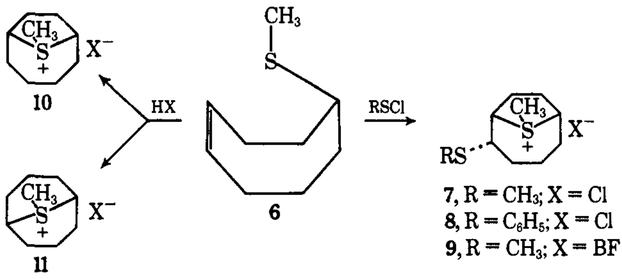
Table I. Nmr Parameters of Bicyclic Sulfonium Ions

Compound[b]	Solvent	Group assignments and chemical shifts,[a] ppm				
		$-SCH_3$	$>^{+}SCH_3$	$>CHS^{+}<$	$>CHS-$	$>CHCl$
3	SO_2	1.96 s	2.78 s	4.37 m	3.25 m	4.50 m
7	SO_2	2.08 s	2.74 s	4.28 m	3.18 m	
8	SO_2		2.52 s	3.85–4.42 m	3.62 m	
9	CD_3CN	2.15 s	2.72 s	4.35 m	3.28 m	
10	SO_2		2.51 s	4.18 m		
11	SO_2		2.65 s	3.41 m		
11	CF_3CO_2H		2.99 s	3.77 m		
12	$CDCl_3$	2.16 s			3.01 dq	4.20 dq
13	$CDCl_3$		2.62 s	~4.3 m		

[a] Spectra were determined on a Varian A-60 instrument at ambient temperature. Chemical shifts are measured in parts per million downfield from TMS as internal standard. With SO_2 as solvent, $CHCl_3$ (at 7.20 ppm) was used as internal standard. [b] All compounds gave satisfactory elemental analyses.

mediate such as **2** would be expected.[2,6] Consequently slow formation of the crystalline sulfonium chloride **3** should occur. This was indeed observed on standing at room temperature.

The addition of methane- and benzenesulfenyl chloride to 5-methylthiocyclooctene-1 (**6**) was chosen to support the proposed mechanism for the formation of **3** and to aid its structural assignment. The closely related bicyclic sulfonium chlorides **7**, mp 162–164° dec, and **8**, mp 151–152° dec, were isolated in addition to some oily adducts which corresponded to **4** and **5**.



10

11

6

7, R = CH_3; X = Cl
8, R = C_6H_5; X = Cl
9, R = CH_3; X = BF_4

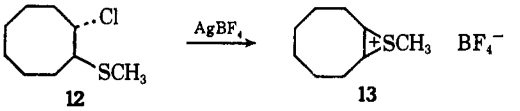
11, **10**, X = Cl or I

Reaction of **7** with silver tetrafluoroborate afforded **9**, mp 103–105° dec.

A more general verification of transannular π-bond activation by the methylthio group as suggested in **1** was obtained from the unusually rapid addition of hydrogen iodide and hydrogen chloride to compound **6**. While sulfenyl chloride additions produced essentially a single sulfonium salt, mixtures of the isomeric products **10** and **11** were obtained with hydrogen halides. Both mixtures, the sulfonium chlorides (mp 184–191° dec) and the sulfonium iodides (mp 198–208° dec), exhibit nearly identical nmr spectra. The chemical shifts of the pertinent signals for the minor product (*ca.* 20–25%) are in excellent agreement with those previously reported for 9-methyl-9-thiabicyclo[3.3.1]-nonanesulfonium iodide (**11**).[7a]

