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RING CLEAVAGE REARRANGEMENT OF CYCLOBUTYLMETHYL-BORANES *

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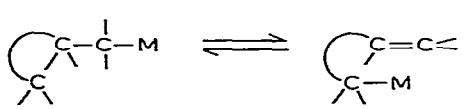
Summary

Boranes derived from hydroboration of methylenecyclobutane with borane/THF, 9-borabicyclo[3.3.1]nonane, and borane-methyl sulfide rearranged on heating in situ at 100—160°C to open chain structures. Products after oxidation were the unrearranged cyclobutylmethanol, and 4-penten-1-ol, 1,4-pentanediol and 1,5-pentanediol. The unsaturated alcohol was the major product in reactions with a stoichiometric ratio of alkene to BH bonds, and the diols were formed with excess borane. With borane-methyl sulfide as hydroborating reagent, the rate of rearrangement at 100°C in triglyme was not significantly dependent upon the initial alkene/borane ratio (3/1 or 1.15/1) or the presence of excess methyl sulfide. However, an equivalent amount of pyridine prevented rearrangement. Rearrangement in THF using borane/THF also occurred at comparable rates in the presence and absence of excess borane. Little or no isomerization of the boron function into the cyclobutane ring was observed. Results are interpreted on the basis of a concerted four-center mechanism which requires a vacant boron orbital.

Introduction

A substantial variety of ring cleavage or cyclization rearrangements involving cycloalkylmethyl organometallic compounds have been reported [1] (eq. 1).



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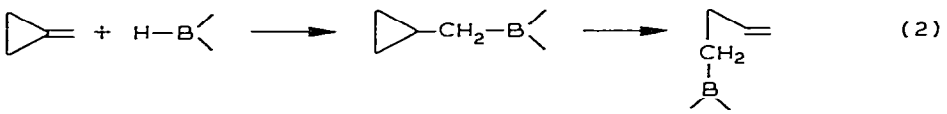
* Taken in part from the M.S. Thesis of Patricia A. Nylen, University of Wisconsin, Milwaukee, 1980. Reported in preliminary form at the 181st American Chemical Society National Meeting, Atlanta, Georgia, 1981, No. ORGN-62.

In the case of cyclopropylmethyl or cyclobutylmethyl systems, ring-strain considerations usually dominate, so that this equilibrium lies in the ring-opening direction.

Organomagnesium compounds have been studied in the greatest detail, but similar rearrangements are found for a number of other metals. In particular, Koster, Arora and Binger [2] reported in 1969 that ring-opened products were obtained on hydroboration of methylenecyclopropane with diborane or diethylborane (eq. 2). In the latter case, hydroboration at −10 to 0°C gave (cyclopropylmethyl)diethylborane, which rearranged at room temperature to (3-



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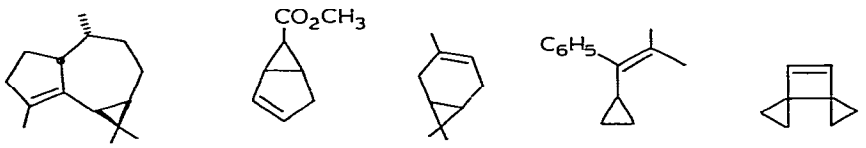
buten-1-yl)diethylborane. Pyridine was reported to prevent rearrangement. Similar cyclopropylmethyl group ring cleavages have been reported [3—7] in the hydroborations of compounds **1**—**5** (In the cases of compounds **1**—**3**, a direct 1,4-BH addition to a vinylcyclopropane was proposed, rather than rearrangement of a cyclopropylmethylborane). In addition, cleavage of a cyclo-

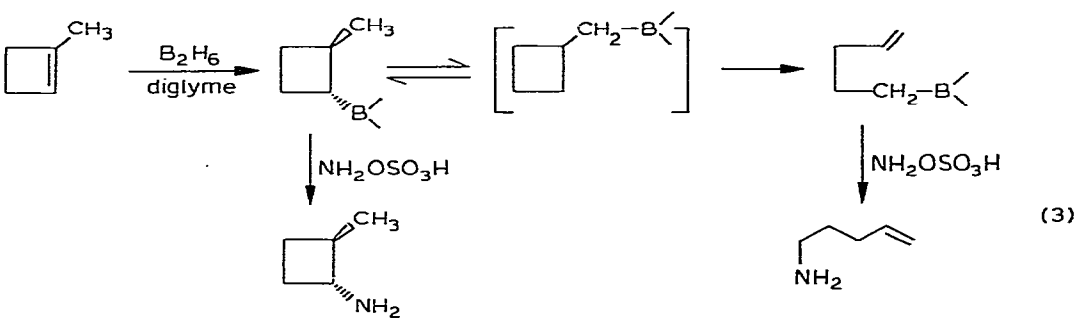


(1) (2) (3) (4) (5)

propylmethylborane is proposed as a step in some more complex reaction sequences [8,9].

Two results, both appearing only in footnotes, suggest similar ring cleavages in cyclobutylmethylboranes. Brown and Zweifel, in a 1967 study of borane isomerization [10], heated the solution resulting from hydroboration of methylenecyclobutane. They found only a low yield (22%) of alcohols after oxidation. However, the presence of some 1,5-pentanediol in the aqueous phase suggested that ring opening and further hydroboration might have occurred (see Scheme 1, formation of products 6, 7 and 9).

