corresponding to the vinyl group of **6-BR$_2$** appeared after short periods of heating at 85 °C and increased more slowly thereafter, along with the resonances assigned to the minor borane isomer, **5-BR$_2$**. ^{13}C NMR assignments are listed in Table 1, and approximate analyses in Table 2C. The ring-cleaved alcohol **6-OH** was isolated after oxidative work-up at the conclusion of heating, and its structure was confirmed by comparison of NMR spectra with literature data [19]. The alcohol mixture also had several extra resonances, which were found by molecular distillation to belong to less volatile constituents. The chemical shifts were consistent with estimates for the diol structures **8** and **9**, and resonances also appeared in the last two spectra of the borane mixture which were at appropriate shifts for their borane precursors; similar minor peaks were found in the run with excess 9-BBN. The alcohol also had about 3% of **7-OH**, which was isolated and compared with an authentic sample.

Hydroboration using borane-methyl sulfide in THF also gave ^1H NMR evidence of ring-cleavage rearrangement. After heating for 2 h at 105 °C, weak resonances typical of a vinyl group attached to a quaternary carbon were observed. Their intensity increased little on further heating (up to 14 h), and corresponded to only a small fraction of the original reactant.

The mixture of *trans*- and *cis*-2,3-dimethylmethylenecyclopropanes (**2** and **3**) was hydroborated with borane-methyl sulfide solutions in THF and methylene chloride. Oxidative work-up as above produced an alcohol mixture consisting principally of **10-OH** from **2** and **11-OH** via addition to the less hindered side of **3**. There was no



(5)

(10-BR$_2$) (11-BR$_2$) (12-BR$_2$)

10-BR$_2$, 11-BR$_2$, 12-BR$_2$ $\xrightarrow[OH^-]{H_2O_2}$ 10-OH, 11-OH, 12-OH

(R = alkyl group of 10, 11, or 12)

evidence for addition to the more hindered side of **3**. With an excess of the alkene mixture in THF, the NMR of the mixture before oxidation indicated that **3** was hydroborated in preference to **2**.

When the solutions were heated for several hours at 60 °C, the ^{13}C NMR spectra clearly indicated formation of a vinyl group, and resonances assigned to *trans* borane **10-BR$_2$** decreased. Little or no decrease was seen for the *cis* borane **11-BR$_2$**. Qualitatively, the ring opening of **10-BR$_2$** appeared to occur rapidly at first, but then more slowly with further heating, as though approaching an equilibrium mixture short of completion. However, splitting of the resonances, apparently as a result of mixed borane species present, and some general deterioration of resolution with heating made it difficult to compare intensities quantitatively. The rearrangement reaction occurred at comparable rates in the two solvents, with loss of about half of the **10-(BR$_2$)** after about 8 h at 60 °C. ^{13}C NMR assignments are listed in Table 1.

Oxidative work-up after heating gave an alcohol mixture depleted in **10-OH**, and containing a new product. The latter had ^{1}H and ^{13}C NMR spectra consistent with the structure of 3-methyl-4-penten-2-ol (**12-OH**). Comparison with authentic samples showed that it was the *threo* isomer. The NMR spectra [20, 21] of the *threo* and *erythro* isomers are quite similar, and solvent dependence of the chemical shifts made it impractical to base the identification solely on comparisons with the literature. However, there were some consistent differences in the proton spectra, and the retention time of the *threo* isomer on polar GC columns is reported to be characteristically shorter [22]. A minor component appeared to be consistent with the *erythro* isomer, in an amount up to 15% as much as the *threo*.

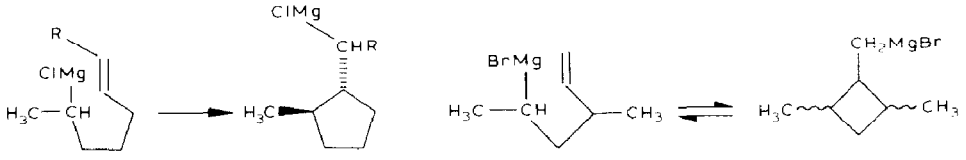
Discussion

Several conclusions may be drawn from the results of this study. First, rearrangement with cleavage of a ring bond occurs most readily if the borane produced is primary, and least readily if it is tertiary. Unsubstituted cyclopropylmethylboranes rearrange at room temperature or below to primary open-chain product (eq. 2) [2]. In contrast, the methyl-substituted analogs in eq. 4 and 5, which all rearrange to secondary open-chain boranes, require heating. Boranes **4** and **5** might rearrange to produce either the secondary ring-opened borane **6** or the tertiary isomer **7**. Little or none of the latter was formed. (A minor amount of **7** was found in two instances. However, it is not clear that its presence was significant, since it might have resulted from inadequate exclusion of air during work-up. A free radical intermediate, believed to be involved in air oxidation [23], should cleave largely to a tertiary radical).

