vinylcyclohexene.[21] A mixture of *cis*- and *trans*-2-hydroxycyclohexaneethanol (**31** and **32**) was obtained by the reduction of commercially available ethyl 2-ketocyclohexaneacetate.

Preparation of Hydroxy-α-methylcyclohexanemethanols. A mixture of *cis*- and *trans*-3- and *cis*- and *trans*-4-hydroxy-α-methylcyclohexanemethanols was prepared by the hydroboration of α-methyl-3-cyclohexenemethanol. The presence of two of these isomers in the diol products derived from a distilled methanolysis product of the hydroboration of 4-vinylcyclohexene led to the assignment of the *cis*-3- and *cis*-4- structures to these compounds. The *trans*-3- and *trans*-4- structures were, therefore, tentatively assigned to the remaining two products.

Preparation of Limonene-2,9-diols. An authentic sample of D-(−)-(1*S*,2*R*,4*R*)-limonene-2,9-diol (**36**) was prepared as described previously,[4] mp 92–92.5°. Its identification was carried out by C. D. Pfaffenberger by converting the diol to the known D-(−)-carvomenthol[22] by the following sequence[4]

$$\mathrm{ROH} \xrightarrow{\mathrm{TsCl}} \mathrm{ROTs} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{RH}$$

The isomeric diol (**37**) was not prepared as a pure substance. A mixture of **36** and **37** was prepared by the hydroboration of D-(+)-limonene with borane. Two major diol products were obtained in the ratio of 84:16, the major component of which was **36**. The structure **37** was, therefore, tentatively assigned to the minor component.[4]

Acknowledgment. The authors are indebted to Drs. E. F. Knight and C. D. Pfaffenberger for the information provided by them in certain phases of the present study. Support of this research by the U. S. Army Research Office (Durham) and the National Institutes of Health is gratefully acknowledged.

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[21] Kindly supplied by Professor C. A. Brown of Cornell University.

[22] D. K. Shumway and J. D. Barnhurst, *J. Org. Chem.*, **29**, 2320 (1964).

Hydroboration. XXXII. The Cyclic Hydroboration of Dienes with Thexylborane

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Contribution from the Richard B. Wetherill Laboratory,
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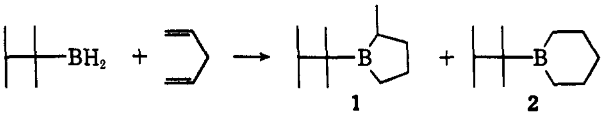
Received July 6, 1971

Abstract: Glpc conditions for determining the exact quantities of *B*-thexylboracyclanes present in the diene–thexylborane reaction mixtures are established. Glpc examination using the established conditions reveals that the hydroboration of 2,3-dimethyl-1,3-butadiene with thexylborane is 93% cyclic, whereas that of 1,3-butadiene is only 17% cyclic. An explanation for the marked difference in the extent of cyclic hydroboration is given. The extent of cyclic hydroboration with 1,4-pentadiene and 1,5-hexadiene is at least 80% in each case. In the competitive formation of five- and six-membered boracyclanes, there exists a strong preference for the formation of the five-membered ring. On the other hand, in the competitive formation of six- and seven-membered boracyclanes, neither is strongly favored over the other, and the usual directive effect appears to control the product distribution. These findings appear to provide a simple explanation for the initial 78:22 distribution of *B*-thexyl-9-borabicyclo[4.2.1]nonane and its [3.3.1] isomer in the highly cyclic hydroboration of 1,5-cyclooctadiene. In most cases examined, the *B*-thexylboracyclanes are isolated in excellent yields by distillation without noticeable isomerization of either the thexyl group or the ring moiety. Even from the largely polymeric 1,3-butadiene–thexylborane reaction mixture is isolated a 71% yield of *B*-thexylborolane. The distilled *B*-thexylboracyclanes are identified and characterized.

In our earlier study on the hydroboration of dienes with thexylborane, 2,3-dimethyl-2-butylborane,[2] it was found that the hydroboration of 1,4-pentadiene with an equimolar quantity of thexylborane yielded, after oxidation, 70% of 1,4- and 30% of 1,5-pentanediols, whereas the monofunctional disiamylborane, bis(3-methyl-2-butyl)borane, afforded mainly the 1,5-diol (85%).[3] This notable difference was rationalized in terms of a cyclization reaction, favoring the formation of a five-membered ring, in the case of hydroboration with thexylborane (eq 1). However, the hydroboration of 1,3-cyclopentadiene with thexylborane yielded, after oxidation, mainly *trans*-1,3-cyclopentanediol (trans:cis = 87:13).[2] Clearly, cyclization cannot be the major path in this case. Similarly, 1,4-cyclohexadiene did not appear to yield the corresponding cyclic organoborane by the hydroboration with thexylborane.[2] Consequently, these earlier observations did not encourage us to utilize thexylborane as a cyclic hydroborating agent to form *B*-thexylboracyclanes.