Rossi and Diversi, in 1970, reported the hydroboration of 1-methylcyclobutene [11]. Side products with apparent olefinic ^{1}H NMR signals led them to postulate isomerization followed by ring cleavage (eq. 3).



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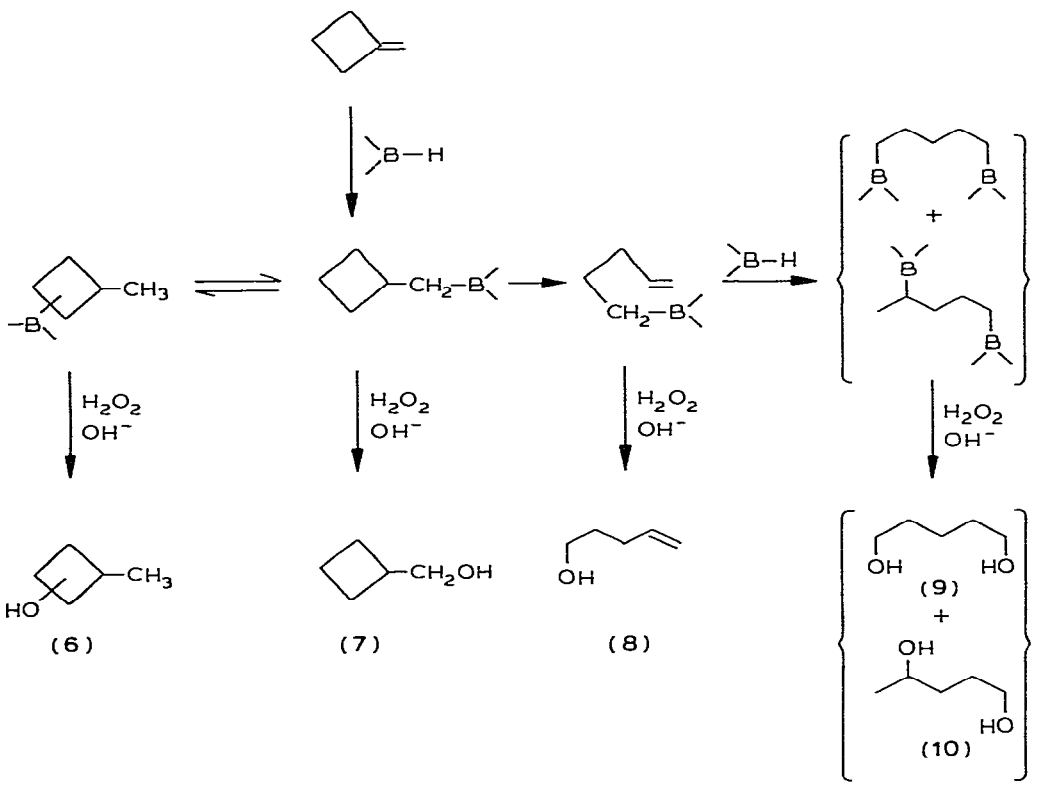
SCHEME 1



We have initiated a study of the ring cleavage rearrangements of cycloalkylmethylboranes. Major goals of this research are to examine the parallel between organoboron and organomagnesium derivatives and to explore the effect of solvent on these rearrangements. In this paper, we report the rearrangement of boranes produced by hydroboration of methylenecyclobutane.

Results and discussion

A number of systems were explored to determine their suitability for more detailed mechanistic studies. Our initial hope was that rearrangement of the product from hydroboration of methylenecyclobutane with 9-borabicyclo-[3.3.1]-nonane (9-BBN) would be clean and conveniently rapid. The incorporation of two of the three carbon—boron bonds into the stable bicyclic ring system was expected to simplify interpretation of results.

NMR samples were prepared by reaction of equivalent amounts of methylenecyclobutane and 9-BBN in benzene and in THF. No olefinic proton NMR resonances could be detected in the benzene solution after heating for up to 5 days at 130°C, although some change in the envelope of aliphatic hydrogens was apparent. In the THF solution, a typical vinyl coupling pattern appeared, and increased with heating over several days. Oxidative work-up without heating produced a good yield of cyclobutylmethanol. After heating at tempera-

tures between 100 and 130°C in THF, solutions prepared with an equivalent or slight excess amount of the borane yielded also the rearranged products 4-penten-1-ol and 1,5-pentanediol. The same products were also found after 4 h reflux in diglyme (160°C), but the solvent interfered with quantitative GC analysis of the products. After heating 96 h at 110°C and oxidation, a sample with a two-fold excess of 9-BBN in THF yielded 30% of cyclobutylmethanol and 59% of 1,5-pentanediol. No rearrangement was found after 48 h reflux in THF. In most of these experiments, cyclooctanone and cyclooctanol were also found in amounts ranging up to about 20% of the original borane. Because of the vigor of the conditions required for rearrangement, 9-BBN was abandoned in favor of other hydroborating agents.

A number of preliminary experiments established that rearrangement occurred in a similar fashion at temperatures between 100 and 160°C using borane-methyl sulfide for the hydroboration. A series of three kinetics experiments were carried out using this reagent in triglyme, followed by heating in sealed tubes at 100°C. Results of these are listed in Table 1.