A second conclusion is that a *cis* ring substituent has a major additional retarding effect on rearrangement toward the carbon to which it is attached. Boranes **5** and **10** each have an adjacent ring carbon without a *cis* methyl substituent. The former was largely rearranged after 12 h heating at 60 °C (see Table 2A) and the latter was half rearranged after about 8 h. In contrast, **4** and **11**, which have *cis* methyl groups on both adjacent ring carbons, did not react significantly beyond experimental error during the same periods; **4** appears to have a half-life in excess of 200 h at 85 °C.

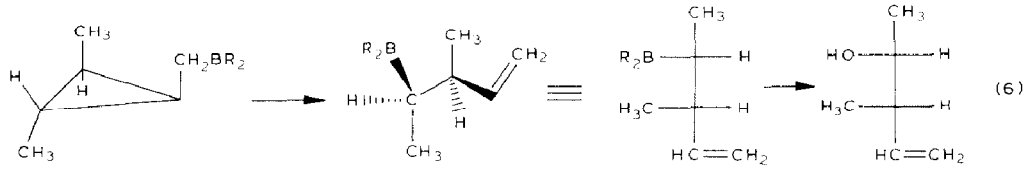
Organomagnesium ring cleavage rearrangements are similarly sensitive to substitution around the reacting centers [1,24]; in addition, cyclization/cleavage equilibria seem to be especially slow in situations involving a *cis* substituent on the ring.

For example, cyclization of **13** has a strong preference for formation of the *trans* product [25]. Heating of **14** produces an equilibrium mixture with cyclic compounds in which the all-*cis* isomer was not detected [24], and in some other examples producing four-membered rings the location of a *cis* methyl substituent may be avoided [26]. It has been proposed that the *trans* preference in cyclization may imply a preferred transition state geometry in which the carbon–metal bond is more nearly perpendicular, rather than parallel, to the carbon–carbon double bond [1b]. The same considerations may apply to the organoborane rearrangement.



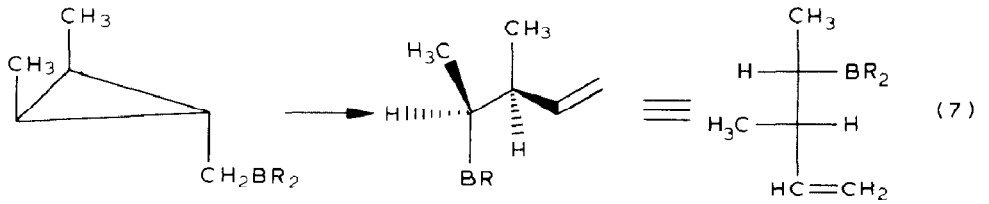
(13) (14)

A third conclusion is that the rearrangement occurs stereoselectively with retention of configuration at the ring carbon to which the boron migrates. In the rearrangement of **10**, the *threo* isomer of 3-methyl-4-penten-2-ol (**12-OH**) was formed exclusively or predominantly (> 87%) as the product of oxidation after rearrangement. Eq. 6 illustrates the formation of the *threo* isomer by cleavage of the



(6)

bond toward the *trans* methyl group. Since borane oxidation takes place with retention of configuration, this result implies that the cleavage must also occur with retention. The same isomer would be formed by cleavage of the other ring bond, but rearrangement of either of the isomers from hydroboration of **3** would form the *erythro* alcohol. A minor constituent was identified as the *erythro* isomer. It comprised about 2% of the total and 12% of the rearranged material. Its presence might indicate that the reaction of **10** is not completely stereoselective. It might also have come from the slow rearrangement of **11** or by more rapid rearrangement of a small amount of **15**, the minor hydroboration isomer from **3**, which was otherwise undetected (eq. 7).

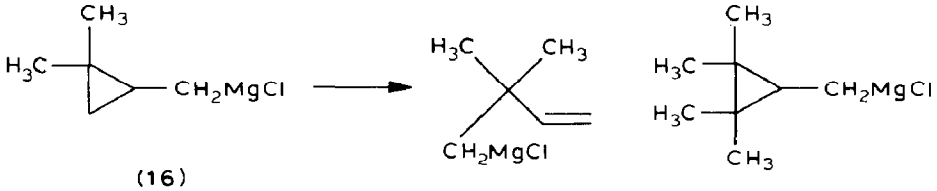


(15) (7)

A rather surprising result was the observation that the ring cleavage rearrangements with the tri-methyl compounds approach an equilibrium short of complete rearrangement. The data in Table 2 show that while **5** rapidly rearranges to **6**, **4** is then more slowly converted to a mixture of **6** and **5**, which remain in a constant

ratio. In the reaction with 9-BBN, the equilibrium between **5** and **6** appeared to favor the ring-opened isomer **6** by a margin of about 3/1, but the ratio was reversed in the reaction with $BH_3 \cdot THF$. Because of the slowness of the reaction and the semiquantitative nature of the analysis, it was not clear whether the borane **4** was approaching a significantly non-zero equilibrium concentration. In the rearrangement of **10** (from hydroboration of **2**), an apparent rapid initial burst of reaction might imply a similar situation, but present results are too rough to be certain.