1 major

2 minor

(1)

On the other hand, our recent stoichiometry study[4] indicated that the hydroboration of dienes with thexylborane in many cases must be highly cyclic and that the results with 1,3-cyclopentadiene and 1,4-hexadiene did not reflect the entire picture.

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[1] Postdoctoral research associate on a research grant, DA 31-134 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

[2] G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 2066 (1963).

[3] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 190 (1962).

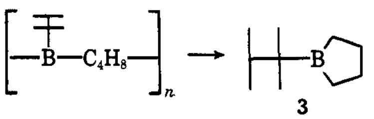
[4] H. C. Brown and C. D. Pfaffenberger, *ibid.*, **89**, 5475 (1967); for the experimental detail, see C. D. Pfaffenberger, Ph.D. Thesis, Purdue University, 1967.

Our recent finding that the carbonylation–oxidation of thexyldialkylboranes provided in high yields the corresponding ketones[5] suggested its application to the transformation of dienes into the corresponding cyclic ketones.[6] Consequently, it became highly desirable to define the exact nature of the hydroboration of dienes with thexylborane.

Results and Discussion

Our stoichiometry study[4] indicated that the hydroboration with thexylborane of 1,4-pentadiene, 1,5-hexadiene, 1,5-cyclooctadiene, and D-(+)-limonene must be highly cyclic, whereas the corresponding reactions of 1,7-octadiene and 1,4-cyclohexadiene are not. Accordingly, in this study 1,4-pentadiene, 1,5-hexadiene, 1,5-cyclooctadiene, and D-(+)-limonene were selected in addition to three conjugated dienes, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, which could not be examined by the methods utilized in the previous stoichiometry study.

Methods of Analyses. Glpc Examination and Distillation of *B*-Thexylboracyclanes. Each diene was hydroborated with an equimolar quantity of thexylborane at 0°. Since our previous work[4] and a preliminary experiment with 1,5-hexadiene indicated that the simultaneous addition of thexylborane and a diene did not offer any noticeable advantage over the use of borane-to-diene mode of addition (Table II), the more convenient borane-to-diene mode of addition was adopted in all cases. At the completion of hydroboration, the reaction mixture was analyzed by glpc on a 2-ft SE-30 column. Glpc examination of *B*-alkylboracyclanes[7,8] offers a highly convenient direct means of determining the exact quantity of a *B*-alkylboracyclane formed in the reaction. Analysis of distilled *B*-alkylboracyclanes does not usually offer any serious difficulty. The distilled *B*-thexylboracyclanes handled in the present study gave constant areas relative to that of an internal standard at various temperatures below 150° in most cases. On the other hand, in the glpc examination of hydroboration mixtures, it is essential to avoid the conversion of acyclic boranes into *B*-alkylboracyclanes during the glpc analyses. Presence of such a conversion would be detected by the temperature dependence of glpc analyses. A notable example is the glpc analysis of 1,3-butadiene–thexylborane reaction mixture. The results are summarized in Table I. A sudden increase in the amount of *B*-thexylborolane above 75° observed in this case must be the result of a thermal conversion of polymeric organoboranes to *B*-thexylborolane (**3**) (eq 2).



3

(2)

Quite significantly, however, at or below 75° the amount of **3** was constant. Another significant observation is that under identical conditions highly reproducible results were obtained. These results seem to assure that under the glpc conditions employed the amount of **3** observed at or below 75° represents its actual amount present in the reaction mixture at 0° or room temperature.

Table I. Temperature Dependence of Glpc Analysis of 1,3-Butadiene–Thexylborane Reaction Mixture[a]

Injection block and detector temp, °C	*B*-Thexylborolane,[b] %	Injection block and detector temp, °C	*B*-Thexylborolane,[b] %
50	17	125	75
75	17	150	63
100	31	200	59

[a] Analysis carried out on a Varian Model 1400 using a 2-ft 10% SE-30 column (Chromosorb W), column temperature 50°. [b] An average value of at least two analyses. At each temperature the values for the amount of *B*-thexylborolane fell within a range of 3%.

Similar experiments testing the validity of glpc examination were made whenever the technique was employed. In the other cases, the results of glpc analyses were essentially constant below 150°. However, this may merely be the consequence of the highly cyclic nature of hydroboration reaction in these cases.

Distillation of the diene–thexylborane reaction mixture as a method of determining the exact quantity of *B*-thexylboracyclanes seems less satisfactory than the glpc analysis. However, it is important from a synthetic point of view that in most cases examined the *B*-thexylboracyclanes could be obtained by distillation in excellent yields (Table II) without involving detectable isomerization of either the thexyl group or the ring moiety, provided that the distillation temperature was kept below ~100°.