In the first run, alkene and borane were used in the stoichiometric 3/1 ratio, so that the rearranging species should be a trialkylborane with no excess BH bonds present. Products isolated were cyclobutylmethanol, 4-penten-1-ol, and 1,4- and 1,5-pentanediols. Table 2 shows the variation in product composition with time. Methyl sulfide and its oxidation products dimethyl sulfoxide and dimethyl sulfone were also present in varying amounts. The formation of diols requires some elimination of alkene to free the necessary additional BH bonds. This result is consistent with decreasing alcohol yields at longer times; there was also indication of an increase in a low-boiling component with retention time appropriate for a C_5 hydrocarbon, but it was not determined quantitatively. It is also possible that some diene was formed and polymerized. A first order plot of the fraction of unrearranged cyclobutylmethanol in the products was satisfactorily linear through four days (about 75% reaction). However, points for 8 and 16 days fell above the line, with the yield of cyclobutyl-

TABLE 1

KINETICS OF REARRANGEMENT OF ORGANOBORANES PREPARED FROM HYDROBORATION OF METHYLENECYCLOBUTANE WITH BORANE-METHYL SULFIDE [a]

Reactants (*M*)					
Methylene-cyclobutane	$BH_3 \cdot S(CH_3)_2$	other	*n* [b]	% [c]	$10^6 k(sec^{-1})$ [d]
0.88	0.29	—	7 [e]	76	4.2 ± 0.2
0.84	0.73	—	6 [f]	88	3.45 ± 0.1
0.80	0.69	$(CH_3)_2S$, 0.69	5	95	4.5 ± 0.2
0.80	0.69	pyridine, 0.69	3	— [g]	— [g]

[a] Borane solutions were prepared at room temperature in 6 ml of triglyme. Aliquots were heated in sealed tubes at 100°C. See Experimental section for details. [b] Number of tubes. [c] Percent of reaction at last point. [d] Uncertainties are standard deviation in the rate constant as estimated from linear unweighted least squares treatment. [e] See Table 2; two samples from a separate preparation were included, but tubes heated for 8 and 16 days were omitted. [f] Times of heating from 0—7 days; a point at 14 days which was omitted corresponded to 96% rearrangement. [g] No rearrangement detected up to 8 days.

methanol appearing to approach a limiting value between 5 and 10%. This deviation may perhaps be attributed to the presence of a small amount of the monomethyl ether of triethyleneglycol (equivalent to about 5% of the methylenecyclobutane) which was identified in the oxidized reaction solutions. Its presence, either in the original solvent or from cleavage of the solvent, could have produced a less reactive alkoxyborane.

It has been reported that the isomerization reaction of boranes requires catalysis by excess BH bonds [10,12]. In order to determine whether the present rearrangement has a similar requirement, a run was performed with a large excess of borane, corresponding to a stoichiometry $R_{1.15}BH_{1.85}$. With the excess of BH bonds, pentanediols were formed to the exclusion of the 4-penten-1-ol. At long reaction times, up to about 7% of 1-pentanol was also isolated. The rate of rearrangement (Table 1) was not greatly different from that in the previous run. Therefore, catalysis by BH bonds does not appear to be important. It may also be noted that a slight, accidental excess of borane could not be responsible for catalysis in the first run; olefinic functions generated in the rearrangement would quickly reduce the concentration of BH bonds to a small value.

A complication in reactions using borane-methyl sulfide is the presence of the methyl sulfide in the reaction mixture. Trialkylboranes seem to coordinate strongly only with amines and other strong Lewis bases [13]. However, it appeared desirable to consider a scheme in which a borane-methyl sulfide complex must dissociate in order to rearrange (eq. 4).

(4)

(Base = $S(CH_3)_2$, pyridine)

In this case, increasing the concentration of methyl sulfide would decrease the concentration of free borane, and hence the observed rate of rearrangement. A run carried out in the presence of an added 100% excess of methyl sulfide proceeded at a rate similar to the two previous runs. We may thus conclude that coordination to methyl sulfide does not influence the rearrangement process.

Although the weak Lewis base methyl sulfide has no effect on the rearrangement rate, the stronger base pyridine does. In the presence of one equivalent of pyridine per boron, no rearrangement was detected in a sample heated for 8 days at 100°C. A similar inhibiting effect of pyridine has been found in the rearrangement of (cyclopropylmethyl)diethylborane [2]. This result is most satisfactorily explained on the basis of the scheme in eq. 4, in which a free orbital on the boron atom is a requisite for the rearrangement (base = pyridine).

As noted above, the rate of rearrangement was found to be largely independent of the stoichiometry of the hydroboration using borane-methyl sulfide. One interpretation of this result might be that cyclobutylmethyl groups in the mono- or dialkylboranes rearrange at a rate virtually identical to those in a trialkylborane. Alternatively, the strength of coordination between BH_3 and methyl sulfide may result in a hydroboration mixture which consists largely of free trialkyl borane and the BH_3-methyl sulfide complex, so that the same

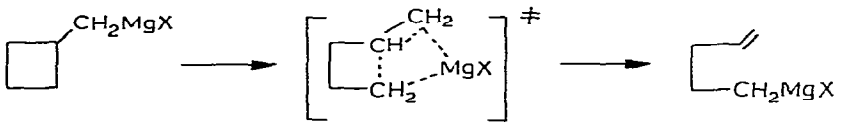
reacting species is present in both solutions (Consideration of dimerization equilibria for mono- and dialkylboranes would further complicate the picture).

