tassium carbonate. The organic layer was dried over 4-Å molecular sieves and analyzed by GC.

(ii) The following is the typical procedure for the hydroboration of pyridine–BF_3 complexes. In the usual experimental setup was placed 5 mmol of olefin in THF. The reaction flask was cooled to 0 °C, and to it was added 5 mmol of boron trifluoride etherate. The reaction mixture was stirred at 25 °C for 15 min. To it was added 1.66 mmol of BMS. The reaction was followed by analysis for residual hydride. Following completion of the reaction, the volatiles were removed under reduced pressure at 25 °C. To it was added 5 mL of THF, followed by 2.5 mmol of tetramehtylethylenediamine. The reaction mixture was oxidized with 3 N sodium hydroxide and 30% hydrogen peroxide. The aqueous layer was saturated with anhydrous potassium carbonate and the organic layer was dried over 4-Å molecular sieves and analyzed by GC.

Hydroboration with 9-BBN, Chx_2BH, and Sia_2BH. The reactions were carried out as described above for BMS.

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Hydroboration. 76. Hydroboration of Cyclic Dienes with Representative Hydroborating Agents

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A detailed study was made of the hydroboration of cyclic dienes with representative hydroborating agents: borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), disiamylborane (Sia_2BH), dibromoborane–methyl sulfide ($Br_2BH{\cdot}SMe_2$), and dibromoborane (Br_2BH). 1,4-Cyclohexadiene essentially undergoes monohydroboration with a stoichiometric amount of the representative hydroborating agents, whereas 1,5-cyclooctadiene gives the dihydroboration product predominantly. The rapid dimerization of 1,3-cyclopentadiene introduces a complication into its hydroboration. However, monomeric cyclopentadiene undergoes hydroboration primarily to the homoallylic derivative with little of the desired allylic product. Hydroboration of 1,3-cyclohexadiene with a stoichiometric amount of the hydroborating agent furnishes mainly the allylboranes, which upon treatment with acetaldehyde followed by oxidation, furnishes 1-(2-cyclohexenyl)-1-ethanol in good yield. Similarly, hydroboration of 1,3-cycloheptadiene and 1,3-cyclooctadiene furnished dihydroborated products preferentially, with lower yields of the corresponding allylboranes, characterized as 1-(2-cycloheptenyl)-1-ethanol and 1-(2-cyclooctenyl)-1-ethanol, respectively, following reaction with acetaldehyde.

The hydroboration of olefins, followed by oxidation with alkaline hydrogen peroxide of the intermediate organoborane, provides a convenient method for the stereospecific cis- and anti-Markovnikov hydration of double bonds.[2,3] A detailed study of directive effects in the hydroboration of olefins revealed that simple 1-alkenes, $RCH{=}CH_2$, undergo reaction to form predominantly the primary alcohols. 93–94%, accompanied by minor amounts, 6–7%, of the corresponding secondary alcohols.

It was evident that the extension of the hydroboration reaction to dienes probably would involve difficulties. First, the reaction of a polyfunctional olefin such as a diene with the polyfunctional borane molecule could result in the formation of polymers which might not exhibit the customary behavior of organoboranes. Secondly, conjugated dienes are less reactive toward simple addition reactions than related olefins. Consequently, the controlled monohydroboration of such dienes was a questionable possibility. Further, in the past, the hydroboration of symmetrical dienes has been studied in our laboratory.[4] In general, these studies have revealed little hope that this reaction might be synthetically useful. Reports of low conversions, mixtures of products, and substantial amounts of dihydroboration support this conclusion.[5] This is unfortunate, since the hydroboration of symmetrical dienes, if it could be controlled to give monohydroboration products, would provide a general synthesis of valuable allyl or homoallylboranes.[6] Accordingly, we undertook a systematic study of the hydroboration of cyclic dienes with representative hydroborating agents. The results of this study are reported in the present paper.