The experimental results of glpc examination and distillation of the diene–thexylborane reaction mixtures are summarized in Table II along with the results of characterization of the distilled products. These results clearly indicate the following. (1) Hydroboration of dienes examined in the present study is largely cyclic except with 1,3-butadiene and possibly with isoprene. (2) Even when the initial product is not highly cyclic, as in the case of 1,3-butadiene, the cyclic product can be obtained in high yield by distillation. (3) Glpc examination of the reaction mixtures and the distilled products revealed that the isomer distribution was essentially unchanged before and after distillation except for the case of 1,5-cyclooctadiene. This strongly supports that no extensive isomerization took place during distillation.

Conjugated Dienes. Conjugated dienes are unique in that the reactivity of conjugated double bonds toward hydroboration is much less than the corresponding isolated double bonds.[3,9] Thus, there is a large increase in reactivity of the second double bond of a conjugated diene after the hydroboration of the first.

As is clear from Table II, the hydroboration of 2,3-dimethyl-1,3-butadiene with thexylborane must be a simple cyclization, following the initial attack of thexylborane almost exclusively at one of the terminal positions (eq 3). On the other hand, the product from 1,3-butadiene was largely polymeric (~80%). This rather unexpected result may be readily accounted for on the basis of the enhanced reactivity of the second and iso-

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[5] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **89**, 5285 (1967).

[6] H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967).

[7] G. Schomburg, R. Köster, and D. Henneberg, *Z. Anal. Chem.*, **170**, 285 (1959).

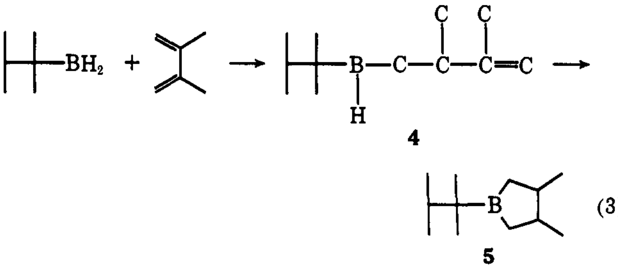
[8] H. C. Brown, E. Negishi, and S. K. Gupta, *J. Amer. Chem. Soc.*, **92**, 2460 (1970).

[9] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, pp 218–226.

Table II. Glpc Examination and Distillation of the Hydroboration Mixtures Derived from Dienes and Thexylborane and Characterization of the Distilled Products[a]

	Total yield of *B*-thexylboracyclane, %		Product				
Diene	Glpc[b]	Isolated[c]	Isomer distribution[d]	%	Bp, °C (mm)	Diol distribution[e]	%
1,3-Butadiene	17	71[f]	*B*-Thexylborolane	100	72 (19)	1,4-Butanediol	100
Isoprene	*g*	54[f,h]	*B*-Thexyl-3-methylborolane	100	55 (4)	*i*	
2,3-Dimethyl-1,3-butadiene	93	89	*B*-Thexyl-3,4-dimethylborolane[j]	100	72–74 (4)	2,3-Dimethyl-1,4-butanediol[k]	100
1,4-Pentadiene	81	83	*B*-Thexylborinane	28	57–58 (4)	1,5-Pentanediol	29
			B-Thexyl-2-methylborolane	72		1,4-Pentanediol	71
1,5-Hexadiene	85 (87)[l]	82	*B*-Thexylborepane	90	79–80 (4)	1,6-Hexanediol	90
			B-Thexyl-2-methylborinane	2		1,5-Hexanediol	2
			B-Thexyl-2,5-dimethylborolane	8		2,5-Hexanediol	8
1,5-Cyclooctadiene	*g*	91	*B*-Thexyl-9-borabicyclo[3.3.1]nonane	80[m]	93–94 (0.4)	1,5-Cyclooctanediol	80[n] (20)[o]
			B-Thexyl-9-borabicyclo[4.2.1]nonane	20[m]		1,4-Cyclooctanediol	20[n] (80)[o]
D-(+)-Limonene	*g*	72[h]	*B*-Thexyl-4,8-dimethyl-2-borabicyclo[3.3.1]nonane[g]	100[m]	88 (0.4)	D-(−)-(1*S*,2*R*,4*R*)-Limonene-2,9-diol[p,q]	100[n]

[a] The hydroboration was carried out by the addition of thexylborane in THF to an equimolar quantity of a diene in THF at 0°. [b] On a 2-ft 10% SE-30 column (Chromosorb W). [c] By distillation. [d] By glpc analyses of the distilled products. However, the glpc analyses of the reaction mixture gave essentially the same distribution (±2%) except in the case of 1,5-cyclooctadiene. [e] By glpc analyses of the oxidation products of distillates. Diols silylated in most cases before glpc analysis on a SE-30 column. Total yield of diols in each case 90–100%. Yield of thexyl alcohol in each case 95–100%. [f] A highly viscous residue obtained after evaporation of solvent. [g] Glpc examination not performed. [h] No attempt made to maximize the yield of *B*-thexylboracyclane. [i] Product not oxidized, but identified by elemental analyses. *Anal.* Calcd for $C_{11}H_{23}B$: C, 79.53; H, 13.95; B, 6.51. Found: C, 79.27; H, 13.93; B, 6.25. [j] A 63:37 mixture of cis and trans isomers by glpc. The cis structure was tentatively assigned to the isomer with the longer retention time. [k] Separation of diasteriomeric isomers not achieved. [l] Number in parenthesis obtained by simultaneous addition of 1,5-hexadiene and thexylborane. [m] Based on the diol distribution. [n] Diols acetylated before glpc analysis on a 150 ft × 0.01 in. capillary column coated with polyphenyl ether. [o] Number in parentheses obtained by oxidation of the hydroboration mixture. [p] Presumably a mixture of cis and trans isomers. [q] Oxidation and glpc analyses of oxidized products carried out by C. D. Pfaffenberger, Ph.D. Thesis, Purdue University, 1967.

