Table VII. Thermal Equilibration of
Cyclopropylidenecycloalkanes, $n = 5$

Temp, °C	$(k_1 + k_{-1}) \times 10^5 \text{ sec}^{-1}$	K_{eq}
211	1.95 ± 0.07	1.23
220	4.76 ± 0.20	1.15
225	7.13 ± 0.73	1.20
229.9	12.2 ± 0.65	1.14
239.9	27.6 ± 1.4	1.06

did occur. Glpc analyses on a 0.25 in. × 15 ft 10% dimethyl-
sulfolane on 60–80 Chromosorb P column indicated that 92% **2**
remained with two products being formed in a ratio of 7:1. A
good recovery yield was obtained in this case. When heated to
320 ± 2° for 20 hr, only a 40% recovery of volatile materials was
possible. The volatile mixture was shown to consist of 60.6% **2**,
15.8% 1,2-dimethylenecyclobutane, and 18.8% 1,3-dimethylene-
cyclobutane. The nmr and ir spectra of the former product
were identical with those of an authentic sample, while those of
the latter product were consistent with those in the literature.[13]

Cleavage of Cyclopropanes by Diborane[1]

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Abstract: Cyclopropanes are cleaved by diborane at about 100°. The reaction is quite regioselective, the products being derived from the addition of hydrogen to the most substituted and boron to the least-substituted carbon. In contrast to the hydroboration of olefins, the cyclopropane cleavage reaction is inhibited by ethereal solvents. The reaction with 1-methylnorcarane was studied in detail; the predominant products after oxidation are (initially) *cis*-(60%) and *trans*-2-methylcyclohexylmethanol (40%). Nonstereospecificity is inherent in the cleavage reaction, and a planar intermediate is proposed. Tetraborane (B_4H_{10}) is comparable to, or somewhat more reactive than diborane. Pentaborane (B_5H_9) under similar conditions does not cause cleavage. The rearrangement of 1,2-di-methylcyclohexylborane (from hydroboration of 1,2-dimethylcyclohexene) was found to occur with initial high selectivity, giving up to 97% *cis*-2-methylcyclohexylmethylborane. An intramolecular borane–olefin complex mechanism is proposed to account for this observation.

Cyclopropane cleavage reactions are of special in-
terest as potential models for the stereochemical
study of electrophilic substitution at saturated carbon.[2]
Numerous Lewis acid reagents will open the three-
membered ring, but in general these give complex mix-
tures of products.[3] The analogy between olefins and
cyclopropanes has often been drawn, and the reactions
of one group frequently are paralleled by those of the
other. In view of the synthetic importance of hydro-
boration,[4] it was of interest to explore the reaction of
diborane with cyclopropanes. Graham and Stone[5]
some time ago reported that unsubstituted cyclopropane
reacts in the vapor phase with diborane to give moderate
amounts of tri-*n*-propylborane.[6] Apparently no other
studies of this reaction have been made.

Regioselectivity of the Cleavage Reaction. Norcarane
(**1**) reacts smoothly with diborane at 100° (sealed tube),
in a highly regioselective cleavage process.[10] Rep-
resentative results, obtained by analysis of the alcohols
obtained after alkaline peroxide oxidation of the
boranes, are shown in Table I. The borane leading to
cyclohexylmethanol (**2**) comprises $\geq 95\%$ of the initially
formed cleavage product; scission of the interior C_1–C_6
bond (giving cycloheptanol **4**) occurs to the extent of at
most a few per cent. The methylcyclohexanols **3** result
largely or exclusively from rearrangement of the ini-
tially formed cyclohexylmethylborane (see Table I,
footnote *a*, and later discussion).

The runs shown in Table I were carried out to explore
the effects of changes in variables on product distri-
bution. Increasing temperature and time, while
causing greater reaction, do not appreciably affect the
regioselectivity of the reaction. The addition of pen-
tane (run 9) has little effect; the hydrocarbon apparently
functions only as a diluent. The oxygen-containing sol-
vents ether, THF, and diglyme, on the other hand, all

(1) This work was supported in part by the Petroleum Research Fund (1442-A4), administered by the American Chemical Society, and by the National Science Foundation (GP 6043).

(2) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

(3) See, for example, (a) R. T. LaLonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.,* **89,** 6651 (1967), and earlier references; (b) R. J. Ouellette, R. D. Robins, and A. South, Jr., *ibid.,* **90,** 1619 (1968); (c) S. Moon, *J. Org. Chem.,* **29,** 3456 (1964); (d) R. Ya Levina, V. N. Kostin, P. A. Gembitskii, and A. D. Vinogradov, *Vestn. Mosk. Univ., Khim.,* **16** (II), 67 (1961) (*Chem. Abstr.,* **56,** 14091*b* (1962)); (e) D. J. Abraham and W. E. Truce, *J. Org. Chem.,* **28,** 2901 (1963).

(4) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(5) W. A. G. Graham and F. G. A. Stone, *Chem. Ind. (London),* 1096 (1957).

(6) The cleavage of unsubstituted cyclopropane by lithium aluminum

hydride in ether has also been reported.[7] However, later work[8] and our own attempts[9] indicate that this reaction is not general.
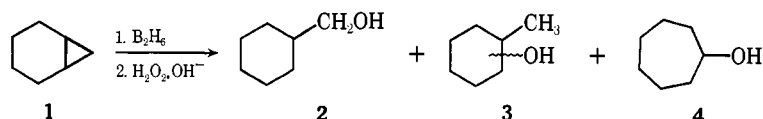
(7) C. F. H. Tipper and D. A. Walker, *Chem. Ind. (London),* 730 (1957).