Some exploratory ^{13}C NMR experiments with hydroboration mixtures from cyclopentene suggest that the trialkylborane may indeed be the principal alkylated borane produced in hydroboration with borane-methyl sulfide, independent of the stoichiometry. Incremental addition of cyclopentene to a solution of borane/tetrahydrofuran led initially to a pair of strong resonances, which were supplanted by two different resonances as the stoichiometry approached that of the trialkylborane. The former were altered on addition of methyl sulfide, but the latter were unchanged. Hydroboration with borane-methyl sulfide in THF produced the trialkylborane at all stoichiometries. (Details are included in the experimentel section.) It is quite possible that redistribution equilibria between BH_3 and the trialkylborane would also be thermodynamically disfavored in the presence of methyl sulfide.

Since the foregoing results did not clearly provide a comparison of the rearrangement of trialkylborane with less alkylated boranes, two rough experiments were carried out using borane/THF in THF solution. Hydroborations were run with methylenecyclobutane/borane ratios of 3/1 and 1/1. In the former, 4-penten-1-ol was, as expected, the major rearrangement product, although with longer heating significant amounts of diols were formed. After five days at 100°C, the ratio of cyclobutylmethanol/4-penten-1-ol/diol was 46/46/8. With the excess of BH bonds, the ratio of products after seven days was 54/3/43. In the latter run, there were indications that reaction between borane and the solvent was occurring. Addition of water during work-up to samples heated for several days evolved little hydrogen, and the detection of 4-penten-1-ol (at five days, but not at two) may also indicate consumption of the excess BH bonds. GC peaks corresponding in retention time to n-butanol and 1,4-pentanediol appeared, and an additional sizeable peak was tentatively identified as 4-butoxy-1-butanol (from dimerization and reduction of the THF). In both runs, the fraction of cyclobutylmethanol in the products decreased somewhat erratically with time, and appeared to be stopping short of completion, rather than following a clean first order decay.

Although the reactions in THF were not as clean as those with borane-methyl sulfide in triglyme, it is clear that the reaction does not require catalysis by excess BH bonds, and is likely a bit slower with the monoalkylborane stoichiometry. The relative insensitivity to the stoichiometry, and the first order kinetics observed in triglyme both imply that rearrangement of a cyclobutylmethyl group attached to boron occurs at a rate fairly independent of the other groups (rearranged or unrearranged alkyl, or hydrogen). It might also be noted that the reactions in THF were somewhat slower than those in triglyme (by a factor of two to three). This could be a general solvent effect, or it might imply weak association of the borane with THF, as in eq. 4.

In the more extensively-studied ring cleavage and cyclization rearrangements of organomagnesium compounds (eq. 5), we have concluded that mechanisms involving initial heterolytic or homolytic dissociation of the carbon—magnesium bond are inconsistent with experiment [2a, 14]. We have favored a four-centered transition state (11) in which changes in carbon—carbon bonding are concerted with the shift of the magnesium. It is reasonable (though not proven)



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that the transition state may electronically resemble a π complex between the metal and the forming double bond, or that a π complex intermediate may actually intervene. Since four-centered and π-complex mechanisms are also frequently discussed for hydroboration and other borane reactions [15,16], they must be considered as likely candidates for the rearrangement of cyclobutylmethylboranes. Furthermore, the alternative heterolytic or homolytic dissociations would appear less likely for boron than for magnesium; boron is more electronegative than magnesium *, and the carbon—boron bond should be stronger than the carbon—magnesium bond **.

If the rearrangements of cyclobutylmethyl-magnesium and -boron compounds occur by the same mechanism, it is appropriate to compare their rates. For cyclobutylmethylmagnesium chloride in THF at 100°C, a rate constant of 2.2×10^{-4} sec^{-1} has been reported [20]. At 60°C in the same solvent, the dialkylmagnesium rearranges about 20—50% faster than the chloride [2a]. It does not appear that organomagnesium rearrangement rates have been measured in triglyme, but a number of such rearrangements appear to be faster in 1,2-dimethoxyethane (DME) or THF/DME than in THF alone, by factors of 3—20 [2a]. It thus appears that the organomagnesium rearrangement occurs some two to three powers of ten more rapidly than the corresponding organoboron rearrangements. This difference might be taken as a lower limit, since it is known that the magnesium is strongly solvated by ethers, while the boron of a trialkylborane is (at most) weakly solvated [13]. If the organomagnesium rearrangement requires a vacant coordination site on the metal, then a hypothetical unsolvated organomagnesium compound should rearrange much more rapidly.

It may be interesting to note another parallel between magnesium and boron organometallics. Allylmagnesium compounds undergo a rapid allylic shift of the metal (eq. 6), at a rate which remains rapid on the NMR time scale down to the lowest temperatures studied [21]. Allylboranes undergo a similar though

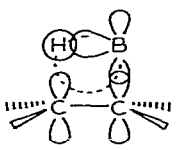
(6)

much slower "permanent allylic rearrangement" [22,23]; the transition between "slow" and "fast" on the NMR time scale is between —25 and +100°C for triallylborane. Like the ring cleavage rearrangements, complexation with a

* Electronegativities of boron and magnesium on various scales are approximately 2 and 1.25, respectively [17].

** Although appropriate thermodynamic quantities are not available for organomagnesium compounds, the variation in carbon—metal mean bond dissociation energies with location in the periodic table strongly suggests that the carbon—boron bond should be the stronger [18,19].