Results

A major consideration in the successful monohydroboration of cyclic dienes with a hydroborating agent would be a suitable choice of the reagent. Reaction of a difunctional substrate, the cyclic dienes, with a borane reagent (R_2BH) can and apparently frequently does lead to polyhydroboration, depending upon the nature of R. The resulting polymeric organoboranes are difficult to characterize. A second source of difficulty in the earlier work involved a lack of appreciation for the high reactivity of the allylboranes, one of the products which may be

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(1) Postdoctoral research associate on Grant GM 10937-22 from the National Institutes of Health.

(2) (a) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1956**, *78*, 5694; (b) *J. Org. Chem.* **1957**, *22*, 1135; (c) *J. Am. Chem. Soc.* **1959**, *81*, 6423, 6428.

(3) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 247, 4106; (b) *Ibid.* **1960**, *82*, 4708; (c) *Ibid.* **1961**, *83*, 2544.

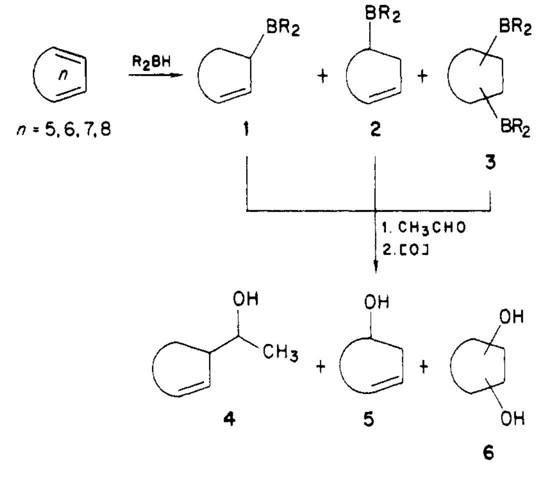
(4) (a) Zweifel, G.; Nagase, K.; Brown, H. C. *J. Am. Chem. Soc.* **1962**, *84*, 183, 190. (b) Zweifel, G.; Brown, H. C. *Ibid.* **1963**, *85*, 2066. (c) Brown, H. C.; Liotta, R.; Kramer, G. W. *J. Org. Chem.* **1978**, *43*, 1058. (d) Liotta, R.; Brown, H. C. *Ibid.* **1977**, *42*, 2836.

(5) Cragg, G. M. L. "Organoboranes in Organic Synthesis"; Marcel Dekker, Inc.: New York, 1973; p 208.

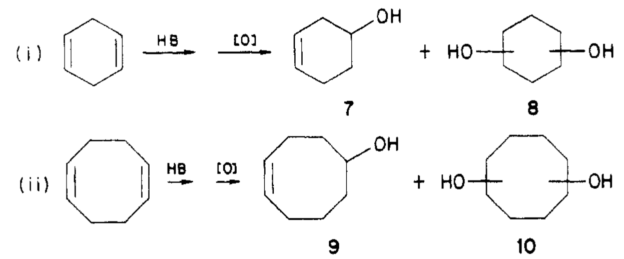
(6) (a) For example, the reaction product of 1,3-cyclohexadiene and diisopinocampheylborane reacts with aldehyde to provide 1-(2-cyclohexenyl)-1-alkanol, diastereomeric products of high optical purities. Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 2564. (b) Brown, H. C.; Jadhav, P. K. *Tetrahedron Lett.* **1984**, *25*, 1215.

0022-3263/86/1951-0445$01.50/0

Scheme I



Scheme II



formed. Mikhailov[7] and others[8] have shown that allylboranes, especially those with low molecular weights and nonsterically hindered allyl groups are rapidly hydrolyzed. Accordingly, such allylboranes will produce olefins rather than the expected allylic alcohols under the usual oxidation conditions utilizing alkaline hydrogen peroxide.