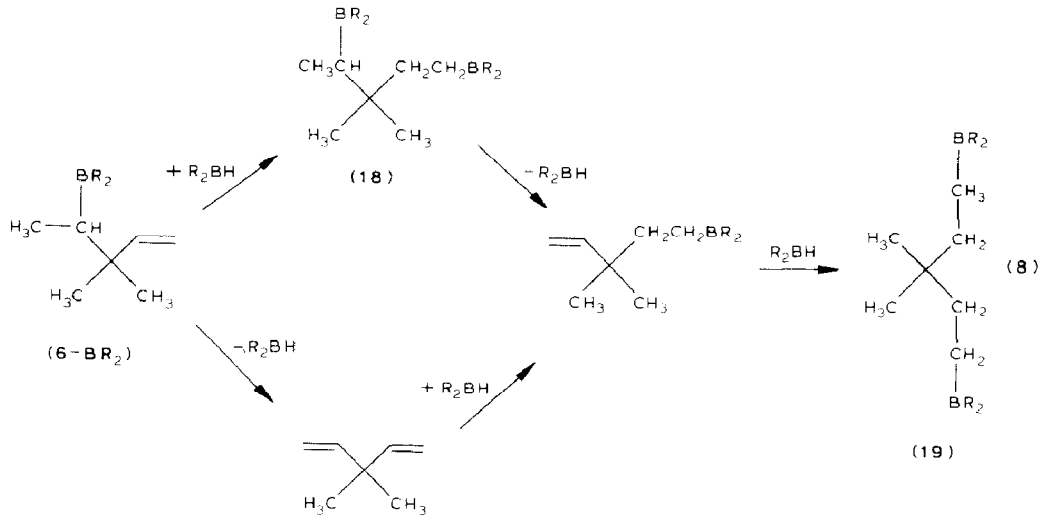
The significant equilibrium concentration of the substituted cyclopropylmethylborane may be compared with related systems. For the corresponding hydrocarbons, experimental heats of formation are not available, but molecular mechanics estimates suggest that cleavage should be exothermic by several kcal/mol. In most cyclopropylmethyl Grignard reagent cyclization-cleavage rearrangements which have been reported, the equilibrium strongly favors the ring-opened isomer in the absence of special structural features [1]. Although there appears to be no direct information on magnesium analogs of **4** or **5**, it is found that **16** is present to an extent of only 0.07% relative to its primary ring-opened isomer. However, **17**, whose open-chain isomer must necessarily be tertiary, is favored to an equilibrium extent of over 99.9% [27]. Several cyclopropylmethyl titanium compounds are reported to



(16) (17)

undergo a comparable ring cleavage [28]. The analog of **4** or **5**, along with others having *gem*-dimethyl substitution on the ring, fails to rearrange; however, the relevance to the present result is uncertain, since the lack of reaction is likely to be kinetic rather than thermodynamic. To the extent that the customary organometallic stability order, $1° > 2° > 3°$, is ascribed to the low electronegativity of the metal and consequent "carbanionic" nature of the alkyl group, we would expect that the *primary* cyclopropylmethyl structure should be more heavily favored with magnesium than with boron. It is probable, then, that steric effects play a major role. Since the alkyl group of **6** is both secondary and "neopentyl", it is likely that this group in a trialkylborane experiences very considerable steric repulsions. The congestion in **6-(9-BBN)** may be smaller that in **6-BR_2**, resulting in more complete ring-opening reaction in the former case.

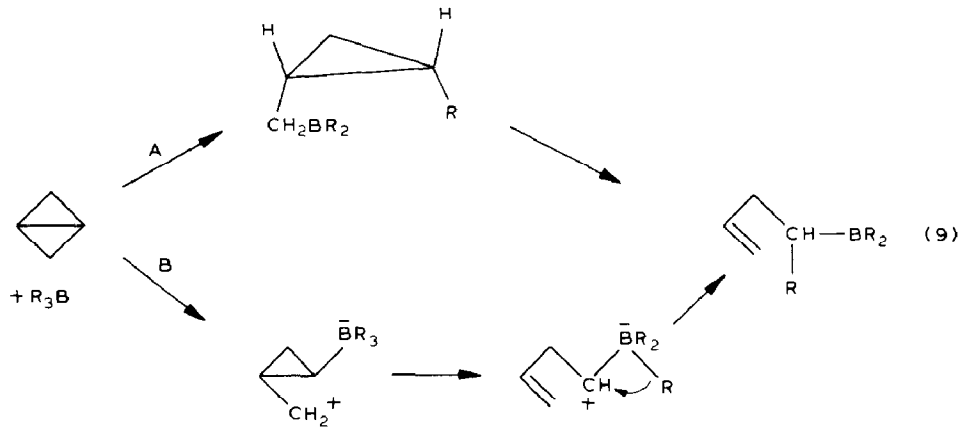
Another interesting observation in the rearrangement of **4-BR_2** and **5-BR_2** is that the product of oxidative work-up contained the diols **8** and **9**. The ^{13}C NMR spectrum of the borane solution at long heating times also had peaks reasonably attributed to **18** and **19**, the borane precursors to these diols. Diol formation in the absence of excess hydroborating agent implies that some trialkylborane present must be decomposing to alkene by elimination of a BH function. If, as suggested earlier, these boranes are quite hindered, such elimination may be sterically accelerated. The ^{13}C NMR spectra of the borane solution and the alcohol products gave no clear indication of the ultimate disposition of the alkene which formed in the generation of the necessary BH groups.