Lewis base markedly slows the borane process. Cyclic four-centered mechanisms for either the ring cleavage or allylic rearrangements or for hydroboration are formally forbidden by orbital symmetry [24]. It has been pointed out in discussions of hydroboration [25—27] and of the cyclization cleavage rearrangements of organomagnesium compounds [2a] that the utilization of an additional (vacant) orbital on the metal would avoid the orbital symmetry constraint. Because orbitals on the same atom are orthogonal, there is no longer the cyclic array of overlapping orbitals which is responsible for that constraint. Transition states incorporating two orthogonal metal orbitals are illustrated for hydroboration (12), allylic shift (13), and for cyclobutylmethyl cleavage (14).



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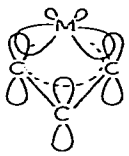

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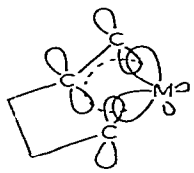

(14)

(Similar considerations apply to a π complex; it is also possible that the vacant orbital on the metal might be generated by displacement of solvent in approaching the transition state.) The inhibition of the ring cleavage and allylic rearrangements of boranes by Lewis bases is consistent with the need for a vacant metal orbital. It is not yet clear whether the vacant orbital is a requirement for the corresponding processes with magnesium.

A brief comment is in order concerning the distribution of pentanediols produced in the rearrangements. With 9-BBN as the hydroborating reagent, 1,5-pentanediol was essentially the exclusive isomer, as expected from the high selectivity of that reagent [28]. With borane-methyl sulfide or borane-THF, the 1,4-diol was initially produced in amounts similar to the 1,5-diol, but decreased with longer heating times. These observations are consistent with previous studies on the hydroboration of 1,4-pentadiene [29]. The 1,4-diol results from the kinetically-favored formation of a 5-membered borolane ring, which is preferentially destroyed or isomerized to the 6-membered borinane.

The rearrangements of cyclobutylmethylboranes presently observed may be compared with previous proposals of such rearrangements. As noted earlier, Rossi and Diversi detected some unsaturated products in their synthesis of 2-methylcyclobutylamine (eq. 3) and suggested borane isomerization to produce cyclobutylmethyl groups, which underwent ring cleavage [11]. It is questionable whether the temperature and heating time in their synthesis would have been vigorous enough to result in a significant amount of rearrangement (e.g. our observation of 6% rearrangement after 4 h at 100°C in triglyme starting with cyclobutylmethyl groups).

Brown and Zweifel [10] hydroborated methylenecyclobutane in diglyme with 20% excess hydride, generated in situ from sodium borohydride and boron trifluoride. Oxidation after heating for 2 h at 160°C produced a 22% yield of alcohols. These were reported to consist of cyclobutylmethanol and alcohols resulting from isomerization of the boron into the ring, in a ratio of 17/83 (see Scheme 1). In the present study, the principal process observed on

heating the hydroboration mixture was the ring cleavage rearrangement, leading after oxidation to the unsaturated alcohol 8 and the pentanediols 9 and 10. Authentic samples of 1-methylcyclobutanol and *trans*-2-methylcyclobutanol were found to have shorter GC retention times than either cyclobutylmethanol (7) or (8). Only minor components (1—2%) in this range were commonly detected in the products. With an excess of BH bonds present, a significant increase in amount of a component with retention time similar to *trans*-2-methylcyclobutanol was observed. However, isolation by preparative GC showed it to be largely 1-pentanol. (The formation of 1-pentanol has precedent in hydroboration studies with 1,5-pentadiene [29]). In a number of reactions under varied conditions (including heating for at 130 or 160°C in diglyme or triglyme with stoichiometric and excess borane), the reaction mixture after oxidation was examined by ^{13}C NMR. Resonances observed were identified with the alcohols 7, 8 and 1-pentanol, diols 9 and 10, and dimethyl sulfoxide and sulfone (from borane-methyl sulfide). However, in no instance were there prominent resonances attributable to the products of borane isomerization. From the hydroboration of 1-methylcyclobutene (heated 4 h at 160°C in diglyme), the diols and 1-pentanol were the principal products); a small amount of *trans*-2-methylcyclobutanol was probably present, but little or no cyclobutylmethanol. We conclude that under a variety of conditions, isomerization of the boron function into the ring occurs to (at most) only a limited extent in competition with ring cleavage rearrangement. It is possible that 1-pentanol or 4-penten-1-ol, both of which have shorter GC retention times than cyclobutylmethanol, may have been mistaken for products of the isomerization in the studies of Brown and Zweifel, or that the reaction follows a distinctly different course when the hydroboration is carried out using $NaBH_4/BF_3$.

Experimental

IR spectra were run on a Beckman Model IR-8, and NMR spectra on Varian Associates T-60 and CFT-20 spectrometers. ^{13}C NMR assignments were assisted by off-resonance decoupling. Gas chromatograms were run on Varian Aerograph A90-P3 instruments, using the following columns: A, 4′ × 1/4″, DC 200 on 60/80 mesh Chromosorb W; B, 5′ × 1/4″, $AgNO_3$/glycerine on 30/65 mesh Chromosorb P; C, 10′ × 1/4″, 15% Carbowax 20M on 60/80 mesh Chromosorb W; D, 10″ × 1/4″, 5% Carbowax 20M on 40/60 mesh Chromosorb T. The detector response was calibrated with known mixtures for quantitative analyses. Boiling points are uncorrected.