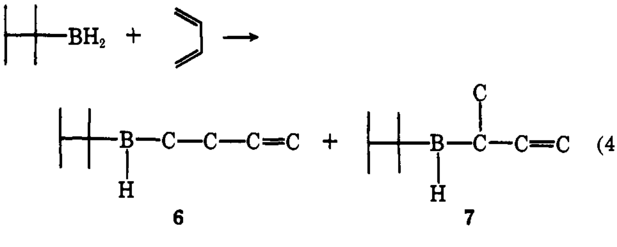


4

5

(3)

lated double bonds of intermediate species (**6** and **7**). The initial products of the 1,3-butadiene–thexylborane reaction must be a mixture of **6** and **7**. Each of these

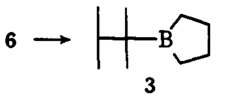


6

7

(4)

intermediates now has a considerably more reactive double bond than the parent 1,3-butadiene and therefore must react preferentially. It is reasonable to assume that **6** is almost exclusively transformed into **3** according to eq 5. Since there has been no evidence for the formation of four-membered organoboranes in the present study, formation of **8** from **7** is ruled out.



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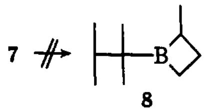
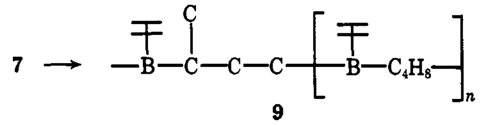
(5)



8

(6)

Polymerization, which may or may not involve formation of macrocyclic ring structures, is the only possibility (eq 7).



9

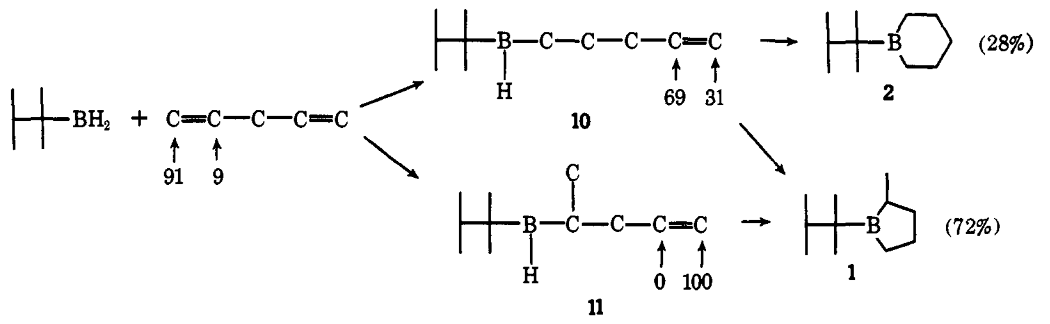
(7)

1,4-Pentadiene and 1,5-Hexadiene. Hydroboration of a terminal olefin with thexylborane, after oxidation, yields a 95:5 mixture of the corresponding 1- and 2-alcohols,[2] whereas the ratio obtained by employing dialkylboranes, such as disiamylborane,[10] 9-BBN,[11] and diethylborane,[12] is ~99:1, irrespective of the structure of dialkylboranes. It follows that the first step of the hydroboration of a terminal olefin with thexylborane yields an approximately 91:9 mixture of thexylmonoalkylboranes, each of which hydroborates the remaining 1-alkene to place the boron atom almost exclusively (~99%) at the terminal position in the second step.