A kinetic uncertainty exists in the interconversion of boranes **4**, **5** and **6**. Are **4** and **5** equilibrated via their rearrangements, so that the rate-determining step for disappearance of **4** is its slow rearrangement to **6** (i.e. **4** → **6** ⇌ **5**)? Or is there an alternative pathway between **4** and **5** which is faster than the slow rearrangement of **4**? A possible alternative pathway may be a dehydroboration–hydroboration sequence, so that the rate-determining step for disappearance of **4** is the re-hydroboration of a small equilibrium concentration of **1** (i.e. **4** ⇌ **1** → **5** ⇌ **6**). The double of **1** should be more reactive than that of **6**, so that early in the reaction, the BH bonds produced by the dehydroboration should be efficiently scavenged by a low concentration of **1**. Later, the increased concentration of **6** would compete more effectively for the BH bonds, leading to the diol products.

A referee has pointed out that *B*-3-pinanyl-9-BBN undergoes unusually facile alkyl group-olefin exchange via dehydroboration in refluxing THF, with a half-life of less than 10 h [29]. *B-cis*-myrtanyl-9-BBN is also largely isomerized to the *trans* isomer in 4 h at 125 °C by a similar dehydroboration–hydroboration route. In other hindered instances, hydroboration product mixtures appear to result from rapid partial isomerization of the initially-produced borane under the conditions of the hydroboration [29]. Therefore, there is reasonable precedent for the isomerization of **4** to **5** by a dehydroboration–hydroboration sequence. A similar process could lead to conversion of **11** to **15**, with formation of the small amount of *erythro* alcohol when the mixture of **10** and **11** was heated.

Our observation that ring cleavage occurs preferentially toward the less-substituted ring carbon allows us to make a comment concerning the reaction of bicyclo[1.1.0]butane with organoboranes, reported earlier by Kazansky et al. [3]. One mechanism, which those authors preferred, was initial addition to a side bond of the bicyclobutane, followed by ring-cleavage rearrangement of the 2-substituted cyclopropylmethylborane thus formed (eq. 9, path A). In this mechanism, formation of the observed product would require rearrangement toward the substituted ring carbon. Furthermore, if the initial addition of the alkyl group occurs with retention of configuration, the rearrangement would have to occur toward a ring carbon with



a *cis* substituent. An additional observation by Kazansky et al. is also inconsistent with their preferred mechanism. They followed formation of the product via NMR at $-60\,^{\circ}C$ without seeing any evidence for the cyclopropylmethyl intermediate. Since Koster et al. [2] found that unsubstituted cyclopropylmethylboranes rearrange slowly below $0\,^{\circ}C$, and we find that rearrangement toward a substituted ring carbon is still slower, the intermediate in path A should have been spectroscopically observable.

We suggest that a more likely mechanism (eq. 9, path B) is a variant on another proposed in the original paper. Electrophilic attack of the boron on the bridgehead carbon of the bicyclobutane would generate a cyclopropylmethyl cation (or "incipient" cation, or bicyclobutonium ion). Homoallylic rearrangement of this cation would form a dipolar intermediate in which alkyl migration from boron to carbon should occur readily. This mechanism would further be consistent with the absence of "allylic inversion" with R = crotyl.

Experimental

NMR spectra were run on Varian Associates EM-360L and CFT-20 and Bruker WM-250 spectrometers. ^{13}C NMR assignments were assisted by single frequency off-resonance decoupling (SFORD) and carbon–proton correlation spectra, by comparison with chemical shifts estimated using additive parameters [15, 30, 31], and by analogy with published spectra of other cyclopropanes and cyclopropylmethanols [32]. The ^{13}C data are collected in Table 1. Multiplicities given were observed with SFORD. Mass spectra were obtained on a Hewlett-Packard 5985 gas chromatograph-mass spectrometer with electron impact or methane chemical ionization, using a capillary column, 0.25 mm ID × 30 m, 0.25 μm coating of 5% diphenyl/95% dimethylpolysiloxane. Gas chromatography was on Varian Aerograph A90-P3 instruments, using the following columns: A, 10′ × 1/4″, 20% Carbowax 20 M on 60/80 mesh Chromosorb P; B, 10′ × 1/4″, 15% Ucon 50-HB-5100 on 60/80 mesh Chromosorb W, AW-DMCS; C 10′ × 1/4″, 10% Ucon 50-HB-2000 on 60–70 mesh Chromosorb W, AW-DMCS. Boiling points are uncorrected.

