Hydroboration. 51. Hydroboration of Representative Allenes with 9-Borabicyclo[3.3.1]nonane. An Exceptional Directive Effect Providing a Direct Synthesis of *B*-Allyl-9-borabicyclo[3.3.1]nonane Derivatives

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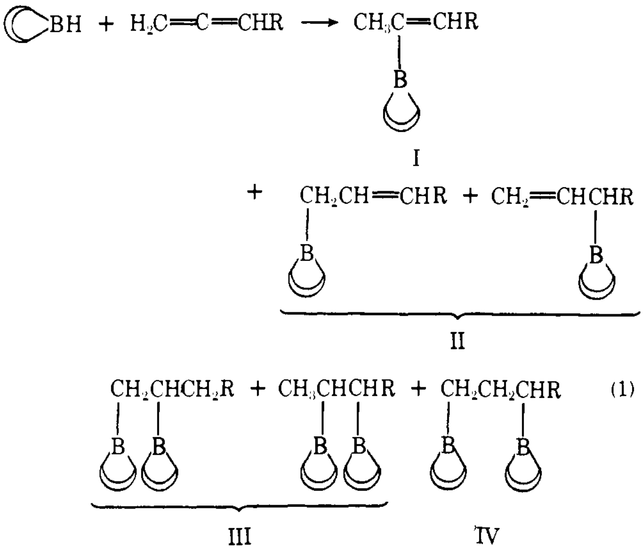
Abstract: The exceptional sensitivity toward structure exhibited by 9-borabicyclo[3.3.1]nonane (9-BBN) in the hydroboration of simple olefins, conjugated and nonconjugated dienes, and acetylenes carries over to the hydroboration of allenes. With few exceptions, the 9-BBN hydroboration of allenes results in the attack of boron at the end carbons of the allene moiety giving the *B*-allyl-9-BBN derivative. Hydroboration of an unsymmetrical allene could lead to two allylboranes. However, only the one with boron bound to the less substituted position is produced. For example, hydroboration of 2-methyl-2,3-pentadiene with 9-BBN affords only the 2-bora-4-methyl-3-pentenyl adduct. This may not reflect solely the initial position of boron attack on the allene since such allylboranes possess a permanent allylic rearrangement whereby the boron can easily migrate to the less substituted site. Simple control of the stoichiometry of these hydroborations appears to lead primarily to monohydroboration products. Only propadiene exhibits exclusive dihydroboration. In sharp contrast to the behavior of 9-BBN, hydroboration of internal allenes with other dialkylboranes, such as disiamylborane or dicyclohexylborane, reveals preferential attack of the boron at the central carbon of the allenic chain, forming vinylboranes. For example, 2,4-dimethyl-2,3-pentadiene (tetramethylallene) is converted essentially quantitatively to the vinylborane with dicyclohexyl- and disiamylborane, but exclusively to the allylborane with 9-BBN. Allylboranes formed via hydroboration of allenes with 9-BBN may be used for the allylboration of carbonyl derivatives (transferring the allyl group in the common organometallic manner from boron to the carbonyl carbon). The sequence allene hydroboration/carbonyl allylboration provides an attractive alternative to the familiar Grignard allylation scheme.

In previous studies, it has been demonstrated that 9-borabicyclo[3.3.1]nonane (9-BBN) is a most useful hydroboration agent which exhibits unusual regio-[2] and stereospecificity[3] and remarkable sensitivity to the structures of olefins.[4] In view of these outstanding characteristics, it appeared desirable to examine the utility of this reagent for the hydroboration of other representative unsaturated moieties: nonconjugated dienes,[5] conjugated dienes,[6] acetylenes,[7] and allenes (present study).

The hydroboration of allenes has been studied by several workers.[8] 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. This is unfortunate, since the hydroboration of allenes, if it could be controlled to give monohydroboration products, would provide a general synthesis of valuable allyl- or vinylboranes. It appeared to us that there may have been experimental complications in the previous studies. One problem is inherent in the choice of substrates. Reaction of a difunctional substrate (the allene) with a trifunctional reagent (borane-THF) can, and apparently does, lead to polyhydroboration. The resulting polymeric organoboranes are difficult to characterize. A second source of difficulty involves a lack of appreciation for the high reactivity of the allylboranes which may be formed. Studies by Mikhailov[9] and others[10] have shown that allylboranes, especially those bearing low molecular weight, non-sterically-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.