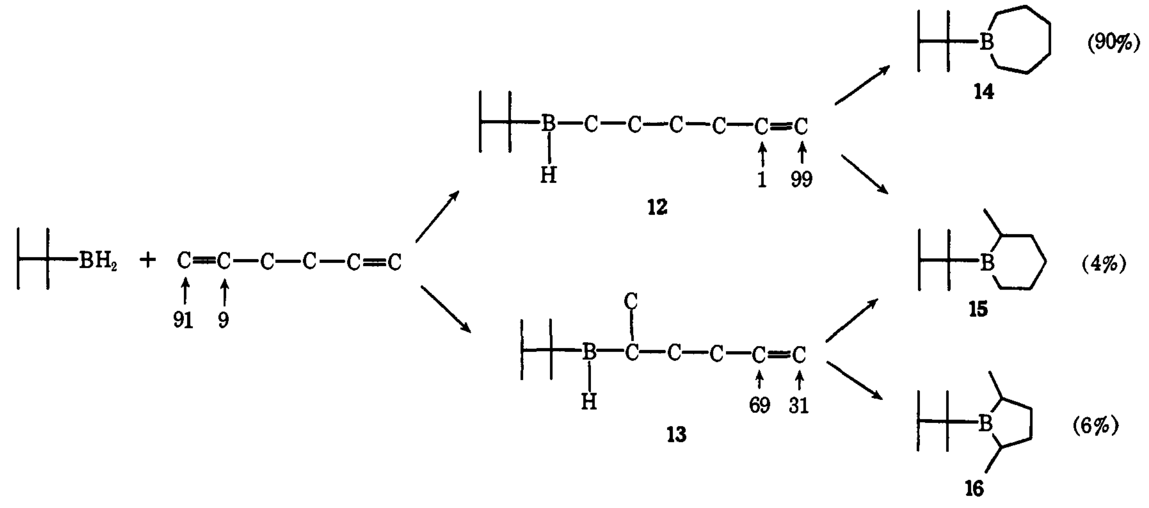
(10) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 1241 (1961).

(11) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281 (1968).

(12) R. Köster, G. Griasnow, W. Larbig, and P. Binger, *Justus Liebigs Ann. Chem.*, **672**, 1 (1964).



(8)

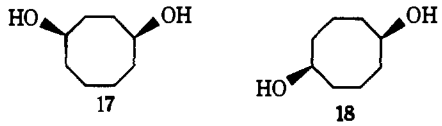


(9)

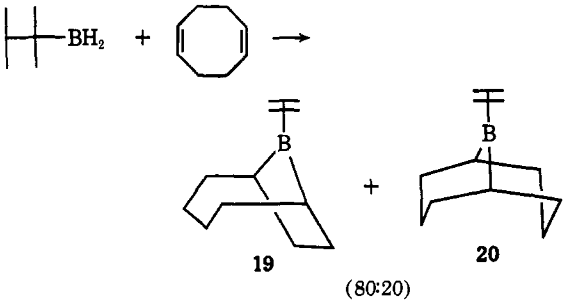
The same 91:9 ratio must also be applicable in the first step of the hydroboration of terminal dienes with thexylborane in cases in which there is little or no effect of the second double bond. Thus, the hydroboration of 1,4-pentadiene with thexylborane should yield a 91:1 mixture of **10** and **11** as intermediates (eq 8). Since we do not obtain 2,4-pentanediol after oxidation, the cyclization of **11** must proceed to place the boron atom exclusively at the terminal position, providing **1** in 9% yield. In order to account for the observed 72:28 distribution of **1** and **2**, **10** must cyclize to place 69% of the boron atom at the internal position and 31% at the terminal position (eq 8). There must exist a large preference to form the five-membered boracyclane, which more than offsets the usual directive effect of dialkylboranes to place the boron atom almost exclusively at the terminal position,

As in the case of 1,4-pentadiene, the hydroboration of 1,5-hexadiene should yield a 91:9 mixture of **12** and **13** as intermediates (eq 9). The cyclization of **13** must proceed in a manner analogous to that of **10**, yielding **15** and **16** in 3 and 6% yields, respectively. The observed yield of 8% for **16** is in good agreement with the prediction. Since the observed yield of **14** is 90%, **12** must cyclize to place the boron atom almost exclusively at the terminal position. The observed isomer distribution suggests that in the competitive formation of six- and seven-membered boracyclanes, the usual directive effect may be used to predict the product distribution.

Stereospecific Hydroboration of Cyclic and "Mixed" Dienes. The cyclic hydroboration of 1,5-cyclooctadiene with an equimolar quantity of thexylborane followed by oxidation provided an 80:20 mixture of *cis*-1,4- and *cis*-1,5-cyclooctanediols (**17** and **18**) in 93% yield.[13] Only trace quantities of other diol products were detected by glpc. Although we have not been successful in observing the *B*-thexylboracyclanes formed in the hydroboration of 1,5-cyclooctadiene with thexylborane as well-defined peaks by glpc, the almost exclusive formation of *cis*-diols (**17** and **18**) suggests that the reaction is highly cyclic, producing *B*-thexyl-9-borabicyclo[4.2.1]nonane (**19**) and *B*-thexyl-9-borabicyclo[3.3.1]nonane (**20**) in the ratio of 80:20 (eq 10).



17 **18**



(10)

Based on the discussion in the preceding section, it is not unexpected to observe the 80:20 ratio of **19** and **20** as the initial products of hydroboration, since the formation of a five-membered boracyclane should be favored over that of a six-membered ring.[14]

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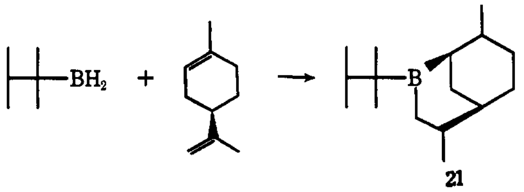
[13] This observation was first made by Dr. E. F. Knights in our laboratories: E. F. Knights, Ph.D. Thesis, Purdue University, 1968.