(8) H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron,* **20,** 1613 (1964).

(9) Unpublished work of J. H. Chan.

(10) A preliminary report of this result has been published: B. Rickborn and S. E. Wood, *Chem. Ind. (London),* 162 (1966).

Table I

	1					2	3	4
Run no.	**1**, mmol	B$_2$H$_6$, mmol	T, °C	Time, hr	% reactn	% **2**	% **3**^{a}	% **4**
1	11	2	100	1	Not det	96.6	1.5	1.9
2	4.4	2	102	1.8	25	91.6	5.0	3.2
3	4.4	0.8	102	1.2	25	98	0.5	1.5
4	12	16	100	0.7	Not det	60	38	2
5	4.4	0.7	100	2.2	60	99	0.5	0.5
6	4.4	2.2	100	4.2	Not det	80	16	3.8
7	8.8	1.6	85	0.8	0			
8	4.4	1	80	6.8	100	95	1	4
9	4.4 (pentane)^b	1	80	6.8	20	95		4
10	4.4 (ether)^b	1	80	6.8	0			
11	8.8 (THF)^b	1.6	100	1	0			
12	4.4 (diglyme)^b	1	94	48	Trace			
13	9 (glass)^c	1.4	100	1.1	20		Not det	

^{a} In runs giving very little **3**, this material consisted nearly exclusively of *trans*-2-methylcyclohexanol. In run 4, the 38% **3** included *trans*-2-(24%), *cis*-3- (10%), and *cis*-2-methylcyclohexanol (4%). ^{b} The sealed tube contained 5–6 ml of the indicated solvent. ^{c} 10 g of powdered Pyrex was used.

strongly inhibit the reaction (best illustrated by run 12). This behavior stands in sharp contrast to hydroboration,[4] where ethereal solvents are known to enhance the reaction.[11] Run 13 was carried out with added crushed glass, to examine the possible effect of glass surface on the reaction. The results (compare with run 3) indicate no appreciable effect on the extent of reaction.

Bicyclo[3.1.0]hexane (**5**) gave similar results, as outlined in Table II. Somewhat more cleavage of the in-
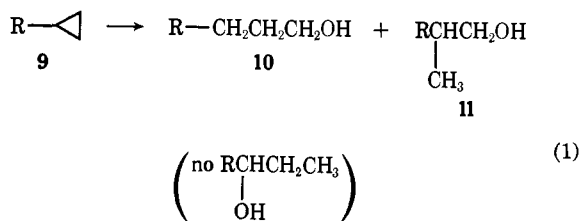
Table II
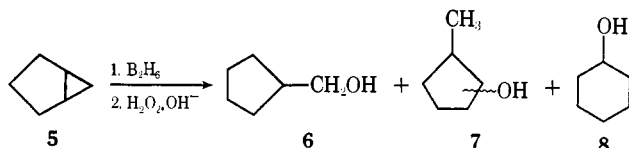
5, mmol	B$_2$H$_6$, mmol	T, °C	Time, hr	% **6**	% **7**	% **8**
3.5	0.8	107	1	95		5
5	2.5	93	1	92	Trace	8
5	2.5	93	1.3	92	1	7

ternal bond (leading to cyclohexanol **8**) occurred than with norcarane.

Three *n*-alkylcyclopropanes were examined. The general reaction is shown in eq 1. Three modes of cleavage are possible with these materials. The major

$$\left(\text{no } \overset{|}{\underset{\text{OH}}{\text{RCHCH}_2\text{CH}_3}}\right) \tag{1}$$

product (**10**) in all three systems was that involving boron addition to the least-substituted carbon, and hy-

(11) Part of the effect in the present study may be due to ether cleavage by borane at these elevated temperatures;[4] however, it is clear that the ethers are not exerting a rate-enhancing effect on the cyclopropane cleavage reaction.

drogen to the most substituted (just as in the bicyclic compounds **1** and **5**). The other directly formed product was that of cleavage of the symmetrical bond, giving **11**. Very little or none of the 3-boranoalkane (see eq 1) is formed directly, although in some instances it is generated by rearrangement of the 1-boranoalkane. Results are given in Table III. Rearrangement products of **11** were not obtained, probably because rearrangement past the tertiary center occurs more slowly than rearrangement of the *n*-alkyl derivatives (**11** is also initially formed in smaller amounts, making observation of rearrangement less likely). All three systems (R = C$_4$H$_9$, C$_5$H$_{11}$, and C$_8$H$_{17}$) give much the same product distribution; the major mode of cleavage accounts for 90% or more of the reaction, although this is diminished by subsequent rearrangement. Somewhat higher regioselectivity appears to be associated with smaller molar amounts of diborane (compare runs 1 and 2, 3, and 4 in Table III).