In this study we undertook to examine the first difficulty as our primary objective. Accordingly, we selected 1,3-cyclopentadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, and 1,4-cyclooctadiene as the diene substrates and BMS, 9-BBN, Sia_2BH, and the haloboranes ($BHBr_2{\cdot}SMe_2$ and $BHBr_2$) as the hydroborating agents. The second difficulty was avoided through the development of a reliable analytical procedure which could be applied to the allylboranes. Hydroboration of cyclic conjugated dienes could afford three major types of organoboranes: allylboranes **1**, homoallylboranes **2**, and dibora species **3** (Scheme I). With such a variety of products possible, conversion to simple, easily analyzed derivatives such as alcohols is highly desirable, but, as mentioned above, the allylborane may not give the desired product on simple oxidation. Accordingly, it seemed appropriate to convert the allylborane into a derivative which would give an unambiguous product upon oxidation. Such a derivative is provided by reaction of the allylborane with a simple aldehyde such as acetaldehyde prior to oxidation. The other potential products, **2** and **3**, are inert to acetaldehyde under these conditions. Following oxidation of this derivatized mixture, the amount of homoallylic alcohol **4** indicates the amount of allylborane, the amount of underivatized homoallylic alcohol indicates the extent of formation of homoallylborane, and the amount of unreacted diene gives the amount of dihydroboration (0% diene = 0% dihydroboration; 50% diene = 100% dihydroboration).

Table I. Stoichiometry of the Reaction of Nonconjugated Cyclic Dienes with Various Hydroborating Agents

diene	reagent	temp, °C	monohydroboration, %	dihydroboration, %
1,4-cyclohexadiene			product **7**	product **8**
	BMS	0	76	24
	9-BBN	25	82	18
	Sia_2BH	0	90	10
	$Br_2BH{\cdot}SMe_2$	40	38	62
	Br_2BH	0	12	88
1,4-cyclooctadiene			product **9**	product **10**
	BMS	0	3	97
	9-BBN[a]	25	9	91
	Sia_2BH[4a]	0	1	99
	$Br_2BH{\cdot}SMe_2$	40	2	98
	Br_2BH	0	2	98

[a] We previously reported that 9-BBN achieves the successful monohydroboration of 1,5-cyclooctadiene (ref 4d), but we have been unable to duplicate this result.

Table II. Reaction of 1,3-Cyclopentadiene (100% Excess) with Various Hydroborating Reagents[a]

reagent	temp, °C	monohydroboration, %: allylic product **12**	monohydroboration, %: homoallylic product **11**	dihydroboration, % product **13**
BMS[9]	0	1.5	55.5	43
9-BBN[b]	25			
Sia_2BH[9]	0	0.6	81.4	18
Br_2BH	0	0	78	22

[a] After hydroboration, the product was directly oxidized with trimethylamine N-oxide.[13] [b] From the earlier studies,[4c] it is evident that hydroboration of 1,3-cyclopentadiene with 9-BBN is slow and dimerization of 1,3-cyclopentadiene competes seriously with the hydroboration, yielding complex products.

Hydroboration of Nonconjugated Cyclic Dienes. 1,4-Cyclohexadiene and 1,5-cyclooctadiene were hydroborated with representative hydroborating agents by utilizing 1 equiv of the hydroborating agent per mole of diene. Following complete hydroboration, the resulting organoboranes were oxidized with alkaline hydrogen peroxide (Scheme II) and the products were analyzed by GC. (In these cases, the formation of allylic organoboranes is not a problem.) The results of these experiments are given in Table I.

Hydroboration of Cyclic Conjugated Dienes. The conjugated dienes 1,3-cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene were hydroborated with representative hydroborating agents. The resulting organoboranes were treated with acetaldehyde (except in the cases of $BR_2BH{\cdot}SMe_2$ and Br_2BH and 1,3-cyclopentadiene) and then oxidized with alkaline hydrogen peroxide (Scheme III). The products, after the usual workup, were analyzed by GC. The results of these experiments are represented in Tables II and III.