[14] In marked contrast, the hydroboration of 1,5-cyclooctadiene with an equimolar quantity of borane in THF, after oxidation, yields 72% *cis*-1,5- and 28% *cis*-1,4-cyclooctanediols: E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968).

Unlike most other cases, distillation of the hydroborating mixture was accompanied by an extensive isomerization of the ring moiety, producing a 20:80 mixture of **19** and **20**, bp 93–94° (0.4 mm), in 91% yield. However, isomerization of the thexyl group was essentially avoided under these conditions.

The cyclic hydroboration of D-(+)-limonene with an equimolar amount of thexylborane followed by distillation yielded *B*-thexyl-4,8-dimethyl-2-borabicyclo[3.3.1]-nonane (**21**), bp 88° (0.4 mm), in 72% yield (eq 11).



(11)

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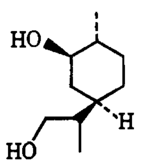
The hydroboration appears highly cyclic. While the oxidation of the reaction mixture provided in 90% overall yield a mixture of cis and trans diols (**22** and **23**)



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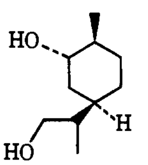

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in the ratio of 85:15, the cis diol, D-(−)-(1*S*,2*R*,-4*R*)-limonene-2,9-diol, was obtained as the only product by the oxidation of the distillate.[15]

Conclusion

Glpc conditions for determining the exact quantities of *B*-thexylboracyclanes present in the diene–thexylborane reaction mixtures have been established. Glpc examination using these conditions revealed that the hydroboration of most dienes examined in the present study was indeed highly cyclic. The cyclic products were isolated by distillation, identified, and characterized. The distillation in most cases did not involve any detectable isomerization of either the thexyl group or the ring moieties. Based on the product study, the following tentative generalization, which would help predict the product distribution in the diene–thexylborane reaction mixture, has been made. (1) Under the usual hydroboration conditions, a four-membered boracyclane would not be formed. (2) Under the usual hydroboration conditions, formation of a five-membered boracyclane is strongly favored in the competitive formation of five- and six-membered rings. (3) Under the usual hydroboration conditions, neither six- nor seven-membered boracyclane formation is strongly favored over the other. Thus, the usual directive effect would be observed in this case. Finally, the cyclic hydroboration of cyclic and "mixed" dienes with thexylborane opened up a useful synthetic possibility of achieving stereospecific hydroboration.

Experimental Section

The organoboranes were always handled under nitrogen with careful exclusion of oxygen and moisture. Pmr spectra were obtained with a Varian T-60 spectrometer, and ir spectra were obtained with a Perkin-Elmer 137B spectrometer.

Materials. The preparation of borane solutions in THF was carried out as described previously.[16] Commercially available 2,3-dimethyl-2-butene (Chemical Samples), isoprene (Aldrich), 2,3-dimethyl-1,3-butadiene (Chemical Samples), 1,4-pentadiene (Aldrich), and 1,5-hexadiene (Aldrich) were used without further purification after checking the refractive indeces. 1,5-Cyclooctadiene (Columbia) (bp 56–57° (25 mm), $n^{20}\text{D}$ 1.4938) and D-(+)-limonene (Minute Maid) (bp 55° (5 mm), $n^{20}\text{D}$ 1.4724, $[\alpha]\text{D}$ +99°) were distilled from lithium aluminum hydride. 1,3-Butadiene (Matheson) was used from the cylinder without further purification.

Preparation of Thexylborane. In a 300-ml, three-necked flask, fitted with a magnetic stirring bar, a thermometer well, a septum inlet, and a condenser, the tip of which was connected to a mercury bubbler, was placed 74 ml (200 mmol) of 2.71 *M* borane in THF. To this was added at 0° 16.8 g (200 mmol) of 2,3-dimethyl-2-butene. The reaction mixture was stirred for 1 hr at 0° and used as a stock solution of thexylborane in THF after determining the concentration.

Hydroboration of Dienes with Thexylborane. The following procedure for the hydroboration of 1,5-hexadiene is representative. In the same setup described for the preparation of thexylborane were placed 8.2 g (100 mmol) of 1,5-hexadiene and 50 ml of THF. To this was added at 0° 48.2 ml (100 ml) of 2.08 *M* thexylborane in THF over 15–20 min. A 1-ml aliquot was tested for the residual hydride. The hydroboration of 1,5-hexadiene was shown to be essentially complete as soon as the addition of thexylborane was over. The reaction mixture was then allowed to stand at room temperature (25°) and used for further experiments.