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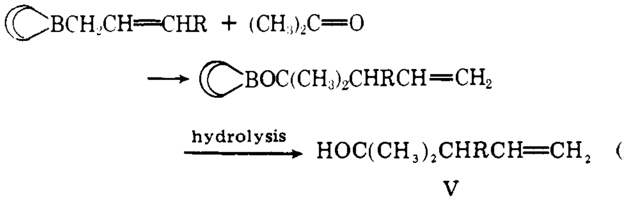
In this study we sought to avoid the first complication through the use of a monofunctional hydroboration reagent—9-BBN. The second pitfall was avoided through the development of a reliable analytical procedure. Hydroboration of an allene with 9-BBN could afford four types of organoboranes: vinylborane (I), allylboranes (II), 1,2-dibora species (III), and a 1,3-dibora moiety (IV) (eq 1). With such a variety of structures possible, conversion to simple, easily analyzed derivatives, such as alcohols, is desirable, but, as mentioned above, the allylborane may not give the expected product on oxidation. Accordingly, it seemed appropriate to convert the allylborane into a derivative which would give an unambiguous product on oxidation. Such a derivative is provided by reaction of the allylborane with a ketone, such as acetone, prior to oxidation.[11] In the case of *B*-allyl-9-BBN derivatives, this allylboration reaction has been shown to be quantitative. The other potential products (I, III, and IV) are inert to acetone under these conditions. After oxidation of this derivatized mixture, the amount of homoallylic alcohol (V) indicates the amount



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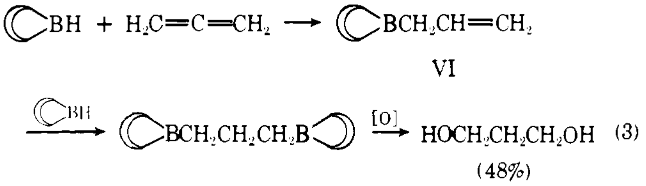
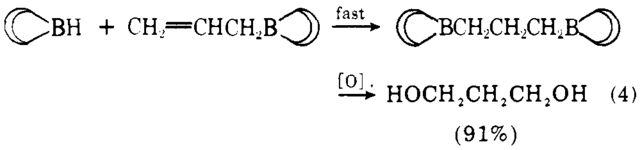
of attack at the terminal carbon of the allenic system (allylborane), the amount of ketone indicates the extent of internal attack (vinylborane), and the amount of unreacted allene shows the amount of dihydroboration (0% allene = 0% dihydroboration, 50% allene = 100% dihydroboration); the diol distribution reveals the points of attack in dihydroboration.

Results and Discussion

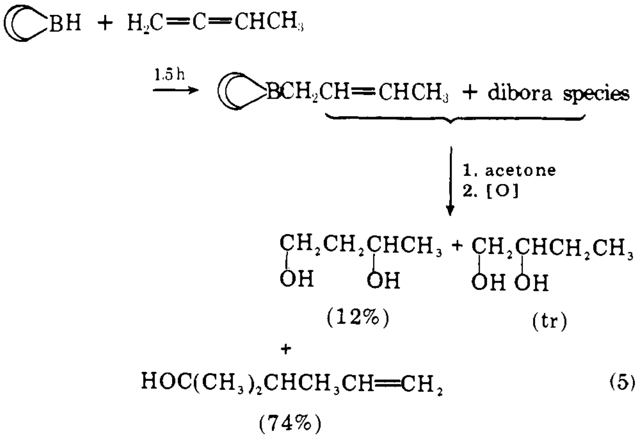
A standard reaction procedure was utilized in this study. An equivalent of allene was added to a standard solution of 9-BBN in tetrahydrofuran (THF) containing an internal standard suitable for GC analyses. The reaction mixture, 0.5 M in each reactant, was allowed to stir at room temperature. GC analyses were performed periodically on the mixture until the level of residual allene remained constant. One equivalent of acetone was added to derivatize any labile allylborane formed, and the mixture was then oxidized with alkaline hydrogen peroxide in the usual manner.[12] GC analyses were used to determine the relative amounts of products formed.[13] For comparison purposes, certain allenes were hydroborated with disiamylborane and dicyclohexylborane under similar conditions.