Borane reagents 9-borabicyclononane (9-BBN), borane-methyl sulfide, borane-methyl sulfide in THF, and borane/THF were all purchased from the Aldrich Chemical Company and used without further treatment. Purity and concentration were determined by hydrolysis and measurement of the volume of hydrogen evolved [30]. Hydrogen peroxide was standardized by permanganate titration [31]. Tetrahydrofuran was dried by distillation under nitrogen in small batches from lithium aluminum hydride and used immediately. Diglyme and triglyme were stirred over calcium hydride for one day and distilled at 2.5—3 mm pressure; b.p. 39—40°C and 90—95°C respectively. Benzene was washed with concentrated sulfuric acid several times and distilled from sodium under nitrogen.

All reactions were run under a nitrogen atmosphere, using glassware and transfer syringes which had been dried at 140°C. 9-BBN was transferred in a glove bag under nitrogen. Tubes for heating sealed samples were oven-dried, flushed with nitrogen and capped with a rubber septum. Reactants were introduced by syringe. Tubes were sealed after chilling with liquid nitrogen and partial evacuation, and were heated in an oven or the cone of a steam bath.

Methylenecyclobutane was prepared from pentaerythrityl tetrabromide following the procedure of Roberts and Sauer [32]. The product was found from GC (Columns A and B) and proton NMR spectroscopy to be about 80% methylenecyclobutane and 20% 2-methyl-2-butene; a trace of spiropentane was evident from its NMR signal at 1.38 ppm. The methylenecyclobutane was obtained in 99% or greater purity by fractionation through a 60 cm column packed with glass helices; b.p. 40—41°C (Lit. b.p. 41.5—42°C [32]); ^{13}C NMR ($CDCl_3$) 150.19 (C=CH_2), 105.28 (=CH_2), 32.43 (2C) and 17.27 ppm (1C). A commercial sample from Aldrich Chemical Company was used for studies with borane/THF; it was sold as 80% purity, but was found by GC to be 93% pure.

1-Methylcyclobutanol was prepared by oxymercuration/demercuration of methylenecyclobutane, following the general procedure of Brown and Geoghegan [33]. Methylenecyclobutane (4.6 ml, 50 mmol) was added over a period of 10 min to a mixture of mercuric acetate (15.95 g, 50 mmol), water (50 ml) and THF (50 ml). After 0.5 h, there was added 50 ml of 3 *M* sodium hydroxide followed by 50 ml of 0.50 *M* sodium borohydride in 3 *M* sodium hydroxide. After 0.5 h, the mixture was saturated with sodium chloride, and the organic layer was separated, dried ($MgSO_4$) and the solvent stripped; IR (neat) 3450, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.6 (s, 1, OH), 2.5—1.4 (m, 6, CH_2), 1.35 ppm (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) δ 72.84 (*C*OH), 37.64 (2C, CH_2), 26.95 (CH_3), 11.84 (1C, CH_2).

1-Methylcyclobutene was prepared by isomerization of methylenecyclobutane, as described by Brown [34]. The product, found by GC (Column A) to be 89% 1-methylcyclobutene and 11% methylenecyclobutane, was used without further purification; ^{1}H NMR ($CDCl_3$) δ 5.6 (m, 1, CH), 2.4 (s, 4, CH_2), 1.7 (s, 3, CH_3).

trans-2-Methylcyclobutanol was produced along with some cyclobutylmethanol by hydroboration of the above mixture with 9-BBN, following standard procedures [29]. The product was shown by GC (Column C) to be 90% pure; ^{1}H NMR ($CDCl_3$) δ 3.6 (m, 2, O*H* and *CH*OH), 2.5—1.5 (m, 5); 1.1 ppm (d, 3, J 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 73.00 (*C*OH), 41.28 (CH), 29.25 (CH_2), 19.78 (CH_3), 18.13 ppm (CH_2).

Reaction of methylenecyclobutane with 9-BBN in THF

Methylenecyclobutane (0.27 ml, 2.9 mmol) was added to a solution of 9-BBN (0.772 g, 6.3 mmol) in 6 ml THF. After 1.5 h stirring at room temperature, the solution was transferred by syringe to two glass tubes and sealed. After heating for 96 h at 110°C, one tube was opened, and worked up by addition of 1.2 ml of 3 *M* aqueous NaOH followed by careful addition of 1.2 ml of 30% hydrogen peroxide. After stirring for 1 h at 50—60°C, 15 ml of water was added, and the mixture was extracted with three 20 ml portions of ethyl ether. The ether solution was washed with water, dried ($MgSO_4$), and concentrated by

distillation of the solvent. The aqueous layer was saturated with potassium carbonate, extracted with 40 ml of THF, dried ($MgSO_4$) and concentrated. The ether and THF fractions were separately analyzed by GC (Column D), using benzyl alcohol as an internal standard. Yields of 59% of 1,5-pentanediol and 31% of cyclobutanemethanol were determined, along with a peak corresponding to 1.4% at the retention time of *trans*-2-methylcyclobutanol and a similar unidentified peak of shorter retention time. Cyclooctanone and cyclooctanol were present in amounts corresponding to 11.5 and 4% based on 9-BBN. 1,5-Cyclooctanediol has a considerably longer retention time, and was not analyzed quantitatively. The pentanediol was mostly in the THF extract, while the other components were almost exclusively in the ether. In earlier experiments, it was shown that substantial losses and poorer material balances were obtained when solvent was stripped from the extracts with a rotary evaporator, or when 1,5-cyclooctanediol was precipitated by addition of pentane. A number of similar experiments were carried out with a smaller (or no) excess of 9-BBN, with different times and temperatures of heating, or with refluxing diglyme as the solvent. The work-up was similar in all cases, but in earlier experiments lower recovery of products resulted from inefficiency in extraction or solvent removal. 4-Penten-1-ol was found in experiments without an excess of borane. Products were isolated by preparative GC, and identified by comparison of IR and proton and carbon NMR spectra with authentic samples or published spectra [36].