Spiro[2.5]octane (**12**) was briefly examined, giving the results shown in eq 2. Only products derived from scission at the spirano carbon were observed. Com-


$$\tag{2}$$
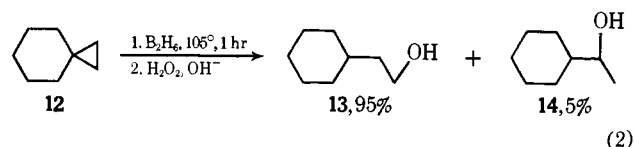
pound **14** is presumably formed by rearrangement of **13**. No 1-methylcyclohexylmethanol was produced, indicating that the reaction of **12** was regiospecific.

Stereochemistry of the Cleavage Reaction. The reaction of diborane with 1-methylnorcarane (**15**) also proved to be highly regioselective, with ≥97% of cleavage of the C$_1$–C$_7$ bond occurring (eq 3). Less than 3% of combined alternate rupture leading to materials **17** and **18** (these were not separable under the vpc conditions employed) occurred. Since **16** can exist as two geometrical isomers, this offered an excellent substrate for examination of the stereochemistry of the cleavage reaction (or more exactly, the stereochemistry at one end of the cleaved bond). Although the reaction of **15**
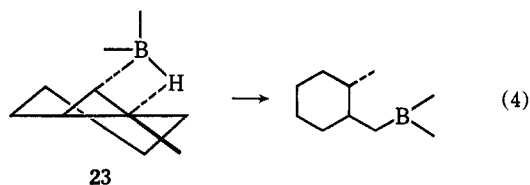
Table III

Run no.	9, R =, mmol	B₂H₆, mmol	T, °C	Time, hr	% reactn	10, %	11, %	Other products
1	n-Butyl, 4.8	1	106	1.5		90	5	5% 2-heptanol
2	n-Butyl, 4.8	2	102	1.6		81	17	2% 2-heptanol
3	n-Pentyl, 3.2	0.5	110	1		90	10	
4	n-Pentyl, 3.2	0.1	110	1		100		
5	n-Pentyl, 3.2	2.5	100	0.25	49	81	8	8% 2-, 3%-3-octanol
6	n-Pentyl, 3.2	0.8	100	0.25	0			
7	n-Pentyl, 3.2	0.8	107	1	90	85	12	
8	n-Pentyl, 5	2.5	97	0.85	100	75	11	7% 2-, 6% 3-, 1% 4-octanol
9	n-Pentyl, 5	2.5	102	0.5	80	75	8	9% 2-, 7% 3-, 1% 4-octanol
10	n-Octyl, 5	2.5	105	0.5	70	72	8	20% combn 2- and 3-undecanols
11	n-Octyl, 5	2.5	86	0.25		81	9	8% 2-, 2% 3-undecanol

$$(3)$$
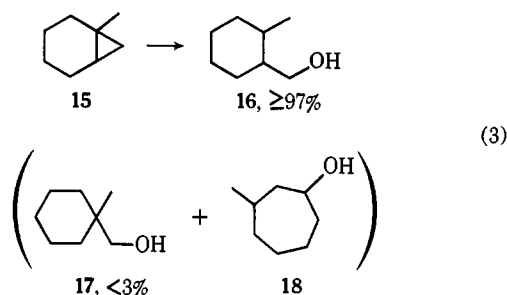
was quite regioselective, it was stereochemically very complex. The results of a thorough study of this system are given in Table IV.
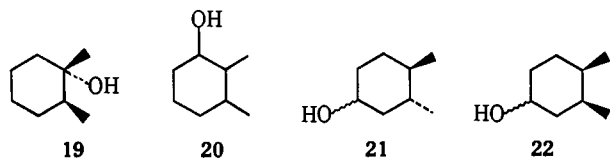

The data indicate that the analogy between olefins and cyclopropanes does not extend to reaction with diborane. A four-center mechanism in hydroboration of olefins, giving clean cis addition of the elements of B and H, is supported by all available evidence. A similar mechanism in the present cleavage reaction (*cf.* structure **23**) would lead to *trans*-2-methylcyclohexyl-methanol (*trans*-**16**), as indicated in eq 4. This mechanism clearly cannot hold for the diborane cleavage

$$(4)$$

reaction, since *cis*-**16**, rather than *trans*-**16**, is the major product of scission of **15**. An attempt was made to determine the cis–trans ratio as initially formed by carrying the reaction to only very low extents of conversion (runs 1, 3, 9, and 13 of Table IV). The maximum selectivity observed was 60% cis, 40% trans. Prolonged treatment gave, along with rearrangement products **19–22** (see Table IV for yields), an isomeric mixture enriched in *trans*-**16**. This is best shown by runs 4 and 11, where the cis–trans ratio has been altered to 25–75%. Clearly equilibration favors the trans isomer,

and the formation of *cis*-**16** as the major initial product rules out the concerted process of eq 4, followed by equilibration, as the correct mechanism.