A priori one is tempted to infer a [3.3.1] structure for sulfonium salts **3** and **7–9** from the previously reported formation of this ring system in transannular additions of sulfur dichloride to COD.[7] However, the predominant formation of the [4.2.1] compound **10** in hydrogen halide additions coupled with a comparison of the nmr data in Table I seems convincing evidence in favor of the [4.2.1] ring system. Bridgehead protons appear in general around 4.2–4.4 ppm while they are located *ca.* 0.7 ppm upfield for the [3.3.1]nonane **11**. This sizable deshielding effect seems to be diagnostic for the more strained ring system since it is also found in 7-methyl-7-thiabicyclo[2.2.1]heptanesulfonium iodide[7a] and the corresponding bridged sulfides.[7a,b]

Significant activation of **6** toward methanesulfenyl chloride addition was also observed in competition with cyclooctene. Within the experimental accuracy only **6** (>90%) was consumed from an equimolar mixture of the substrates. The methanesulfenyl chloride–cyclooctene adduct **12** is a nonionic, oily compound which excludes the remote possibility of a stable episulfonium salt rather than the transannular bridging in compounds **3** and **7**. It was, however, possible to generate the stable episulfonium tetrafluoroborate **13**, mp *ca.* 106° dec.



12

13

Work to independently synthesize some of these sulfonium salts and thus affirm the [4.2.1] ring system is in progress. Attempts will be made to define the scope of this transannular π-bond activation.

Acknowledgment. The author gratefully acknowledges the assistance of Mr. R. Kelly.

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Received December 11, 1968

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(6) J. F. King and K. Abikar, *Can. J. Chem*, **46**, 1, 9 (1968).

(7) (a) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966); (b) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966); (c) F. Lautenschlaeger, *Can. J. Chem.*, **44**, 2813 (1966).

Conversion of Linear Trienes into Bicyclic Boranes *via* Hydroboration–Isomerization and Their Carbonylation. A Simple Synthesis of Angularly Substituted Bicyclic Alcohols

Sir:

We reported recently that certain cyclic polyenes can be readily converted into polycyclic tertiary alcohols *via* hydroboration–carbonylation–oxidation.[1,2] Earlier, Köster and his coworkers reported the syntheses of

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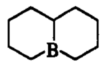
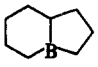
(1) H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5478 (1967).

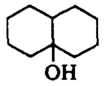
(2) E. Knights and H. C. Brown, *ibid.*, **90**, 5283 (1968).

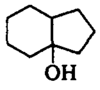
9-boradecalin (I) and 8-borahydrindan (II) from 1-nonene and 1-octene, respectively, *via* hydroboration–pyrolysis.[3]


I


II

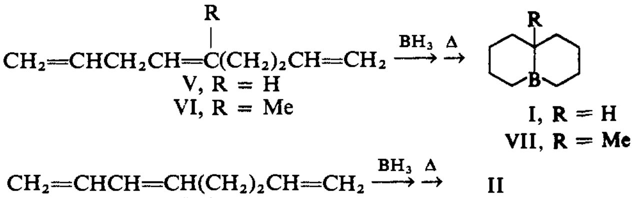
It appeared that carbonylation–oxidation of such bicyclic boranes might produce the corresponding angularly substituted alcohols (III, IV) and provide a convenient synthetic route to these derivatives.


III


IV

Unfortunately, the pyrolytic preparation of bicyclic boranes from terminal olefins is not simple. The reaction requires a very high temperature, ≥300°, and the borane products are obtained only as impure mixtures in low yield, unless a specially designed circulating apparatus[3] is used for the pyrolysis. For example, the yield of 8-borahydrindan from 1-octene was reported to be only about 5%.[3] Similarly, in our study a glpc analysis of the carbonylation–oxidation products from the boranes produced in the simple pyrolysis of tri-*n*-nonylborane revealed the presence of more than ten peaks, in addition to the desired *cis*- and *trans*-9-decalols. It was evident that this synthesis of angularly substituted bicyclic alcohols required an improved route to the bicyclic bridgehead boranes.