Reaction of methylenecyclobutane with borane-methyl sulfide

Methylenecyclobutane (0.56 ml, 6.0 mmol) was added to a solution of borane-methyl sulfide (0.22 ml, 2.0 mmol) in 6 ml of triglyme and the mixture was stirred for 15 min at 40°C. Aliquots (1 ml) were transferred by syringe to each of six tubes, which were sealed and heated at 100°C for various periods of time ranging from 12 h to 16 days. The contents were transferred to a small flask and worked up by addition of a few drops of water, 0.125 ml of 3 *M* aqueous sodium hydroxide, and then 0.10 ml of 30% H_2O_2. The mixture was maintained at 40—50°C for 20 min, and then anhydrous K_2CO_3 was added until excess solid remained. Products were analyzed by GC on column C after addition of benzyl alcohol or diethylene glycol as a standard. Results are listed in Table 2. In addition to the products shown, there were also variable amounts of dimethyl sulfoxide and dimethyl sulfone (from oxidation of methyl sulfide) and the monomethyl ether of triethyleneglycol. All were identified by collection of the corresponding GC peak and comparison of spectra and retention times with authentic materials or published spectra [36]. (The last indicated substance was produced by partial hydrolysis of triglyme with hydriodic acid.) A rate constant was derived from least squares analysis of a plot of the logarithm of the fraction of cyclobutylmethanol in the products vs. time.

A similar run was prepared, in which 0.57 ml (5.2 mmol) of borane-methyl sulfide was used. Work-up of sealed 1 ml aliquots utilized 0.23 and 0.21 ml of 3 *M* NaOH and 30% H_2O_2, respectively. 4-Penten-1-ol was absent from the product mixture. A third set of tubes was prepared using 0.83 ml (9.0 mmol) of methylenecyclobutane and 0.86 ml (7.8 mmol) of borane-methyl sulfide in 9 ml triglyme. To each 1 ml aliquot was added 0.054 ml (0.73 mmol) of methyl sulfide or 0.059 ml (0.73 mmol) of pyridine. Tubes were worked up as in the second run.

TABLE 2

HYDROBORATION, HEATING, OXIDATION PRODUCTS FROM METHYLENECYCLOBUTANE AND BORANE-METHYL SULFIDE IN TRIGLYME AT 100°C [a,b]

Heating time (days)	Cyclobutyl-methanol	4-penten-1-ol	1,4-pentane-diol	1,5-pentane-diol
0	92	0	—	—
0.17	80 [c]	5 [c]	—	—
0.5	58	13	1	1.5
1	56	23	2	3
2	36, 43 [c]	37, 40 [c]	4, 3 [c]	6, 9 [c]
4	16	42	4	7
8	10	56	3	12
16	8	30	2	13

[a] Concentration calculated as trialkylborane: 0.29 *M*; see experimental section for details of preparation and work-up. [b] Yields based on methylenecyclobutane, determined by gas chromatography. Methyl sulfide, dimethyl sulfoxide and dimethyl sulfone were also present in variable amounts; the monomethyl ether of triethylene glycol was present in 5 ± 2% yield. [c] Sample from a different hydroboration preparation.

Reaction of methylenecyclobutane with borane/THF

Commercial borane in THF (4.2 ml, 4.6 mmol) was added to methylenecyclobutane (0.81 g, 11.9 mmol). One-ml aliquots were sealed in tubes and heated for various periods up to 10 days at 100°C. After opening, tubes were washed out with an additional 1 ml of THF, and worked up with 1 ml of water, 7 ml of 0.1 *N* NaOH and 0.30 ml of 30% H_2O_2. After stirring for 30 min, weighed quantities of cyclohexanol and *p*-methoxybenzyl alcohol were added as standards, and solid anhydrous K_2CO_3 was added to saturate the aqueous phase. A second set of tubes was prepared similarly using 9.0 ml (9.9 mmol) of the borane in THF, and worked up similarly with 3 ml of 0.1 *N* NaOH and 0.20 ml of 30% H_2O_2. Two substantial components were detected by GC in the runs with excess borane, which had not been found in reactions carried out in diglyme or triglyme. One of these was identified by retention time comparison as 1-butanol. The other had a retention time the same as a product prepared by reaction of the sodium alkoxide of 1,4-butanediol with 1-bromobutane.