It is more difficult to rule out a mechanism involving stereospecific formation of *cis*-**16** followed by isomerization to the observed mixture. Such a stereospecific process, involving inversion at the cleaved quaternary center, has ample precedent in the mixed hydride reduction of epoxides.[12] However, the data in Table IV show that borane rearrangement is occurring, but the rate of change of the *cis–trans*-**16** ratio suggests that such rearrangement is too slow to account for all of the *trans*-**16** obtained at low conversion. If the low-conversion cis–trans ratio is indeed intrinsic to the cleavage reaction, it is particularly interesting to note that hydroboration of methylene-2-methylcyclohexane (**24**) under a variety of conditions gives essentially the same ratio of these two materials (eq 5). This suggests that the

$$(5)$$
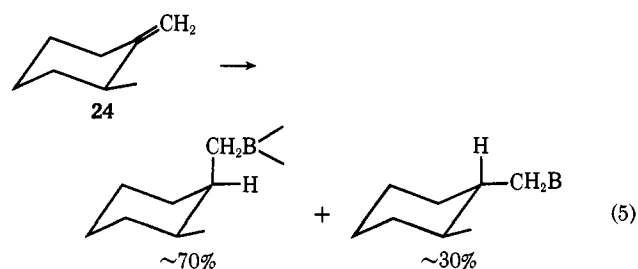
olefin **24** may serve as a reasonable model for either the transition state or an intermediate in the cleavage reaction. Either the olefin itself or a carbonium ion or radical at the tertiary center would have the appropriate geometry. Data on the hydroboration of **24** are given in Table V. It is interesting that hydroboration using diborane (no solvent), $BH_3 \cdot THF$ in THF, and dicyclohexylborane all give effectively the *cis–trans*-**16** product ratio shown in eq 5.

Rearrangement of *cis*-1,2-Dimethylcyclohexylborane. In connection with the cleavage of 1-methylnorcarane and the subsequent equilibration of borane products from this reaction, the hydroboration–rearrangement of 1,2-dimethylcyclohexene (**25**) was examined. An unexpected observation was made, as indicated by the data in Table VI.

(12) D. K. Murphy, R. L. Alumbaugh, and B. Rickborn, *J. Amer. Chem. Soc.*, **91**, 2649 (1969).

Table IV. Cleavage of 15[a]

| Run no. | B₂H₆, mmol | T, °C | Time, hr | % reactn | %16 | | % | | | | |
					Trans	Cis	(17 + 18)	19	20	21	22
1	1	106	1	5	35	50		4	5	8	
2	2.5	106	1	80	47	43	2	1	1	6	
3	1	106	0.5	1	40	60					
4	2.5	106	0.5	17	35	52	1	2	2	8	
5[b]	12.5	104	0.5	30	47	16	1	0.5	5	16	10
6[b]	12.5	88	0.3	1							
7	2.5	90	3	40	37	56	1	0.5	0.6	5	
8	2.5	90	5	55	46	46	1	0.5	0.5	6	
9	1	90	5	8	44	53	1			2	
10	2.5	106	3	80	46	40	3	1	3	5	2
11	2.5	106	24	90	64	20	3	0.5	3	4	5
12	2.5	105	0.5		38	52	1	2	4	3	
13	2.5	105	0.9	10	37	46	3	2.5	2.5	9	
14	2.5	102	1	75	43	51					6
15[c]	2.5	102	1	25	42	58					Trace

[a] All runs involved 4.8 mmol of **15**. [b] A sealed tube of 4.5 times the usual volume was employed. [c] A tube of twice the usual volume was used.

Table V. Hydroboration of **24**

| Run[a] no. | B₂H₆, mmol | T, °C | Time, hr | %16 | |
				Cis	Trans
1	2.5	25	26	70	30
2	2.5	25 then	20		
		93	0.25	70	30
3	2.5	25 then	24		
		93	14.5	62	36
4	2.5	25 then	20		
		94	24	50	40
5[b]	0.7	100	5 min	49	36
6[c]	2.75	100	10 min	19	52
7[d,f]	2 (BH₃·THF)	25	5 min	73	27
8[e]	3 (R₂BH)	100	5 min	40	24

[a] All runs involved 4 mmol of methylene-2-methylcyclohexene (**24**). [b] 15% dimethylcyclohexanols also formed. [c] 28% dimethylcyclohexanols also formed. [d] Carried out in THF, using BH₃·THF for hydroboration. [e] The reagent used here was dicyclohexylborane; extensive rearrangement into the ring (36%) was evident in this run. [f] Similar results have recently been reported for the solution hydroboration of 3- and 4-alkylmethylenecyclohexanes, i.e., approximately twice as much a,e as e,e product is formed; J. Klein and D. Lichtenberg, J. Org. Chem., **35**, 2654 (1970).

Although the olefin employed in these studies was only 77% pure, the remainder being 1,6-dimethylcyclohexene (cf. run 1, Table VI), the data clearly indi-

OH
B

HO⟍
C

HO⟍⟍
D

ŌH
E

HO⟍⟍
F
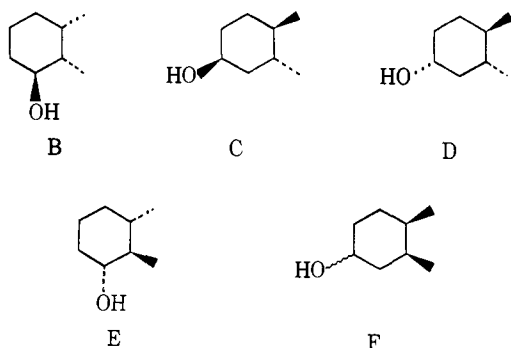
cate that the rearrangement of the tertiary borane to the primary borane is a highly selective process. This is shown by runs 3 and 5, where the extent of rearrangement, although extensive (see per cent of product A), is far from approaching equilibrium (compare run 9).