Borane reagents were purchased from the Aldrich Chemical Company and used without further treatment. In some cases, purity and concentration were determined by hydrolysis and gas volume measurement [33]. Tetrahydrofuran was purified by reflux and distillation under nitrogen from benzophenone ketyl. Reactions were run under a nitrogen atmosphere, using glassware and transfer syringes which had been oven-dried. Tubes for heating or storing borane solutions were dried, connected with a short length of Tygon tubing to a manifold, evacuated, refilled with nitrogen, loaded by syringe through an opening on the top of the manifold, and sealed under a slight negative pressure. In some cases, screw-capped, septum-sealed NMR tubes were used.

2,2,3-Trimethylmethylenecyclopropane (1)

1-Chloro-1,2,2,3-trimethylcyclopropane was prepared from 2-methyl-2-butene and 1,1-dichloroethane with butyllithium via the procedure of Arora and Binger [13]. Product was obtained in 41% yield; b.p. 114–115 °C (lit. 116 °C [13]); 2/1 mixture of stereoisomers by GC on column C. This was dehydrochlorinated with potassium t-butoxide in dimethyl sulfoxide by a modification of the procedure of Arora and Binger [13], using a 200% excess of the base. The product was obtained in 70% yield; b.p. 74–76 °C (lit. 75 °C [13]); ^{13}C and ^{1}H NMR spectra identical to literature spectra [34]. Because of the similar boiling points of product and t-butyl alcohol, modifications were explored using sodium t-amyloxide [35] as base. These offered no advantage in obtaining an easily-purified product. Little contamination by the alcohol was found when a large excess of potassium t-butoxide was used.

2,3-Dimethylmethylenecyclopropane (2 and 3)

1-Chloro-1,2,3-trimethylcyclopropane was prepared from 2-butene and 1,1-dichloroethane with butyllithium [13] in 24% yield. Dehydrochlorination [13] as in the preceding preparation produced a 76% yield of product, which was found by GC (column C) to consists of two components in a ratio of 2.5/1. The ^{13}C NMR spectrum had resonances corresponding to published spectra [34a] of the *trans* and *cis* isomers, with the former predominating.

Hydroboration reactions of 1

A. A sample of **1** (0.96 g, 10 mmol) was added to 9-borabicyclo[3.3.1]nonane (9-BBN, 1.34 g, 11 mmol) and 10 ml of THF, maintained below 25 °C. After stirring for 2 h at room temperature, the reaction was worked up by addition of 4 ml of 3 *M* NaOH followed by 5 ml of 30% hydrogen peroxide (dropwise, with cooling below 30 °C on an ice bath), stirring for 1 h, addition of 7 ml of water, and saturation with K_2CO_3. After separation of the organic layer, the aqueous phase was extracted twice with 15 ml of ether, and the combined organic phase was dried over $MgSO_4$ and distilled under vacuum. The distillation residue consisted largely of 1,5-cyclooctanediol (NMR [36]). The distillate consisted of two components in a ratio of 7/93 (in order of elution, GC column C), which were separated preparatively; major isomer (**4-OH**): ^{1}H NMR ($CDCl_3$): δ3.71 (b, 1H, O*H*), 3.62 (2H, AB part of ABX spectrum, J_{AB} 11.3, δ_{AB} 9.4, J_{AX} 7.25, J_{BX} 7.5 Hz; d, J 6.5 Hz at 60 MHz, CH_2OH), 1.06 (s, 3H), 0.98 (d, J 6.5 Hz, 3H), 0.97 (s, 3H) and 0.63–0.86 ppm (m, 2H, J_{AB} 8.7, δ_{AB} 0.10 ppm, J_{AX3} 6.45, J_{BY2} 7.2 Hz); MS (EI, 15v), *m/e* (*I*): 99(3), 96(6), 85(5), 84(7), 83(100), 81(16), 79(6), 71(49), 70(11), 69(3), 67(3), 59(61), 55(62)

(lit. [18]); minor isomer (**5-OH**): ^{1}H NMR ($CDCl_3$): δ4.0 (b, O*H*), 3.4–3.8 (m, CH_2), 1.08 (s,3), 1.05 (s,3), ca. 1.04 (d, partly obscured), ca. 0.5 ppm (m); MS: same as major isomer. ^{13}C NMR spectra of both isomers are in Table 1.