Hydroboration of cyclopentene

Reactions were run in a 10 mm septum-capped NMR tube, with a sealed inner tube with the D_2O lock sample. To the tube, 2 ml of a 1 *M* borane/THF solution was added, followed by increments of cyclopentene. Two prominent peaks appeared at 0.98 and 5.77 ppm down field from the higher-field THF resonance, reaching maximum intensity at about 1.5 mol of alkene per BH_3. With more alkene, these diminished in intensity and were replaced by resonances at 1.95 and 3.33 ppm downfield from THF. No changes in the latter were produced when one mol of methyl sulfide was added to the solution after an excess of cyclopentene. In a similar solution, methyl sulfide was added after 1.5 mol cyclopentene per BH_3. The peaks at 0.98 and 5.77 ppm from THF were largely replaced by a strong peak at about 1.2 ppm. The spectrum remained essentially unchanged on standing two weeks at room temperature. Addition of

n excess of cyclopentene produced a change to the two bands at 1.9 and 3.33 ppm. Incremental additions of cyclopentene to 2 ml of 2.0 *M* borane-methyl ulfide in THF produced major peaks at only 1.9 and 3.33 ppm. In addition to najor resonances noted above, there were some minor signals, and appropriate peaks were observed for methyl sulfide (broadened, except when cyclopentene had been added in 3/1 stoichiometry or greater) and excess cyclopentene.

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References

1 For reviews, see (a) E.A. Hill, J. Organometal. 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, N.Y., 1977, p. 131; (c) C.J.M. Stirling, Chem. Rev., 78 (1978) 517.
2 R. Koster, S. Arora and P. Binger, Angew. Chem. Internat. Edit., 8 (1969) 205.
3 P. Pesnelle and G. Ourisson, J. Org. Chem., 30 (1965) 1744.
4 W. Cocker, P.V.R. Shannen and P.A. Staniland, J. Chem. Soc. C, (1967) 915.
5 D. Dopp, Chem. Ber., 102 (1969) 1081.
6 E. Breuer, E. Segall, Y. Stein and S. Sarel, J. Org. Chem., 37 (1972) 2242.
7 A.T. Bottini and L.J. Cabral, Tetrahedron, 34 (1978) 3195.
8 R.E. Merrill, J.L. Allen, A. Abramovitch and E. Negishi, Tetrahedron Lett., (1977) 1019.
9 B.A. Kazansky, Y.N. Bubnov, S.V. Zotova, N.M. Abramova, V.G. Kiselev and B.M. Mikhailov, Tetrahedron Lett., (1974) 567.
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 H.C. Brown and G. Zweifel, J. Am. Chem. Soc., 88 (1966) 1433.
13 T. Onak, Organoborane Chemistry, Academic Press, New York, 1975, p. 147—154.
14 E.A. Hill, A.T. Chen and A. Doughty, J. Am. Chem. Soc., 98 (1976) 167.
15 H.C. Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca, N.Y., 1972, pp. 265—266, 284—285.
16 Ref. 13, pp. 30—31, 38—39, 111—115, 188.
17 G. Simons, M.E. Zandler and E.R. Talaty, J. Am. Chem. Soc., 98 (1976) 7869.
18 H.A. Skinner in F.G.A. Stone and R. West (Eds.), Advances in Organometallic Chemistry, Vol. 2, Academic Press, New York, 1964, p. 49.
19 V.I. Tel'noi and I.B. Rabinovich, Uspekhi Khim., 49 (1980) 1137.
20 E.A. Hill and H.-R. Ni, J. Org. Chem., 36 (1971) 4133.
21 G.M. Whitesides, J.E. Nordlander and J.D. Roberts, Discuss. Faraday Soc., 34 (1962) 185; H.E. Zieger and J.D. Roberts, J. Org. Chem., 34 (1969) 1976.
22 B.M. Mikhailov, Yu.N. Bubnov and A.V. Tsyban', J. Organometal. Chem., 154 (1978) 113; B.M. Mikhailov, Uspekhi Khim., 45 (1976) 1102.
23 G.W. Kramer and H.C. Brown, J. Organometal. Chem., 132 (1977) 9.
24 R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Academic Press, New York, 1970.
25 D.J. Pasto, B. Lepeska and T.-C. Cheng, J. Am. Chem. Soc., 94 (1972) 6083.
26 R.A. Jackson, J. Chem. Soc. B, (1970) 58.
27 P.R. Jones, J. Org. Chem., 37 (1972) 1886.
28 H.C. Brown, E.F. Knights and C.G. Scouten, J. Am. Chem. Soc., 96 (1974) 7765.
29 E. Negishi, P.L. Burke and H.C. Brown, J. Am. Chem. Soc., 94 (1972) 7431.
30 H.C. Brown, G.W. Kramer, A.B. Levy and M.M. Midland, Organic Synthesis via Boranes, Wiley, New York, 1976, p. 239—250.
31 J. Rosin, Reagent Chemicals and Standards, 5th ed., Van Nostrand, Princeton, N.J., 1967, p. 228.
32 J.D. Roberts and C.W. Sauer, J. Am. Chem. Soc., 71 (1949) 3925.
33 H.C. Brown and P. Geoghegan, Jr., J. Am. Chem. Soc., 89 (1967) 1522.

34 H.C. Brown, R. Liotta and L. Brener, J. Am. Chem. Soc., 99 (1977) 3427.
35 E. Gil-Av and J. Shabtai, J. Org. Chem., 29 (1964) 257.
36 Sadtler Standard Proton NMR, Carbon-13 NMR and Infrared Spectra, Sadtler Research Laboratories, Philadelphia, Pa.; C.J. Pouchert and J.R. Campbell, The Aldrich Library of NMR Spectra, Aldrich Chemical Company, Milwaukee, 1974; C.J. Pouchert, The Aldrich Library of Infrared Spectra, Aldrich Chemical Company, Milwaukee, 1975.