The ratio of *trans-* to *cis*-16 in these two cases is 3:97. Recall that hydroboration of methylene-2-methylcyclohexane by a variety of reagents, including the bulky dicyclohexylborane, gives a 30:70 ratio of these two materials. The high selectivity for formation of *cis*-16 is not a feature of the solvent-free reaction alone; runs 10 and 11 (Table VI), carried out in THF, demonstrate the same behavior. In order to explain this stereoselectivity, we suggest that an intramolecular process occurs, one which does not involve "free" olefin. One possibility, involving an olefin–borane π-complex, is illustrated in eq 6. Any sort of loose interaction which retains the relative geometry of the boron and C₂-methyl would lead

(6)
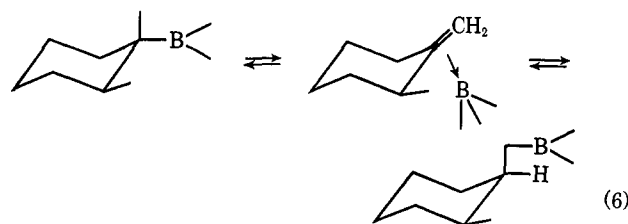
to the observed result. The slower process which leads to complete borane equilibration may in fact occur by "leakage" to the free olefin. Conceivably even higher specificity would be shown by pure 1,2-dimethylcyclohexene, and we plan to explore this system and others in greater detail.

The Nature of the Cleavage Agent. The preceding discussion of the cyclopropane cleavage reaction has specified diborane as the reagent, but it is well known that diborane is thermally unstable, decomposing fairly rapidly at temperatures of about 100° and higher to give, eventually, hydrogen and polymeric borane species. Evidence of such decomposition was obtained in most of the cleavage runs described here. The mechanism of the diborane decomposition is not known with certainty, although several studies of this complex reaction have been made.[13–15] A vpc analysis[15] of the volatile products formed on pyrolysis of diborane indicated that pentaborane(11) was the first detectable ma-

(13) For a review of earlier work, see R. M. Adams, Ed., "Boron, Metallo-Boron Compounds and Boranes," Interscience, New York, N. Y., 1964.

(14) T. P. Fehlner, J. Amer. Chem. Soc., **87**, 4200 (1965).

(15) K. Borer, A. B. Littlewood, and C. S. G. Phillips, J. Inorg. Nucl. Chem., **15**, 316 (1960).

Table VI. Hydroboration–Rearrangement of 1,2-Dimethylcyclohexene[a]

| Run no.	B_2H_6, mmol	T, °C	Time, hr	Products after oxidation,[b] %								16, trans:cis
				A	B[c]	C	D	E[c]	F	G	H	
1	2.75	25	12	77	18			5				
2	0.7	101	0.5	13	28	?	20	3	7	5	23	20:80
3	2.75	100	0.5	54	19			12		Trace	15	3:97
4	0.7	101	1.5	4	16	?	26	2	8	9	34	23:77
5	2.75	100	1.5	23	23	?	1	15	3	1	34	3:97
6	0.7	101	5	3.5	10	3.5	32	2	8	11	30	27:73
7	2.5	106	5	3.2	25	3.2	10	2.5	11	12.5	33	28:72
8	2.5	106	9.5	2.4	13	3.5	18	2.2	12	21	30	41:59
9	2.5	106	36.3	1.8	8.5	3.7	16	2.5	15	40	15	73:27
10[e]	4 ($BH_3 \cdot THF$)	102	0.2	33	16			25	Trace	Trace	26	4:96
11[e]	4 ($BH_3 \cdot THF$)	101	0.75	7	20		1	19	3	1.5	50	3:97
12[e]	5 ($BH_3 \cdot THF$)	110	2.5	1	9	17	17	2	11	25	33	45:57

[a] All runs involved 4 mmol of olefin (77% 1,2- and 23% 1,6-dimethylcyclohexene). [b] A = **19**, B–F in text, G = *trans*-**16**, H = *cis*-**16**. [c] The products are given in order of increasing retention time on a Carbowax 20 M vpc column. B and E are assigned (with reference to the geometry at C_3) on the basis of expected relative vpc retention times, and from the data of run 1; Pasto and Klein[d] have shown that 1,6-dimethylcyclohexene, when hydroborated using $BH_3 \cdot THF$, gives *ca.* 60% B, 40% E. [d] D. J. Pasto and F. M. Klein, *J. Org. Chem.*, **33**, 1468 (1968). [e] Carried out in THF solvent.

terial, followed by pentaborane(9) and tetraborane-(10). For a variety of reasons these higher boranes have received very little attention as reagents in organic chemistry. However, with the hope of gaining further insights into the cyclopropane cleavage reaction, we decided to examine both B_4H_{10} and B_5H_9 as possible cleavage reagents.