In another experiment, a 24.0-ml solution of 1,5-hexadiene (4.1 g, 50 mmol) in THF and 24.1 ml of 2.08 *M* thexylborane in THF were simultaneously added over a period of ∼1 hr to 50 ml of THF maintained at 0°. After the addition was complete, *n*-nonane was added as an internal standard and the mixture examined by glpc. The results indicated that both the total glpc yield of *B*-thexylboracyclanes and the isomer distribution were essentially the same as those observed with the reaction mixture obtained by the addition of thexylborane to 1,5-hexadiene. Therefore, the simultaneous mode of addition was not employed in the other hydroboration experiments.

Glpc Analyses. Glpc examination of organoboranes were generally carried out on a Varian Model 1400 using a 2 ft × $^1/_8$ in. 10% SE-30 column (Chromosorb W). Similar inert liquid-phase materials, such as Apiezon L, and solid support materials, such as Varaport 30, were also satisfactory. In order to remove a trace quantity, if any, of oxygen a few microliters of the trialkylborane to be analyzed was injected prior to the actual glpc examination. In order to determine the actual quantity of *B*-thexylboracyclanes present, a hydroboration mixture was analyzed at various injection block and detector temperatures within the 50–150° range. The column temperature was generally not allowed to exceed these temperatures. When essentially constant values were observed over a certain temperature range between 50 and 150°, it was assumed that the observed values represented the actual amount of the organoboranes in question. The process of finding a temperature range giving the actual quantity of *B*-thexylboracyclane was exemplified by glpc analysis of the 1,3-butadiene–thexylborane reaction mixture summarized in Table I. The results of glpc analyses of the hydroboration mixtures were summarized in Table II. The glpc response ratios of the *B*-thexylboracyclanes were determined using the distilled products. The same response ratios were assumed for the isomeric products.

Glpc examination of thexyl alcohol was carried out on a Carbowax 20M column. In all cases examined, thexyl alcohol (isomerically ∼99% pure) was obtained in 95–100% yields. The diols were generally analyzed on a SE-30 column after silylation using Tri-Sil (Pierce Chemical Co.). Cyclooctanediols and limonenediols were analyzed on a Perkin-Elmer 226 capillary glpc instrument using a 150 ft × 0.01 in. Golay column of polyphenyl ether. The results of diol analyses were summarized in Table II. Total yields of diols in all cases were 90–100%.

Distillation of *B*-Thexylboracyclanes. A usual distillation setup is satisfactory. However, the flasks should be equipped with a septum inlet. In order to avoid possible isomerization of either the thexyl group or the ring moieties the distillation temperature was kept below 100°. Under these conditions no detectable

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[15] These oxidation experiments were performed by Dr. C. D. Pfaffenberger; see ref 4.

[16] G. Zweifel and H. C. Brown, *Org. React.*, 13, 1 (1963).

isomerization of either the thexyl group or the ring moiety was observed except with *B*-thexyl-9-borabicyclononanes. The experimental results were summarized in Table II.

Oxidation of Organoboranes. In most cases oxidation of the reaction mixtures was carried out essentially as described earlier.[16] Oxidation of the distillate was carried out similarly after dissolving the distillate in THF (10 ml per 10 mmol of distillate). *B*-Thexyl-9-borabicyclo[3.3.1]nonane proved to be quite resistant to the usual oxidation conditions. Therefore, 2.06 g (10 mmol) of *B*-thexyl-9-borabicyclo[3.3.1]nonane dissolved in 10 ml of THF was oxidized, after addition of 10 ml of ethanol, with 5 ml each of 30% hydrogen peroxide and 6 *N* sodium hydroxide at 30–40°. After heating the mixture for 1 hr at 50°, it was worked up as usual. The results were summarized in Table II. Authentic samples of the diols were either commercially available or available in our laboratories.

Acknowledgment. The authors are indebted to Drs. E. F. Knights and C. D. Pfaffenberger for the information provided by them in certain phases of the present study. Support of this research by the U. S. Army Research Office (Durham) is gratefully acknowledged.

Reactions of Coordinated Ligands. I. Molybdenum Carbonyl Complexes of Dimethyl- and Diphenylphosphinous Acids and of Several Diphosphoxanes[1]

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Received October 12, 1971

Abstract: The compounds $[Cl(CH_3)_2P](CO)_5Mo$ and $[Cl(C_8H_5)_2P](CO)_5Mo$ react readily with water in the presence of triethylamine to yield $[(CH_3)_2P(OH)](CO)_5Mo$ and $(C_2H_5)_3NH\{[(C_6H_5)_2PO](CO)_5Mo\}$, respectively. In the first product, dimethylphosphinous acid is stabilized as the hitherto unknown tautomer of dimethylphosphine oxide. The corresponding complex of diphenylphosphinous acid was obtained upon base hydrolysis of $[Cl(C_6H_5)_2P](CO)_5Mo$ as well as from the thermal reaction of diphenylphosphine oxide with $Mo(CO)_6$. The two phosphinous acid derivatives react smoothly with $[Cl(CH_3)_2P](CO)_5Mo$ in the presence of triethylamine to yield $(CO)_5MoP(CH_3)_2OPR_2Mo(CO)_5$ with R equal to methyl or phenyl. Reaction between $[Cl(C_6H_5)_2P](CO)_5Mo$ and $(C_2H_5)_3NH\{[(C_6H_5)_2PO](CO)_5Mo\}$ led to $(CO)_5MoP(C_6H_5)_2OP(C_6H_5)_2Mo(CO)_5$. The bridging ligands in the three dimolybdenum complexes contain the very uncommon diphosphoxane linkage.