We wish to report that the hydroboration–isomerization of the corresponding trienes provides a greatly improved synthetic route to these boranes.



$$\mathrm{CH_2{=}CHCH_2CH{=}\overset{R}{C}(CH_2)_2CH{=}CH_2 \xrightarrow{BH_3}\xrightarrow{\Delta}}$$

V, R = H
VI, R = Me

I, R = H
VII, R = Me

$$\mathrm{CH_2{=}CHCH{=}CH(CH_2)_2CH{=}CH_2 \xrightarrow{BH_3}\xrightarrow{\Delta}}\ \mathrm{II}$$

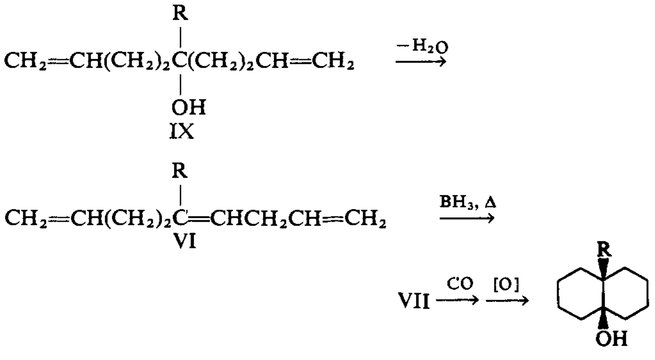
VIII

1,4,8-Nonatriene (V),[4] bp 86–88° (120 mm), $n^{20}\mathrm{D}$ 1.4454, was obtained in 80% yield by dehydration of 1,8-nonadien-5-ol (IX) using an equimolar amount of boric acid for the dehydration. IX, in turn, was prepared in 90% yield from 4-bromobutene and ethyl formate *via* the Grignard reaction (bp 73–76° (5 mm), $n^{20}\mathrm{D}$ 1.4541). Hydroboration of V with diborane in THF gave insoluble products, apparently polymeric boranes. The solvent was removed and the residual mass was heated for 3 hr at 210–220° to form a pale yellow clear liquid. Distillation yielded a colorless liquid, bp 100–105° (100 mm), in 41% yield.[5] The ir spectrum was superimposable with that reported for I.[3] The product was carbonylated at 1000 psi and 150° for 3 hr in the presence of ethylene glycol (300 mole %). Oxidation with alkaline hydrogen peroxide provided *cis*- and *trans*-9-decalols (III) in 89% yield (*cis*:*trans* = 4:1).[6]

Investigation revealed that the isolation of I was not necessary. Indeed, the yield of the decalols from 1,4,8-nonatriene was improved to 73% by hydroborating in diglyme solution and then subjecting the product to refluxing solvent (160°) for 6 hr. The *cis*:*trans* ratio remained the same. Consequently, this provides a simple synthetic route to the 9-decalols.

The synthesis is evidently capable of considerable variation, as shown by the ready preparation of *cis*-10-methyl-9-decalol (X) by the sequence of reactions indicated (R = Me).

$$\mathrm{2CH_2{=}CH(CH_2)_2MgBr + RCO_2C_2H_5 \rightarrow}$$



$$\mathrm{CH_2{=}CH(CH_2)_2\overset{R}{\underset{OH}{C}}(CH_2)_2CH{=}CH_2 \xrightarrow{-H_2O}}$$

IX

$$\mathrm{CH_2{=}CH(CH_2)_2\overset{R}{C}{=}CHCH_2CH{=}CH_2 \xrightarrow{BH_3,\ \Delta}}$$

VI

$$\mathrm{VII \xrightarrow{CO}\xrightarrow{[O]}}$$

X

The triene VI was obtained in an over-all yield of 60%, bp 64° (25 mm), by the dehydration of the intermediate tertiary alcohol with 50% sulfuric acid. The triene was then subjected to hydroboration–carbonylation–oxidation using the simplified procedure described above. Alcoholic products were obtained in a yield of 74%. Glpc analysis indicated that the major peak, amounting to 62% of the alcoholic products, was *cis*-10-methyl-9-decalol (X).[7] The *trans* isomer was present only in trace amounts. Four other products were present in the amounts estimated as 5–12% merely from the areas of the chromatogram. The major product, X, which eluted last over a Carbowax 20M column, was easily isolated by preparative glpc.