Discussion

The above results reveal that monohydroboration is very high in the six-membered diene system. As the ring size increases, dihydroboration increases and the yield of monohydroboration product decreases. Presumably, the high yields of monohydroboration realized is the result of the exceptional inertness of the six-membered ring derivatives toward hydroboration.[4a] For example, under conditions identical with those used for the hydroboration of dienes with disiamylborane, the reaction with cyclohexene is only 61% complete.[4a] Thus, the initial hydroboration step yields cyclohexene derivatives (**23** and **24**), which resists

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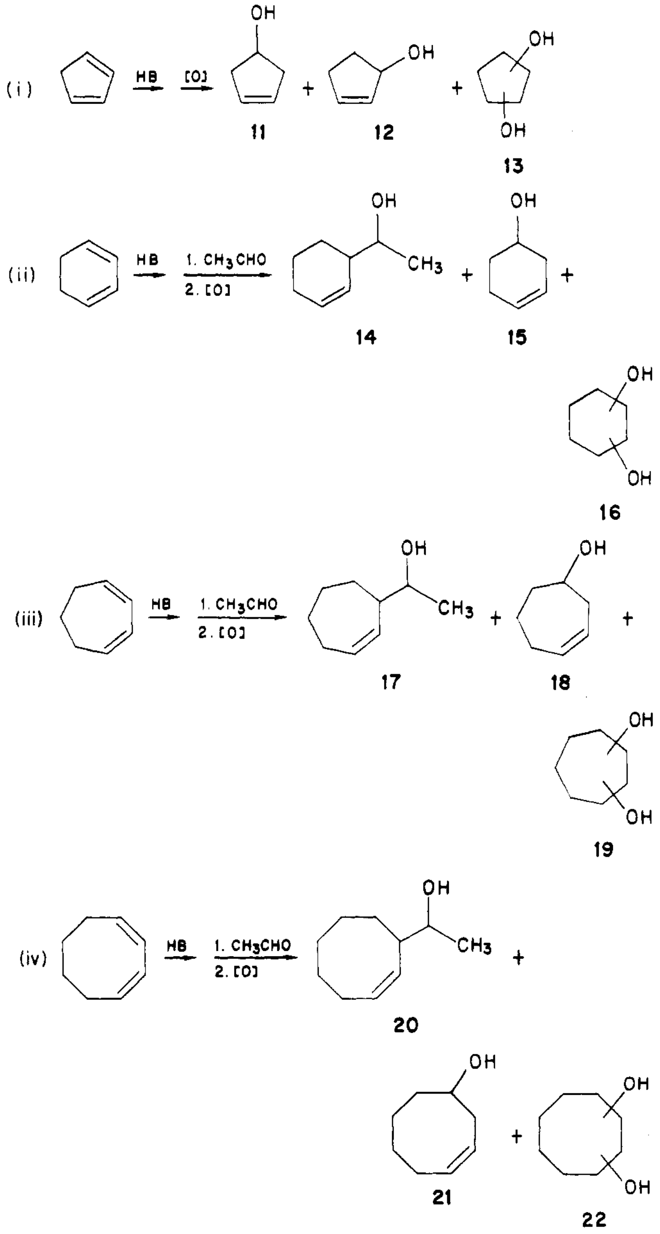
(7) Mikhailov, B. M. *Organomet. Chem. Rev. Sect. A* **1972**, *8*, 1.
(8) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1977**, *132*, 9.

Table III. Stoichiometry of the Reaction of Conjugated Cyclic Dienes with Various Hydroborating Reagents

diene	reagent	temp, °C	monohydroboration, % allylic	monohydroboration, % homoallylic	dihydroboration, %
1,3-cyclohexadiene			product **14**	product **15**	product **16**
	BMS	0	74	14	12
	9-BBN[4b]	25	85	10	5
	Sia_2BH[4a]	0	90	10	0
	$Br_2BH\cdot SMe_2$	40	11	63	26
	Br_2BH	0	0	20	80
1,3-cycloheptadiene			product **17**	product **18**	product **19**
	BMS	0	21	3	76
	9-BBN	25	42	4	54
	Sia_2BH	0	47	3	50
	$Br_2BH\cdot SMe_2$	40	0	7	93
	Br_2BH	0	0	2	98
1,3-cyclooctadiene			product **20**	product **21**	product **22**
	BMS	0	18	2	80
	9-BBN[4c]	25	0	0	100
	Sia_2BH	0	30	2	68
	$Br_2BH\cdot SMe_2$	40	0	4	96
	Br_2BH	0	0	2	98