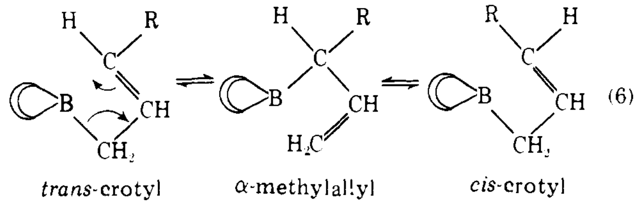
Terminal Allenes. Hydroboration of propadiene with 9-BBN affords only dihydroboration product. Derivatization–oxidation of the reaction mixture produced 1,3-propanediol (48%) and residual propadiene (50%). This result is in good agreement with the previous observation of Cadiot.[14] Apparently, the rate of addition of the second 9-BBN is faster than the rate of the initial hydroboration (eq 3). In a previous study we examined the hydroboration of the proposed intermediate (VI) with 9-BBN.[10] This reaction was complete in a few minutes (eq 4), and oxidation of the mixture gave a 91% yield of 1,3-propanediol. The attack of the boron must occur exclusively at the end of the unsaturated chain in both steps, since no trace of 1,2-propanediol or acetone was detected in either reaction.[15]

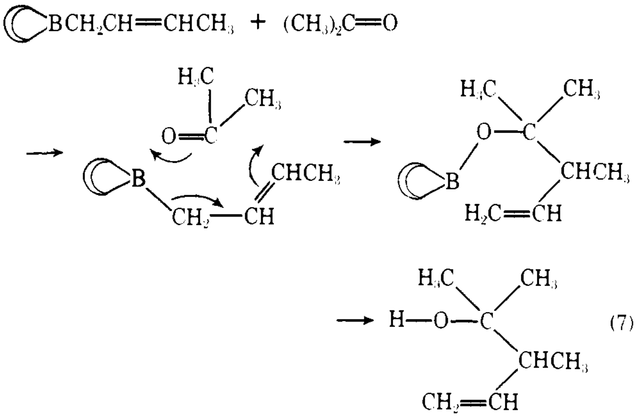




The presence of an alkyl group at one end of the allene chain alters the course of the reaction substantially. Hydroboration of 1,2-butadiene with 9-BBN results in the formation of a significant amount of the allylborane (eq 5). Based on our previous hydroboration studies, it is likely that the initial attack of the 9-BBN is at the terminus of the allene chain. However, in cases where allylboranes are formed, the initial position of attack cannot be definitively established. Allylboranes, such as *B*-crotyl-9-BBN, undergo a permanent allylic rearrangement (eq 6).[9,10] In such equilibrating systems, the boron seems to "prefer" the least substituted position.[17] If any hydroboration occurred at the carbon of the allene bearing the methyl group, the resulting α-methylallylborane would rapidly rearrange to place the boron at the terminal carbon. The permanent allylic rearrangement also scrambles the stereochemistry of the remaining double bond. Mikhailov has determined that tricrotylborane exists at room temperature as a mixture of cis and trans isomers with the *trans*-crotylborane predominating (70%).[9] Finally, it should be pointed out that the allylboration of ketones occurs with complete allylic rearrangement.[9,11] Thus a crotylborane gives the α-methylallyl homoallylic alcohol derivative (eq 7).