Two especially interesting features of this synthesis should be pointed out. First, the synthesis of the borane involves placing the boron atom at the tertiary position of the carbon chain, rather than on the competing isomeric secondary or primary positions. Presumably, the strong tendency to form two fused six-membered rings is responsible. Second, this is the first observation of a successful migration of a tertiary alkyl group from boron to carbon in the carbonylation reaction. We previously noted that a tertiary group, such as thexyl, is reluctant to migrate at 50°,[8] or isomerizes prior to or during migration at 150°.[2,9]

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[3] R. Koster, W. Larbig, and G. W. Rotermund, *Ann.*, **682**, 21 (1965).

[4] All new compounds gave satisfactory elemental analyses and infrared and pmr spectra.

[5] All operations involving the formation, isomerization, and carbonylation of the organoboranes were carried out with protection from atmospheric oxygen.

[6] The products were identified by comparison of their ir and pmr spectra and/or retention times with those of authentic samples. An authentic sample of *trans*-III, prepared by reduction of $\Delta^{9(10)}$-octalin oxide, was kindly supplied by W. C. Dickason, and spectral data for *cis*-III were kindly provided by Professor M. M. Mousseron.

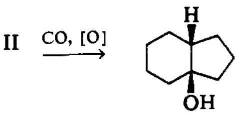
[7] Authentic samples of X and its *trans* isomer were kindly provided by Professor J. A. Marshall of Northwestern University.

[8] We took advantage of this property to develop a highly versatile synthesis of ketones: H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5285 (1967).

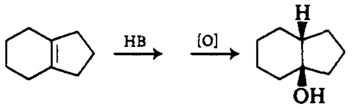
[9] A detailed study of the carbonylation of organoboranes bearing such tertiary groups is currently under way.

Recently, 1,3,7-octatriene (VIII) became readily available by the dimerization of 1,3-butadiene.[10] The hydroboration–carbonylation–oxidation of the triene yielded *cis*-8-hydrindanol (XI) in a yield of 33%.[11] This compound was previously obtained by Criegee and Zogel by the autoxidation–reduction of hydrindan in less than 2% yield.[12] The stereochemistry of XI was established as the *cis* isomer by its dehydration into $\Delta^{8(9)}$-hexahydroindene (XII) followed by hydroboration–oxidation to yield the original alcohol (XI).

$$\underset{\text{VIII}}{CH_2{=}CHCH{=}CHCH_2CH_2CH{=}CH_2} \xrightarrow{BH_3,\ \Delta}$$



XI



XII XI

It is noteworthy that all of these carbonylations take place preferentially from the *cis* side of these bicyclic boranes.[13] We are exploring the stereochemistry of such carbonylations in greater detail in the hope that the study will throw additional light on the mechanism of the carbonylation reaction.

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(10) E. J. Smutny, *J. Am. Chem. Soc.*, **89**, 6793 (1967). We are indebted to Dr. Smutny for a generous gift of the triene.

(11) Glpc analysis of the product revealed a minor peak which presumably is the *trans* isomer.

(12) R. Criegee and H. Zogel, *Ber.*, **84**, 215 (1951).

(13) Compare H. C. Brown and W. C. Dickason, *J. Am. Chem.Soc.*, **91**, 1226 (1969).

(14) Postdoctoral research associate on a grant provided by the National Institutes of Health (GM-10937).