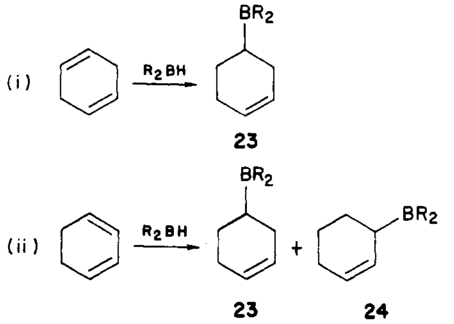
Scheme III



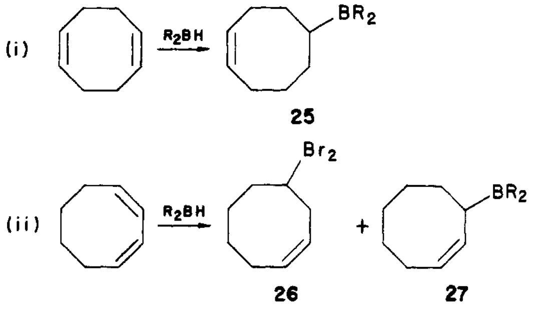
further hydroboration (Scheme IV).

In contrast to the cyclohexadienes, the cyclooctadienes undergo dihydroboration preferentially. Cyclooctene is exceedingly reactive toward the borane reagent.[10] Since the initial product of the hydroboration of cyclooctadienes must be cyclooctene derivatives (**25**, **26** and **27**), the speed of the second stage is not unexpected, thus favoring dihydroboration (Scheme V).

Scheme IV



Scheme V



The increasing yield of the monohydroboration product (allylborane, **27**) in the hydroboration of 1,3-cyclooctadiene, as compared to that realized in the hydroboration of 1,5-cyclooctadiene, probably indicates the initial formation of **27**, which may not be as active as the homoallylborane **25** toward further hydroboration because of steric hindrance afforded by the large BR_2 group on the neighboring double bond. The same interpretation can be extended to the reasonable yields of allylborane provided by 1,3-cycloheptadiene.

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(9) Hess, H. M.; Brown, H. C. *J. Org. Chem.* **1967**, *32*, 4138.

(10) For a discussion of the reactivity of medium ring olefins toward hydride reagents with pertinent literature references, see: Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1961**, *83*, 3417. Dauben, W. G.; Pitzer, K. S. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956.

Conclusion

A high yield of monohydroboration product was realized in the six-membered-ring diene system. As the ring size increases, monohydroboration decreases and dihydroboration increases. Further, the yield of allylborane (monohydroboration product) was very high in the six-membered conjugated diene system but decreased in the seven- and eight-membered-ring conjugated diene systems. In contrast, the five-membered-ring system failed to furnish the corresponding allylborane. Further, the results indicate that the dialkylborane, disiamylborane, furnishes a high yield of monohydroborated product. Finally, the allylboranes can be readily derivatized to the corresponding 1-(2-cyclohexenyl)-1-ethanol or 1-(2-cycloheptenyl)-1-ethanol or 1-(2-cyclooctenyl)-1-ethanol upon treatment with acetaldehyde, followed by oxidation.

Experimental Section

Methods. All glassware was dried at 140 °C overnight, assembled hot, and allowed to cool under a purge of nitrogen. All reactions were carried out under a static pressure of nitrogen in flasks fitted with side arms capped with rubber septa and were stirred magnetically using oven-dried, Teflon-coated stirring bars. All transfers of liquids and solutions of organometallic reagents were done either with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles or by the double-ended needle technique. Special techniques used in handling air-sensitive materials are described in detail elsewhere.[11]

Analyses. ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The chemical shifts are in δ relative to $BF_3 \cdot OEt_2$. IR spectra were recorded on a Perkin-Elmer 137 spectrometer. ^{1}H NMR spectra were recorded on either a Varian T-60 (60 MHz) or Perkin-Elmer R-32 (90 MHz) instrument. ^{13}C NMR spectra were recorded on a Varian FT-80A instrument. All GC analyses were carried out with a Hewlett Packard 5750 chromatograph using 12 ft × 0.125 in. columns packed with 10% Carbowax 20M on Chromosorb W (100–120 mesh) or 12 ft × 0.125 in. column packed with 10% SE-30 on Chromosorb W (100–120 mesh). Analyses were done by the internal standard method by using correction factors determined from authentic samples.