Tetraborane(10), bp 16°, was prepared by the pyrolysis of diborane in a hot–cold reactor (120° − 80°) following the procedure of Klein, Harrison, and Solomon.[16] This relatively unstable material[17] was of special interest as a potential source of BH_2^+, by "asymmetric cleavage"[18] as indicated in eq 7. Pentaborane(9), structure **26**,[19] is somewhat more stable[20] than tetra-

$$B_3H_8^- + BH_2^+ \quad (7)$$
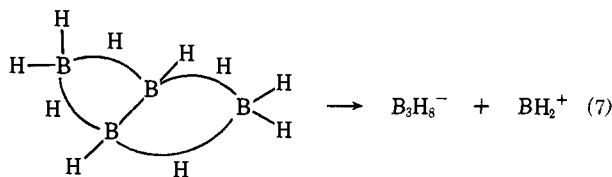
borane. MO calculations have indicated[21] that each of the basal borons bears a formal charge of +0.22, sug-

26
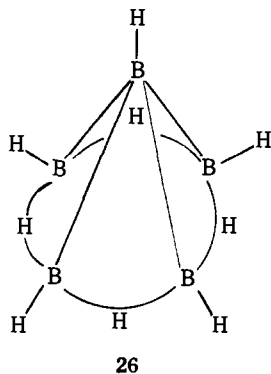
(16) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Amer. Chem. Soc.*, 80, 4149 (1958).
(17) The structure of B_4H_{10} was established by C. E. Nordman and W. N. Lipscomb, *J. Chem. Phys.*, 21, 1856 (1953).
(18) R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, 3, 1475 (1964).
(19) W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.*, 5, 260 (1952).
(20) This material was obtained from the Callery Chemical Co., Callery, Pa.
(21) E. B. Moore, Jr., *J. Amer. Chem. Soc.*, 85, 676 (1963).

gesting that this material might also play a role in cyclopropane cleavage. The regioselectivity of the diborane cleavage is as anticipated for an electrophilic cleavage reaction.

The results of treating 1-methylnorcarane with these materials are given in Table VII. Pentaborane(9) proved to be inert under the usual reaction conditions for cleavage by diborane. Tetraborane(10), on the other hand, was as reactive or slightly more so than diborane. It is not clear whether tetraborane itself is the cleavage agent, or some pyrolysis or disproportionation fragment (borane, BH_2^+, ?), but the general similarity of conditions required for this reaction and those starting with diborane suggests that the latter is the case. In view of the difficulty of preparing, storing, and handling B_4H_{10}, it does not appear to offer any advantages over B_2H_6 for the cleavage of cyclopropanes.

Table VII also contains data on runs made with BF_3. This electrophilic reagent apparently causes a facile rearrangement of 1-methylnorcarane to 1,2- and 1,6-dimethylcyclohexene (runs 7, 8). The hydroboration products of these olefins are the only alcohol products obtained in run 6 where both BF_3 and B_2H_6 were employed. Apparently the BF_3-catalyzed reaction occurs much more rapidly than the direct cleavage by diborane. These data also make it clear that the diborane cleavage reaction is not simply an electrophile-catalyzed rearrangement to olefin, followed by hydroboration.

The question of reaction phase in the cleavage process was explored using *n*-octyl- and *n*-pentylcyclopropane; individually no appreciable difference in rate of reaction was observable. A competition experiment was carried out using equimolar amounts of the two cyclopropanes; at the temperature required for reaction, the two compounds differ in vapor pressure by approximately a factor of 5, while analysis of the alcohol products in this run indicated that the octylcyclopropane had reacted at a rate 75–80% that of pentylcyclopropane. It is clear that at least most of the reaction is occurring in the liquid phase. Although the medium for reaction is clearly nonpolar, an ionic process cannot be excluded.

Experimental Section

Cleavage Reactions. The required amount (usually 5 mmol) of the cyclopropane was vacuum transferred from a calibrated tube to

Table VII. Cleavage of 1-Methylnorcarane with Various Boranes

Run no.	Reagent[a]	Amt, mmol	T, °C	Time, hr	% reactn	Products
1	B₅H₉	5	100	24	0	
2	B₄H₁₀	0.1 ml	25	15	0	
3	B₄H₁₀	0.14 ml	50	0.25	0	
4	B₄H₁₀ B₂H₆ ⎫	0.16 ml	82	0.25	15	37% trans-16, 52% cis-16[b]
5	B₄H₁₀ ⎬ B₃H₉ ⎭	0.1 ml	86	0.1	4.5	42% trans-16, 48% cis-16, 10% misc
6	B₂H₆ ⎫ ⎬ BF₃ ⎭	2.5 ⎫ ⎬ 0.3 ⎭	25 then 97	5 0.1	Large	42% 19, 58% 2,3-dimethyl-cyclohexanols; large hydrocarbon fraction
7	BF₃	2.5	93	4.75	100	85% 24, 15% 1,6-dimethyl-cyclohexene
8	BF₃	0.5	93	0.5	60	50% 24, 10% 1,2-dimethyl-cyclohexene, 40% st mat.

[a] All reactions involved 4.8 mmol of 1-methylnorcarane. [b] Also formed 4% 19, 5% 2,3-dimethylcyclohexanols, and 1% methylcyclo-heptanol (?).

the reaction tube using liquid nitrogen to effect condensation. Diborane was measured as a gas (ideal behavior assumed) and then condensed into the reaction tube. Tetraborane was measured by volume as a liquid at 0° and pentaborane was similarly measured at 25°. The experimentally determined densities of 0.55 and 0.66 g/cm³ were used to calculate mole amounts. The cold tube was then evacuated (to assure removal of all vapor phase diborane) and sealed; heavy wall tubes (volume ca. 30 ml) were used in experiments involving more than 2.5 mmol of diborane. After sealing, the tubes were brought to room temperature, and then immersed in a thermostated oil bath (±0.1°) for the desired time, after which they were withdrawn and allowed to cool to ambient temperature.