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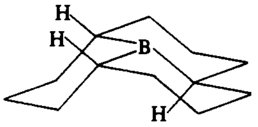
Synthesis of the *cis,cis,cis*-Perhydro-9b-phenalenol, a Very Highly Strained System, *via* the Carbonylation Reaction. A Remarkably High Rate of Solvolysis of the Corresponding *p*-Nitrobenzoate

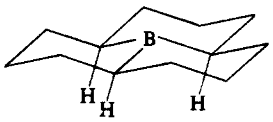
Sir:

Carbonylation–oxidation of *cis,cis,cis*-perhydro-9b-boraphenalene yields the highly strained tertiary alcohol, *cis,cis,cis*-perhydro-9b-phenalenol. This requires that the carbonylation takes place predominantly from the more hindered side of the borane intermediate to give the more strained of the two possible tertiary alcohols. This strained tertiary alcohol is enormously reactive. Its *p*-nitrobenzoate undergoes solvolysis at 25° at a rate 2,000,000 times faster than the *t*-butyl derivative, and 4,000,000 times faster than the *p*-nitrobenzoate of the previously synthesized *cis,cis,trans* isomer.[1]

The two possible isomers of perhydro-9b-boraphenalene have been previously prepared.[2] In an earlier publication[1] we questioned the original structural assignment[2] of these two polycyclic boranes. The accumulated evidence now fully supports our position that the assignments must be reversed.



cis,cis,trans
I



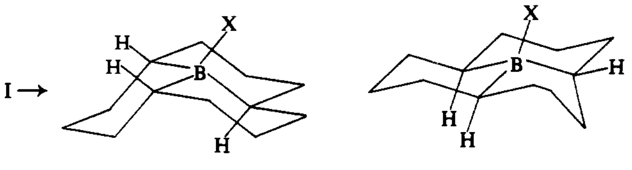
cis,cis,cis
II

Previous methods of preparation and purification of II[2] proved satisfactory. However, utilization of the published procedure for I produced a 92:8 mixture (glpc analysis) of I and an unidentified, presumably isomeric, organoborane.[3,4] However, distillation through a spinning-band column gave a much purer product, with a purity of at least 98% indicated by glpc analysis.

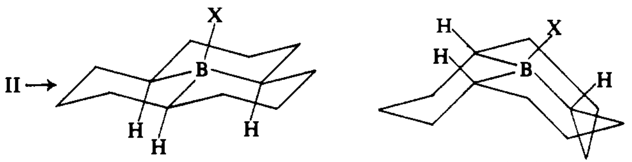
The indicated structures for organoboranes I and II are supported by a detailed pmr investigation of the free boranes and their pyridine addition compounds.

Thus the pmr of I shows a broad peak with a maximum at 1.53 ppm, a value intermediate between what may be considered the "normal" bands for equatorial and axial protons, as determined from the pmr of II. At −60° the pmr showed no evidence of conformational "freezing." Such behavior is expected on the basis of the "axial effect."[5] On the other hand, the pmr of II shows two distinct bands centered at 1.85 and 1.32 ppm, in keeping with its rigid structure and lack of axial substituents. This spectrum resembles that of *all-trans*-perhydrophenalene with two bands centered at 1.65 and 1.03 ppm.[6]

Coordination of each of these boranes with pyridine or carbon monoxide could conceivably take place from either side, producing two possible adducts from each borane.



cis,cis,trans *trans,trans,cis*



trans,trans,trans *cis,cis,cis*

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[1] H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5478 (1967).

(2) G. W. Rotermund and R. Köster, *Ann. Chem.*, **686**, 153 (1965). The symbols I and II correspond to the products (but not the structures) labeled I and II by these authors.

(3) We are indebted to Professor R. Köster for the glpc conditions satisfactory for separating these boranes.

(4) Long heating at 200° did not alter this distribution.

(5) For example, *cis*-decalin, which represents part of the structure of I, shows only a broad peak even at −100°: N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962).

(6) Normal bands for rigid hydrocarbons are 1.65 ppm (equatorial) and 1.17 ppm (axial).[5] Thus these regions are shifted downfield in the borane.