Materials. The *n*-alkanes (Phillips) employed as GC internal standards were kept over 4-Å molecular sieves under nitrogen atmosphere and used as such. Tetrahydrofuran (THF) was distilled over benzophenone ketyl and stored under nitrogen atmosphere in an ampule. Technical grade pentane was stirred over concentrated sulfuric acid, washed with aqueous base, dried over anhydrous magnesium sulfate, distilled under nitrogen from lithium aluminum hydride, and stored under nitrogen atmosphere in an ampule. Acetaldehyde (Aldrich) was used as received. Borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), and dibromoborane–methyl sulfide were purchased from Aldrich Chemical Company. BMS and dibromoborane–methyl sulfide were estimated according to the standard procedure. 1,3-Cyclopentadiene was obtained from dicyclopentadiene (Aldrich) by cracking.[12] 1,4-Cyclohexadiene (Wiley Organics), 1,3-cyclohexadiene (Wiley Organics), and 1,3-cycloheptadiene (Aldrich) were used as received. 1,5-Cyclooctadiene and 1,3-cyclooctadiene used in this study were distilled over lithium aluminum hydride in a nitrogen atmosphere. *n*-Decane and *n*-dodecane were used as internal standard.

Hydroboration with BMS. A general procedure is as follows. In a 50-mL flask fitted with a reflux condenser, septum inlet, and magnetic stirring bar was placed cyclic diene (10 mmol) in 10 mL of tetrahydrofuran and a known amount of internal standard. The flask was immersed in an ice-bath and 3.33 mmol of BMS (10 M) was added dropwise. The temperature was maintained at 0 °C, and the reaction was followed by ^{11}B NMR. After completion of the reaction in the cyclic nonconjugated diene system, the reaction mixture was directly oxidized with alkaline hydrogen peroxide, whereas in conjugated diene system the reaction mixture was treated with acetaldehyde (20 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, slowly warmed to room temperature, and then kept at 25 °C for 3 h. Then the reaction mixture was oxidized with alkaline hydrogen peroxide. After the usual workup, the products were analyzed by GC.

Hydroboration with 9-BBN. A general procedure is as follows. In a 50-mL flask assembled as above was placed solid 9-BBN (10 mmol), THF (10 mL), and a known quantity of internal standard. To it was added 10 mmol of cyclic diene, and the reaction mixture was kept under stirring at 25 °C. The reaction was followed by ^{11}B NMR. After completion of the reaction in cyclic nonconjugated diene system, the reaction mixture was directly oxidized with alkaline hydrogen peroxide and the products were analyzed by GC, whereas in the conjugated diene system the reaction mixture was treated with acetaldehyde (20 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, then slowly warmed to room temperature, and kept at 25 °C for 3 h. The reaction mixture was oxidized with alkaline hydrogen peroxide. After the usual workup, the products were analyzed by GC.

Preparation of Disiamylborane. In a 50-mL round-bottomed flask equipped with a septum inlet and magnetic stirring bar were placed 50 mmol (5 mL of 1 M) of BMS and 18 mL of tetrahydrofuran. The flask was cooled to −5 °C, and 7 g (100 mmol) of 2-methyl-2-butene was added dropwise via syringe. Then the flask was kept at 0 °C under stirring for 3 h. The ^{11}B NMR of the reaction mixture after methanolysis showed a clean signal at δ 53.65, characteristic of $Sia_2B{-}O$ species.