B. In a similar preparation, the ^{13}C NMR spectrum of the hydroboration solution was observed shortly after mixing, and after periods of standing or heating (with 10% C_6D_6 as lock and reference). Before addition of alkene, the 9-BBN had peaks at 33.58 (t, C(2,4,6,8)) and 24.24 ppm (t, C(3,5)); minor oxidation or hydrolysis impurity was seen at 33.77 and 23.63 ppm. On addition of alkene, the corresponding peaks for 9-alkyl-9-BBN derivatives were seen at 33.50 and 23.73 ppm (lit. [16]). The major hydroboration product (**4-(9-BBN)**, see Table 1) was assigned to chemical shifts of the principal new peaks in the spectrum. A number of minor peaks were also present. Several of these (75.62, 34.82, 31.97, 27.86 and 23.08 ppm) were also present before addition of the alkene, and changed little over the course of the experiment. Little change was seen in the peaks assigned to **4-(9-BBN)** over heating periods up to 12 h at 80–90 °C, but some minor peaks which decreased or disappeared after 12 h at 60 °C were assigned to **5-(9-BBN)**. New weak resonances appeared at 10.63, 30.18, 37.85 and about 40 ppm as those decreased, but no olefinic resonances were seen, and little further qualitative change was noted after heating times up to over 100 h at 85 °C. (Minor unassigned resonances at 70.13 and 31.47 ppm persisted.) Semiquantitative analyses from the NMR spectra are listed in Table 2A.

C. A reaction mixture from 11 mmol of **1** and 9.5 mmol of 9-BBN in 8 ml of THF (10% C_6D_6 lock/reference) was sealed into two 10-mm NMR tubes, and ^{13}C NMR spectra were run after periods of heating at 85 °C. Resonances assigned to **6-(9-BBN)** were detected after several hours' heating, but increased slowly thereafter. Semiquantitative analyses based on the NMR spectra and the GC of the alcohols are listed in Table 2B. Both alcohol mixtures contained about 3% of an additional component. This was identified as **7-OH** by comparison of the GC retention time and the ^{1}H NMR of an isolated sample with those of the authentic material prepared by addition of crotylmagnesium chloride to acetone.

D. A nitrogen-filled 10-mm NMR tube was charged with 7.5 mmol of **1**, 2.5 ml of a 1 *M* borane·THF solution and 0.4 ml of C_6D_6, and sealed. The ^{13}C NMR spectrum was observed after periods of heating at 85 °C. The alcohols **4-OH, 5-OH,** and **6-OH** were isolated by preparative GC after oxidative work-up. The latter was identified by comparison of ^{1}H and ^{13}C NMR spectra with published data [19]. At long heating times, the borane spectrum developed significant resonances at about 40, 37.40, 37.19, 28, and possibly at 31 and 22.9 ppm. A residue from molecular distillation of the alcohol mixture appeared to consist of two principal components with resonances at 74.2, 59.2, 42.0, 37.43, 25.0, 23.5 and 17.8, and at 59.7, 44.35 and 28.11 ppm, respectively. Estimated chemical shifts [30] for **8** and **9** are 75, 57, 39, 36, 21.5 (2C), and 16.8 ppm and 56.8, 43.9, 27.9, and 26.4 ppm respectively. Estimated shifts for the boranes **18** and **19** are 38, 32, 25, 23.5 and 14 ppm, and 40, 28, and 28 ppm. In Table 2C, semiquantitative analyses of the borane and alcohol spectra are listed. In addition, the alcohol product contained about 3% of **7-OH** (GC).

E. In a 5-mm NMR tube, 1.5 mmol of **1** was combined with a 1 *M* commercial solution of borane-methyl sulfide in THF until the olefinic proton resonance of the alkene had nearly disappeared. Little change in the spectrum was observed over a period of 20 h at room temperature, but on heating to 105 °C, new multiplets

appeared at 4.7–5.3 and 5.65–6.15 ppm. The latter was a doublet of doublets, with J 9.5 and 17.5 Hz. The new signals corresponded to a maximum of about 10% of the reactant, and were about half this intensity after 2 h.

Hydroboration reactions of 2 and 3. *A.* Samples of **2** + **3** (about 4.5 mmol) were treated with borane-methyl sulfide solutions (1 *M*, about 1.5 ml) in methylene chloride and in THF in septum-capped NMR tubes (containing about 10% C_6D_6 as lock/reference). ^{13}C NMR spectra were run after heating at 60 °C for various periods of time. Resonances assigned to hydroboration products **10-(BR_2)** and **11-(BR_2)** and the rearrangement product **12-(BR_2)** are listed in Table 1. In the THF reaction, an excess of the mixture of **2** and **3** was used; the spectrum after hydroboration showed that the alkene remaining was 90% **2**, and the concentration remained unchanged through the heating. Some additional minor changes in the spectra were evident, but more detailed interpretation was hampered by multiple resonances (see Results section).