Product Isolation. The reaction tubes were CAREFULLY[22] opened, and treated slowly with 2 ml of ethanol to decompose unreacted boron hydrides. The contents of the tubes were then washed into an erlenmeyer flask, a few pellets of potassium hydroxide added, and the mixture then oxidized with 1 ml of 30% hydrogen peroxide. After standing a few minutes, water (75 ml) was added, and the products were then extracted using three 20-ml portions of methylene chloride. The organic phase was dried over K₂CO₃, after which the solvent was evaporated through a Vigreux column. The residue was then diluted to a standard volume for vpc analysis.

Product Identification. Minor products were identified by comparison of vpc retention times of materials prepared by alternate synthetic methods. Major products were isolated by preparative vpc and identified by spectral comparison (ir, nmr) with known samples.

Boron Trifluoride Reactions. Preparation of sample tubes was the same as for the diborane cleavage of cyclopropanes; commercial boron trifluoride gas was used without purification. Transfers were accomplished on a grease-free high vacuum line. After determining that this reagent did not give appreciable organoborane products in reaction with cyclopropanes, a simplified product isolation procedure was adopted. The reaction tube was opened in a fume hood; the contents were taken up in pentane, washed twice with water, dried (K₂CO₃), and subjected to vpc analysis.

Diborane. The procedure of Brown and Tierney[23] was used with minor modifications; helium was used in place of nitrogen as the flushing gas, and the product was passed through a Dry Ice trap and collected in a liquid nitrogen trap. The product was purified by three bulb-to-bulb vacuum transfers from a −126° bath (methylcyclohexane slush) bath to a liquid nitrogen trap. The purified material was then stored at room temperature in a bulb of approximately 5-l. capacity, with a condensing tube on the bottom. Because diborane decomposes slowly at room temperature, it could be repurified by condensing into this tube and evacuating to remove the hydrogen decomposition product. Warming the condensing tube to Dry Ice temperature then allowed the removal of diborane from the storage bulb, while higher boranes were retained.

In a typical synthesis, 11.5 g of sodium borohydride (0.300 mol) gave 190 mmol (95%) of purified diborane.

Tetraborane(10). The hot–cold concentric tube procedure of Klein, Harrison, and Solomon[16] was used to prepare this material. In a typical experiment 40 mmol of diborane on treatment at 135°/−80° for 2 hr gave 0.3 cm³ (3 mmol) of tetraborane, after fractionation from hydrogen, diborane, and higher boron hydrides. The product was kept at liquid nitrogen temperature, where no decomposition was noted over a period of 2 weeks.

Pentaborane(9). Callery Chemical Co. material was purified by distilling twice from a −46° bath (chlorobenzene slush) to −64° (chloroform slush), and discarding the small higher and lower boiling fractions. Although pentaborane(9) is a stable material, it was stored at Dry Ice temperature.

Cyclopropanes. The cyclopropanes used in this study were all prepared from the corresponding olefins using the Simmons–Smith reaction,[24] with the zinc–copper couple prepared according to Le Goff.[25] The bicyclo[4.1.0]heptane (norcarane), bicyclo[3.1.0]-hexane, 1-methylbicyclo[4.1.0]heptane, and spiro[2.5]octane have been described previously.[26] n-Pentylcyclopropane,[24] bp 124.5–125°, and n-octylcyclopropane,[27] bp 122° (130 mm), were both >99% pure by vpc analysis (20% Carbowax 6M).

Comparison Compounds. The Norcarane System. The isomers of 2- and 3-methylcyclohexanol were available from earlier work.[12,28] Cyclohexylmethanol was prepared by LAH reduction of cyclohexanecarboxylic acid, and had bp 187–188°.[29] Cycloheptanol,[30] bp 186–187°, was obtained by LAH reduction of the ketone.

Bicyclo[3.1.0]hexane Comparison Compounds. Cyclopentylmethanol, bp 158–160°, was prepared by the method of Royals and Neal.[30] Addition of methylmagnesium bromide to cyclopentanone furnished 1-methylcyclopentanol,[31] bp 54–55° (23 mm). A portion of this alcohol was dehydrated with hot phosphoric acid[32] to give, after fractionation, 95% pure 1-methylcyclopentene,[33] bp 75–76°. Hydroboration of this olefin furnished trans-2-methylcyclopentanol,[33] bp 147–150°.

1-Methylnorcarane Comparison Compounds. 1-Methylcyclohexanol, bp 73–74° (28 mm), was prepared following the procedure of Nevitt and Hammond.[34] A portion was converted to 1-methylcyclohexyl bromide,[35] which was in turn used to make the corresponding Grignard reagent. The bromide (46 g) was added over a period of 6 hr to 6.5 g-atoms of Mg in ether, to give a 77% yield (by titration) of the organometallic reagent. Treatment with

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formaldehyde gave 1-methylcyclohexylmethanol,[36] bp 98–99° (20 mm).