Hydroboration with Disiamylborane. The following procedure is characteristic. In the usual experimental setup were placed 10 mmol of cyclic diene and a known amount of the internal standard. The flask was immersed in an ice-bath and 10 mmol of disiamylbornae in tetrahydrofuran (prepared as above) was added to the diene dropwise. The temperature was maintained at 0 °C and the reaction was followed by ^{11}B NMR. After completion of the reaction, the contents from the nonconjugated diene systems were directly oxidized with alkaline hydrogen peroxide, whereas the reaction products from the conjugated diene system were treated with acetaldehyde (20 mmol) at −78 °C and then stirred for 30 min, followed by warming to room temperature. At 25 °C it was stirred for 3 h and then oxidized with alkaline hydrogen peroxide. Following the usual workup, the reaction products were analyzed by GC.

Hydroboration with Dibromoborane–Methyl Sulfide. A general procedure is as follows. In the usual experimental setup, a mixture of cyclic diene (5 mmol), a known amount of internal standard, and the dibromoborane–methyl sulfide (5 mmol) in dichloromethane (5 mL) were refluxed. The progress of the reaction was followed by ^{11}B NMR. After completion of the reaction (^{11}B NMR δ +6, $RBBr_2 \cdot SMe_2$ species), the mixture was cooled to 0 °C and tetrahydrofuran (3 mL) added. The reaction mixture was stirred for an additional 30 min (^{11}B NMR δ +30, $-OB(R)O-$ species). In the case of the cyclic nonconjugated dienes, the mixture was directly oxidized with alkaline hydrogen peroxide, whereas in the case of cyclic conjugated dienes the mixture was oxidized with anhydrous trimethylamine *N*-oxide.[13] The product, after the usual workup, was analyzed by GC.

Hydroboration with Dibromoborane.[14] In the usual experimental setup were placed cyclic diene (5 mmol), pentane (5 mL), and dibromoborane–methyl sulfide (neat, 5 mmol). The reaction flask was cooled to 0 °C and the tribromoborane was added dropwise to generate free dibromoborane. After complete addition, the reaction mixture was stirred for 45 min (^{11}B NMR δ +64 to +65; $RBBr_2$ species). THF (3 mL) was added to destroy the boron-bromide bonds. Then the reaction mixture was oxidized with alkaline hydrogen peroxide. The products were isolated and analyzed by GC.

1-(2-Cyclohexenyl)-1-ethanol, 1-(2-cycloheptenyl)-1-ethanol, and 1-(2-cyclooctenyl)-1-ethanol were isolated in a typical hydroboration experiment of 1,3-cyclohexadiene, 1,3-cycloheptadiene,

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[11] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

[12] Moffett, R. B. "*Organic* Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 238.

[13] Zweifel, G.; Polston, N. L.; Whitney, C. C. *J. Am. Chem. Soc.* **1968**, *90*, 6243.

[14] Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384.

and 1,3-cyclooctadiene with disiamylborane. GC pure (100%) compounds were obtained by preparative GC using a 6 ft × 0.5 in. column packed with 20% SP-2100 on Chromosorb W (60-80 mesh).

1-(2-Cyclohexenyl)-1-ethanol: IR (neat) ν_{max} 3359, 1642 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.5-6.0 (m, 2 H), 3.6-3.9 (m, 1 H), 1.4-2.3 (m, 8 H), 1.2 (d, J = 4 Hz, 3 H); ^{13}C NMR (CDCl$_3$) ppm 129.87, 128.34, 70.61, 42.90, 25.32, 23.73, 21.36, 19.95.

1-(2-Cycloheptenyl)-1-ethanol: IR (neat) ν_{max} 3355, 1644 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.6-6.1 (m, 2 H), 3.8 (m, 1 H), 1.3-2.5 (m, 10 H), 1.1 (d, J = 4 Hz, 3H); ^{13}C NMR (CDCl$_3$) ppm 133.41, 132.37, 70.88, 46.97, 30.32, 28.93, 28.67, 26.89, 19.58.