The diol distribution from the dihydroboration products reveals a marked preference for attack at the 3 position of the unsaturated chain (Table I). We have previously examined this aspect of the reaction by treating *B*-crotyl-9-BBN (prepared by another route) with 1 equiv of 9-BBN (eq 8).[10] After oxidation, 1,3-butanediol was found to be the major product (95%) along with a small amount of the 1,2 isomer and trace amounts of the 2,3- and 1,4-diols. The directivity of the attack of the second boron may be due to a favorable combination of both steric and electronic factors. Hydroboration at the 3 position is favored on steric grounds since the boron can be located next to the smaller methyl group. As stated earlier, 9-BBN is especially sensitive to steric effects.[2,4] However,

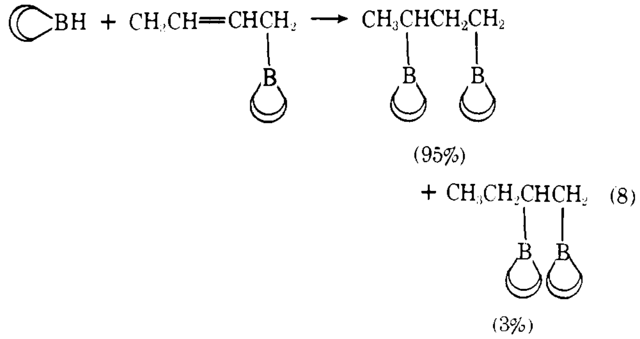


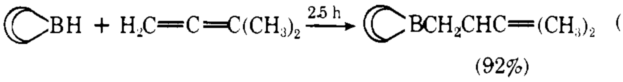
Table I. Hydroboration-Derivatization-Oxidation Product Distribution in the Reaction of Allenes with 1 Equiv of 9-BBN (0.5 M) in THF at 25 °C

allene	reaction time, h	residual[a] allene, %	homoallylic alcohol, %	diols,[b] %	ketone, %
propadiene	2.5	50	0	1,3-diol, 48	0
1,2-butadiene	1.5	7	74	1,3-diol, 12 1,2-diol, tr	tr
1,2-pentadiene	1.5	4	82	1,2-diol and 1,3-diol, 5	2
3-methyl-1,2-butadiene	2.5	tr	92	c	tr
phenylpropadiene	4	11.5	86	1,2-diol and 1,3-diol, 6	tr
p-anisylpropadiene	4	4	87	1,2-diol and 1,3-diol, 6	tr
3-phenyl-1,2-butadiene	4	tr	97	c	c
2,3-pentadiene	2	5	72[d]	2,3-diol and 2,4-diol, 12	0
4-methyl-2,3-pentadiene		c	94[d]	c	c
2,4-dimethyl-2,3-pentadiene	>108	8	86[e]	0	tr
1,2-cyclononadiene	1	tr	83	0	17

[a] Analysis after oxidation with alkaline hydrogen peroxide. [b] Based on diene. [c] No analysis. [d] Mixture of cis and trans homoallylic alcohols. [e] Product was allylic alcohol.

hydroboration is also prone to electronic effects. The boron is directed toward electronegative substituents and away from electropositive groups.[12] In the present case, boron is electropositive toward carbon, so the electronic effect should also direct attack toward the 3 position.

Increasing the steric bulk of the substituent at one end of the allene decreases the amount of dihydroboration. The addition of a single methylene unit in going from 1,2-butadiene to 1,2-pentadiene cuts the amount of dihydroboration by 50% (Table I). Disubstitution at one end of the allenic system further decreases the amount of dihydroboration. For example, 3-methyl-1,2-butadiene affords a nearly quantitative yield of the corresponding allylborane (eq 9). Replacement of the alkyl substituent on the allene with an aryl moiety does not appear to alter the regiochemistry. Phenylallene gives almost the same product distribution as does ethylallene (Table I). Furthermore, the electronic nature of the aryl group does not seem to influence the reaction course since phenylallene and *p*-anisylallene give very similar results (Table I).



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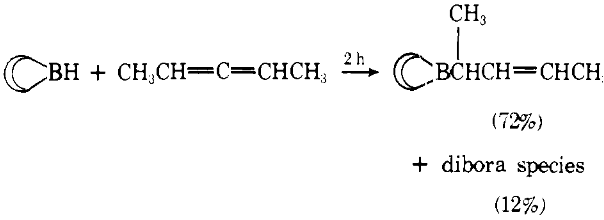
The product distributions from the hydroboration of terminal allenes show that vinylborane formation, resulting from attack of the boron at the 2 position of the allene chain, is unimportant. This observation is in sharp contrast with previous results from allene hydroborations with disiamylborane. For example, 1,2-octadiene, 1,2-nonadiene, and phenylpropadiene give about 17% vinylborane when treated with disiamylborane.[16,20] Thus, for terminal allenes, hydroboration with 9-BBN offers a much cleaner reaction than disiamylborane, affording the allylboron derivative in high yields with only minor contamination by dihydroboration products and vinylboranes.