In general, attempts to synthesize trivalent phosphorus compounds which retain the phosphinous acid structure, R_2POH, have been unsuccessful as the thermodynamically more stable phosphine oxide tautomer, $R_2P(O)H$, is obtained.[2] Bis(trifluoromethyl)phosphinous acid, $(CF_3)_2POH$, is the only well-documented species in this class.[3] However, the rationalization of considerable kinetic exchange data and the nature of numerous reactions of organophosphorus compounds is possible only if the following equilibria are considered to exist: $(RO)_2P(O)H \rightleftharpoons (RO)_2POH$;[4–6] $(C_6H_5)P(O)H(OH) \rightleftharpoons (C_6H_5)P(OH)_2$;[7,8] $(C_6H_5)_2P(O)H \rightleftharpoons (C_6H_5)_2P(OH)$.[9] Each equilibrium is shifted extensively to the left and attempts to obtain physical evidence for the presence of the trivalent tautomer have been unsuccessful.[10] In this paper, we are concerned with the stabilization of the trivalent form of phosphinous acids upon complexation with molybdenum(0).

Two synthetic routes toward obtaining a general complex $L_xMPG_2(OH)$ (where L's are ligands on the metal M, and G may be alkyl, aryl, alkoxyl, hydroxyl, etc.) are apparent: (1) hydrolysis of a phosphorus to halogen bond, or other readily cleaved bond to phosphorus, in a precomplexed ligand; (2) direct reaction of $G_2P(O)H$ with a metal salt or complex in an effort to shift the above-mentioned equilibria to the right by removal of the trivalent tautomer as it is generated. One century ago Schutzenberger and Fontaine[11] reported what may have been the first example of hydrolysis of a phosphorus–halogen bond in a coordinated ligand. They found $PtCl_2(PCl_3)$ and $PtCl_2(PCl_3)_2$ to be readily hydrolyzed to $PtCl_2[P(OH)_3]$ (presumably dimeric) and $PtCl_2[P(OH)_3]_2$ respectively. Although other metal complexes with phosphorus donor ligands that have phosphorus–halogen bonds have been noted to show differing degrees of reactivity toward water, product analysis has not been of interest.[12] More recently, Austin[13] obtained *cis*-$MCl_2[(C_6H_5)_2P(OH)]_2$ and *cis*-$MCl_2[(C_6H_5)ClP(OH)]_2$ (where M is Pt or Pd) upon hydrolysis of the metal complexes of chlorodiphenylphosphine and dichlorophenylphosphine.

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[1] Presented in part at the 6th Middle Atlantic Meeting of the American Chemical Society, Baltimore, Md., Feb 3, 1971, Abstract IN-7.

[2] J. R. Van Wazer, "Phosphorus and Its Compounds, Vol. I: Chemistry," Interscience, New York, N. Y., 1958.

[3] J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, **82**, 1507 (1960); **84**, 3442 (1962).

[4] W. J. Bailey and R. B. Fox, *J. Org. Chem.*, **28**, 531 (1963).

[5] P. R. Hammond, *J. Chem. Soc.*, 1365 (1962).

[6] Z. Luz and B. Silver, *J. Amer. Chem. Soc.*, **83**, 4518 (1961).

[7] I. G. M. Campbell and S. M. Raza, *J. Chem. Soc. C*, 1836 (1971).

[8] J. Reuben, D. Samuel, and B. Silver, *J. Amer. Chem. Soc.*, **85**, 3093 (1963).

[9] I. G. M. Campbell and I. D. R. Stevens, *Chem. Commun.*, 505 (1966).

[10] G. O. Doak and L. D. Freedman, *Chem. Rev.*, **61**, 31 (1961).

[11] P. Schutzenberger and R. Fontaine, *Bull. Soc. Chim.*, **17**, 482 (1872). Presumably, $PtCl_2 \cdot PCl_3$ is actually a dimer with this empirical formula.

[12] W. Strecker and M. Schurigin, *Ber.*, **42**, 1767 (1909); T. L. Davis and P. Ehrlich, *J. Amer. Chem. Soc.*, **58**, 2151 (1936); G. Wilkinson, *ibid.*, **73**, 5501 (1951).

[13] T. E. Austin, Ph.D. Thesis, University of North Carolina at Chapel Hill, 1966.