1-(2-Cyclooctenyl)-1-ethanol: IR (neat) ν_{max} 3358, 1644 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.3-5.9 (m, 2 H), 3.65 (m, 1 H), 1.3-2.6 (m, 12 H), 1.1 (d, J = 4 Hz, 3 H); ^{13}C NMR (CDCl$_3$) ppm 130.60, 130.50, 71.53, 43.94, 31.80, 29.42, 26.91, 26.73, 25.61, 21.30.

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Intramolecular Anionic Cyclization Route to Capped [3]Peristylanes

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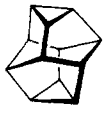
A short route to capped [3]peristylanes, in particular the polycyclic ether **9**, is described. The synthesis begins with the known unsaturated ketone **3** and proceeds by way of a two-carbon chain extension, chemospecific reduction, epoxidation, and anionic cyclization to form the first additional framework C-C bond. Following tosylation, the cyclopropane ring is elaborated under anionic conditions. The regioselectivity of ring closure is discussed in the context of MM2 calculations. Although nitrile **8** could be transformed by conventional methods to the carboxylic acid, subsequent Hunsdiecker degradation of this intermediate proved unworkable. On the other hand, **8** proved subject to decyanation when heated with potassium hydride in tetrahydrofuran. The response of **8** and **9** to the action of trimethylsilyl iodide was briefly examined. In both examples, the cyclopropane ring was cleaved while the ether linkage was unaffected.

The molecular array p-[3^2.5^6]octahedrane (**1**)[1] is the smallest member of a family of polycyclic saturated (CH$_2$)$_n$ systems having a central n-membered ring (for **1**, n = 6) connected by alternate carbon atoms to two (n/2)-membered rings.[2] Dramatic alterations in structural topology are expected to accompany changes in n. To this time, the pentagonal dodecahedrane and select derivatives (n = 5) have been the only representatives studied.[3] We are interested in defining the precise nature of these geometric perturbations and in correlating the various structural features with chemical reactivity.[4] For this reason, **1** has been chosen as a synthetic target of interest, although a less symmetric dimethyl analogue has been recently prepared.[5]



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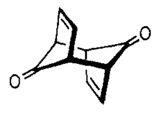

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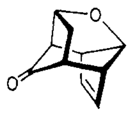

3

Examination of the carbocyclic framework of **1** in a retrosynthetic sense has led us to consider the readily available diketone **2**[6] as a potentially suitable starting material. Two symmetrically disposed carbon atoms are seen to be lacking and these must ultimately serve as the linchpins for construction of the two cyclopropane rings. In the present paper, methods are described that resulted in the desired chemical construction on one surface of **2** *under mild conditions* (thus avoiding framework rearrangement[7,8]).

Ganter and co-workers have convincingly demonstrated that the carbonyl groups in **2** are sterically compressed.[9] This situation, which markedly lowers the reactivity of these centers (particularly following nucleophilic attack at one of them), can be ameliorated by bridging across half of the molecule as in **3**. This substance is prepared from **2** by reduction with lithium tri-*tert*-butoxyaluminum hydride and cyclization with 2 N sodium hydroxide in methanol.[8,9] Accordingly, we have utilized **3** in this initial study. Our investigation has culminated in an eight-step synthesis of **9** via a route potentially applicable to the elaboration of **1**.

Condensation of **3** with the anion of diethyl (cyanomethyl)phosphonate proceeded with customary good efficiency (81%) to give **4** as an inseparable 4:1 mixture of isomers. Reduction of the admixed α,β-unsaturated nitriles with magnesium in methanol[10] occurred with complete

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(1) For an explanation of this nomenclature, see footnote 4 in Paquette, L. A.; Browne, A. R.; Doecke, C. W.; Williams, R. V. *J. Am. Chem.* **1983**, *105*, 4113.

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(4) For preliminary studies aimed at the member of this series where n = 4, consult Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 686.

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(9) (a) Pfund, R. A.; Ganter, C. *Helv. Chim. Acta* **1979**, *62*, 228. (b) Ammann, W.; Ganter, C. *Ibid.* **1977**, *60*, 1924.

(10) Profitt, J. A.; Watt, D. S.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 127.

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