B. To 7 ml of 1 *M* borane-methyl sulfide in THF, cooled in an ice bath, was added 1.15 g (14 mmol) of the mixture of **2** and **3**. After stirring for 45 min, the reaction was worked up as described for **1** and distilled under vacuum. The two major constituents, appearing in a ratio of about 5/2, were isolated by GC (columns A and B) and identified spectroscopically as **10-OH** and **11-OH**, in order of increasing retention time. ^{13}C NMR spectra had, respectively, six and four resonances, with appropriate chemical shifts (see Table 1). The ^1H NMR spectrum of the former had resonances sufficiently separated for complete analysis ($CDCl_3$, 250 MHz): CH_2OH as the AB portion of an ABX pattern (δ_A 3.67, δ_B 3.45 ppm, J_{AB} 11.25, J_{AX} 6.50, J_{BX} 8.50 Hz); O*H* at 1.88 (s); methyl groups at 1.028 (d, J 6.26 Hz, *cis*) and 0.992 ppm (d, J 5.97 Hz, *trans*); and ring methine protons at 0.725 (C_1H), 0.571 (C_3H, with *cis*-methyl) and 0.264 ppm (C_2H, with *trans*-methyl), with $J_{1,2}$ 4.75, $J_{1,3}$ 8.50 and $J_{2,3}$ 5.25 Hz, and coupling to adjacent methyl or methylene groups as reported above (Lit. [37]: 60 MHz spectrum reported with methyls at 1.12 and 1.02 ppm, J 1.6 and 2.6 Hz). The latter had δ3.63 (d, J 7.1 Hz, CH_2OH), 1.46 (s, O*H*), and 0.95 ppm (m); coincidence of methyl and ring methine groups precluded more complete analysis; MS, m/e(*I*), EI (15 V): 100(0.7), 85(6), 83(4), 82(4), 81(2), 71(45), 69(23), 67(24), 57(14), 56(100), 55(9); CI: 101(0.4), 99(1.5), 84(7), 83(100), 81(3), 56(4), 55(8) for **11-OH**; similar intensities for **10-OH**. A minor GC fraction (ca. 7%) was isolated in insufficient amount of characterize; its ^{13}C and ^1H NMR spectra indicated no double bond, and were inconsistent with the oxidation product from **13**. Two other minor shoulders ($\leq 3\%$) were not isolated.

The combined product from the two NMR runs was worked up in similar fashion. The GC had a new important component of shorter retention time, a reduced amount of **10-OH**, and a number of minor new peaks ($\leq 5\%$) which could not be isolated in sufficient amount to characterize. The three major components were isolated, and two were shown to have NMR spectra and GC retention times identical with **10-(OH)** and **11-(OH)** from the unheated reaction. The new component had NMR spectra consistent with the literature for **12-OH** [20, 21]. An authentic sample was prepared by routine Grignard synthesis from crotylmagnesium chloride and acetaldehyde, and the stereoisomers were chromatographed preparatively. The component from the hydroboration reaction was identical in retention time and spectroscopically with the *threo* isomer; ^1H NMR ($CDCl_3$, 250 MHz): δ 5.79–5.64 (m, J 17.9, 9.75 and 8.25 Hz, $=CH$), 5.15–5.06 (m, 2H,

$=CH_2$), 3.54 (quintet, J 6.37 Hz, $CHOH$), 2.11 (sextet, av. J 7.1 Hz, CH), 1.7 (broad, OH), 1.16 (d, J 6.5 Hz, CH_3), 1.00 ppm (d, J 6.89 Hz, CH_3). A minor GC component had retention time similar to the *erythro* isomer and to the minor (7%) component from the unheated reaction. It was collected with the *threo* isomer. The spectrum of the fraction had weaker ^1H NMR signals corresponding to the *erythro* isomer; both GC and NMR were consistent with a ratio of *erythro*/*threo* = 1/7 or less.