Catalytic hydrogenation of σ-toluic acid was carried out as reported earlier[37] to give largely cis-2-methylcyclohexanecarboxylic acid. A portion of this material was further reduced with LAH to give a 94:6 mixture of cis- and trans-2-methylcyclohexylmethanol. A separate portion of the acid was converted to the methyl ester and refluxed for 95 hr with 1% sodium methoxide in methanol to effect isomerization; an 80:20 mixture of methyl trans- and cis-2-methylcyclohexanecarboxylates resulted. LAH reduction gave a corresponding mixture of trans- and cis-2-methylcyclohexyl-methanols; the stereochemical identity was confirmed by conversion to the tosylate derivative and LAH reduction to give cis- and trans-1,2-dimethylcyclohexane, which were compared with known samples.

Addition of methylmagnesium bromide to 2-methylcyclohexanone gave an 80:20 mixture of cis- and trans-1,2-dimethyl-cyclohexanol,[34] bp 71–75° (25 mm). The trans material was separately prepared by hydroboration of 1,2-dimethylcyclohexene, followed by oxidation of the resultant borane.

Dehydration of 1,2-dimethylcyclohexanol with hot phosphoric acid gave a mixture of olefins; a spinning band distillation fraction, bp 132–136°, containing 77% 1,2- and 23% 1,6-dimethylcyclohexane was used in this work (cf. Table VI).

A sample of commercial 2,3-dimethylphenol was sublimed and subjected to catalytic hydrogenation followed by sodium borohydride treatment to further reduce ketone intermediates. Vpc analysis (Carbowax 20M) of the mixed 2,3-dimethylcyclohexanols obtained in this way gave four peaks. A small sample of 1,6-dimethylcyclohexene, isolated by preparative vpc from the olefin mixture described above, was subjected to hydroboration–peroxide oxidation. The product, trans-2-cis,trans-3-dimethylcyclohexanols, exhibited two peaks on vpc analysis, corresponding to the minor products from the catalytic reduction described above. The various isomers of 3,4-dimethylcyclohexanol as well as 2,2-dimethylcyclohexanol were available from earlier work.[38]

1-Methylcycloheptanol[39] was prepared by the addition of methylmagnesium bromide to cycloheptanone, and had bp 91–92° (28 mm). A portion was dehydrated to give 1-methylcycloheptene, which on hydroboration–oxidation gave trans-2-methylcyclo-heptanol,[40] bp 189–191°. Other mixed methylcycloheptanols were prepared by treating 1 ml of 1-methylcycloheptene with 8 ml of 1 M BH$_3$·THF, sealing the mixture in an ampoule, and heating in a steam bath for 12 hr. Subsequent peroxide oxidation showed <5% trans-2-methylcycloheptanol, <5% cycloheptylmethanol (by comparison with commercial material), and another peak (>90%) presumably encompassing a variety of methylcycloheptanols.

Spiro[2.5]octane Comparison Compounds. Addition of acetaldehyde to cyclohexylmagnesium bromide gave 1-cyclohexyleth-anol,[41] bp 95–96° (25 mm). 1-Ethylcyclohexanol,[42] bp 86–87° (30 mm), was similarly prepared by the addition of cyclohexanone to ethylmagnesium bromide. A portion was dehydrated with hot phosphoric acid to give material, bp 132–135°, which consisted of 85% 1-ethylcyclohexene[39] and 15% ethylidenecyclohexane (analysis by vpc on Carbowax 20M and by nmr). Hydroboration of this olefin mixture gave two alcohols (by vpc on Carbowax 20M), bp 95–97° (30 mm), the larger peak being assigned to trans-2-ethylcyclohexanol[43] while the second, smaller peak had the same retention time as 1-cyclohexylethanol.

Commercial cyclohexylacetic acid was reduced by LAH to furnish 2-cyclohexylethanol.[44]

n-Butylcyclopropane Comparison Compounds. 1-Heptanol was commercial material; 2-heptanol was prepared by the LAH reduction of the ketone. 2-Methyl-1-hexanol was not prepared but its retention time deduced by comparison with the homologs 1-octanol and 2-methyl-1-heptanol.

n-Pentylcyclopropane Comparison Compounds. Commercial 1-octanol was used. 2-Octanol[45] was obtained by the addition of methylmagnesium bromide to n-heptanal, and had bp 179–180°. The reaction of propionaldehyde with n-pentylmagnesium chloride furnished 3-octanol,[45] bp 175–177°. 2-Heptanol was successively converted to the bromide, Grignard reagent, and carboxylic acid, which on LAH reduction gave 2-methylheptanol,[46] bp 184–185°. The reaction between n-butylmagnesium bromide and isobutyraldehyde furnished 2-methyl-3-heptanol,[47] bp 92–93° (78 mm).

n-Octylcyclopropane Comparison Compounds. Commercial 1-bromodecane was converted to the Grignard reagent and then carbonated; LAH reduction of the resultant undecanoic acid gave 1-undecanol,[48] bp 146–147° (25 mm). 2-Undecanol was purchased from the Aldrich Chemical Co. Treatment of n-octylmagnesium bromide with propionaldehyde gave 3-undecanol,[49] bp 134–137° (37 mm). Commercial 2-bromodecane was converted as above to 2-methyl-1-decanol,[50] bp 142–144° (30 mm).

Methylene-2-methylcyclohexane (24). The procedure of Schlosser and Christman[51] was generally followed, using 2-methylcyclohexanone and triphenylphosphonium iodide; methylene-2-methyl-cyclohexane,[34] bp 125–126.5°, was obtained in 54% yield.

All other olefins used in this study were either obtained from commercial sources or have been described earlier.[26]

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