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References

1 For reviews, see (a) E.A. Hill, J. Organomet. Chem., 91 (1975) 123; (b) E.A. Hill in F.G.A. Stone and R. West (Eds.), Advances in Organometallic Chemistry, Vol. 16, Academic Press, New York, 1977, p. 131; (c) C.M.J. Stirling, Chem. Rev., 78 (1978) 517.
2 R. Koster, S. Arora, and P. Binger, Angew. Chem. Int. Ed. Engl., 8 (1969) 205.
3 B.A. Kazanski, Y.N. Bubnov, S.V. Zotova, N.M. Abramova, V.G. Kiselev, and B.M. Mikhailov, Tetrahedron Lett., (1974) 567.
4 P. Pesnelle and G. Ourisson, J. Org. Chem., 30 (1965) 1744.
5 W. Cocker, P.V.R. Shannon, and P.A. Staniland, J. Chem. Soc. C, (1967) 915.
6 D. Dopp, Chem. Ber., 102 (1969) 1081.
7 E. Breuer, E. Segall, Y. Stein, and S. Sarel, J. Org. Chem., 37 (1972) 2242.
8 A.T. Bottini and L.J. Cabral, Tetrahedon, 34 (1978) 3195.
9 R.E. Merrill, J.L. Allen, A. Abramovitch, and E. Negishi, Tetrahedron Lett., (1977) 1019.
10 H.C. Brown and G. Zweifel, J. Am. Chem. Soc., 89 (1967) 561.
11 R. Rossi and P. Diversi, Tetrahedron, 26 (1970) 5033.
12 E.A. Hill, P.A. Nylen, and J.H. Fellinger, J. Organomet. Chem. 239 (1982) 279.
13 S. Arora and P. Binger, Synthesis, (1974) 801.
14 B. Wrackmeyer, Progress in NMR Spectroscopy, Vol., 12, Pergamon Press, London, 1979, p. 227; C.D. Blue and D.J. Nelson, J. Org. Chem., 48 (1983) 4538; J.A. Soderquist and M.R. Najafi, J. Org. Chem., 48 (1983) 4538; J.A. Soderquist and M.R. Najafi, J. Org. Chem., 51 (1986) 1330.
15 E.A. Hill and H.R. Guenther, Org. Magn. Reson. 16 (1981) 117.
16 H.C. Brown and J.A. Soderquist, J. Org. Chem., 45 (1980) 846.
17 P.S. Wharton and T.I. Bair, J. Org. Chem., 30 (1965) 1681.
18 J.D. Fourneron, L.M. Harwood, and M. Julia, Tetrahedron, 38 (1982) 693.
19 P.K. Jadhav, K.S. Bhat, P.T. Perumal, and H.C. Brown, J. Org. Chem., 51 (1986) 432.
20 A. Gambaro, D. Marton, V. Peruzzo, and G. Tagliavini, J. Organomet. Chem., 226 (1982) 149.
21 R.W. Hoffmann and H.-J. Zeiss, J. Org. Chem., 46 (1981) 1309; P.A. Bartlett and K.K. Jernstedt, J. Am. Chem. Soc., 99 (1977) 4829.
22 H. Felkin, Y. Gault, and G. Roussi, Tetrahedron Lett., (1981) 2895.
23 H.C. Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca, N.Y., 1972, pp. 320–321, 410–412, 425–441.
24 E.A. Hill and M.M. Myers, J. Organomet. Chem., 173 (1971) 1.
25 H.G. Richey, Jr. and H.S. Veale, Tetrahedron Lett., (1975) 615; W.C. Kossa, Jr., T.C. Rees, and H.G. Richey, Jr., Tetrahedon Lett., (1971) 3455.
26 H. Lehmkuhl, D. Reinehr, D. Schomburg, G. Henneberg, D. Damen, and G. Schroth, Liebigs Ann. Chem., (1975) 615; J. Kang, Organometallics, 3 (1984) 525.
27 A. Maercker, P. Güthlein, and H. Wittmayr, Angew. Chem. Int. Ed. Eng., 12 (1973) 774.
28 H. Lehmkuhl and S. Fustero, Liebigs Ann. Chem., (1980) 1361.

29 M.M. Midland, J.E. Petre, S.A. Zderic, and A. Kazubski, J. Am. Chem. Soc., 104 (1982) 528.
30 R.M. Silverstein, G.C. Bassler, and T.C. Morrill, Spectrometric Identification of Organic Compounds, 4th Ed., Wiley, New York, 1981, pp. 249–303.
31 R. Touillaux, M. Van Meersche, J.M. Dereppe, G. Leroy, J. Weider, and C. Wilante, Org. Magn. Reson. 16 (1981) 71.
32 (a) N.C. Rol and A.D.H. Clague, Org. Magn. Reson., 16 (1981) 187; (b) E.T. Chukovskaya, V.I. Dostovalova, A.A. Kamyshova, and R.K.J. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1801; (c) M. Barfield, E.C. Canada, Jr., D.R. McDaniel, Jr., J.L. Marshall, and S.R. Walter, J. Am. Chem. Soc., 105 (1983) 3411; (d) P. Brun, J. Casanova, J. Hatem, E.-J. Vincent, B. Waegell, and J.-P. Zahra, C.R. Seances Acad. Sci., Ser. C, 288 (1979) 201; (e) M. Brookhart, J.R. Tucker, and G.R. Husk, J. Am. Chem. Soc., 105 (1983) 258; (f) C.H. DePuy, P.C. Funfschilling, A.H. Andrist, and J.M. Olson, J. Am. Chem. Soc., 99 (1977) 6297.
33 H.C. Brown, G.W. Kramer, A.B. Levy, and M.M. Midland, Organic Synthesis via Boranes, Wiley, New York, 1976, pp. 239–250.
34 (a) R.J. Crawford, H. Tokunaga, L.M.H.C. Schrijver, J.C. Godard, and T. Nakashima, Can. J. Chem., 56 (1978) 992; (b) W. von der Saal, W. Risler, J. Stawitz, and H. Quast, J. Org. Chem., 48 (1983) 2374.
35 J.M. Conia, Bull. Soc. Chim. France, (1950) 537.
36 Sadtler Standard Carbon-13 NMR Spectra, Sadtler Research Laboratories, Philadelphia, PA, no. 5523.
37 J. Nishimura, N. Kawabata, and J. Furukawa, Tetrahedron, 25 (1969) 2647.