Internal Allenes. Previous studies on the hydroboration of internal allenes with reagents other than 9-BBN report the predominant attack of boron at the center carbon of the allenic system giving vinylboranes.[18,19] In the present study, it was quite surprising to find that the hydroboration of 2,3-pentadiene with 9-BBN produced only the allylborane (eq 10). No vinylborane was detected. Dicyclohexylborane, on the other hand, reacts with this allene to give a mixture of both vinyl- and allylboranes (eq 11). It has been proposed that the attack at the central carbon of an internal allene is due to the preference for boron occupying the least sterically hindered position.[18] Clearly in the case of 9-BBN hydroborations, such a steric effect plays little or no role in determining the regiochemistry.



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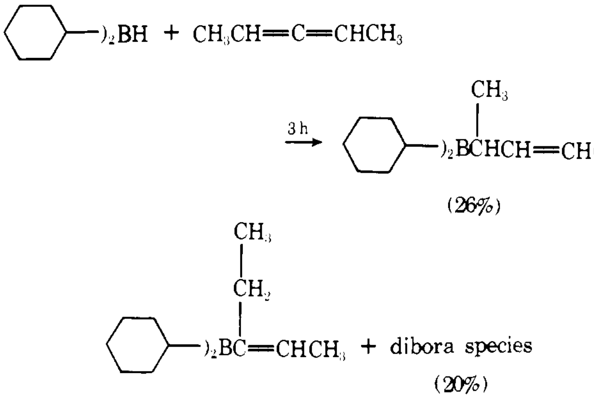

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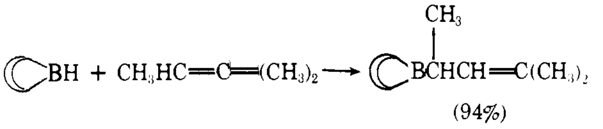
Hydroboration of the trisubstituted allene, 2-methyl-2,3-pentadiene, with 9-BBN leads to exclusive allylborane formation (eq 12). Here, as in the cases of terminal allenes, two allylboranes are possible. However, as expected, only one product was found—the one with the boron bound to the least substituted position.



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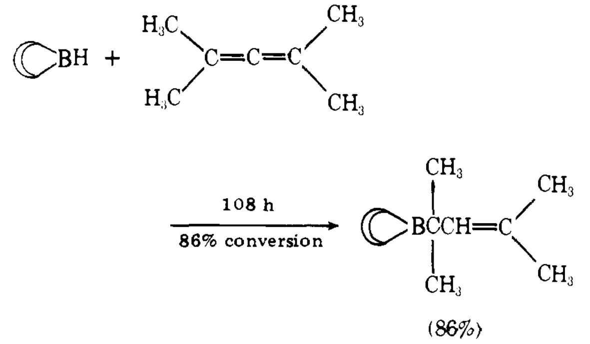
Even the tetrasubstituted allene, 2,4-dimethyl-2,3-pentadiene, is converted to the allylborane by treatment with 9-BBN (eq 13). In this case the boron is bound to a tertiary carbon! Hydroboration of this allene with disiamylborane (eq 14) or dicyclohexylborane shows a complete reversal of the regiochemistry. Here vinylboranes are the predominant products.

Table II. Hydroboration-Derivatization-Oxidation Product Distribution of Reaction of Allenes with Other Dialkylboranes

allene	dialkylborane	reaction time, h	residual allene[a]	homoallylic alcohol, %	diols[b]	ketone, %
2,3-pentadiene	dicyclohexyl	3	2	26	20	28
2,4-dimethyl-2,3-pentadiene	dicyclohexyl	3	3	[c]	5	90
2,4-dimethyl-2,3-pentadiene	disiamyl	14	3	5[d]	5	90

[a] Analysis after oxidation with alkaline hydrogen peroxide. [b] Based on diene. [c] No analysis. [d] Product was allylic alcohol.



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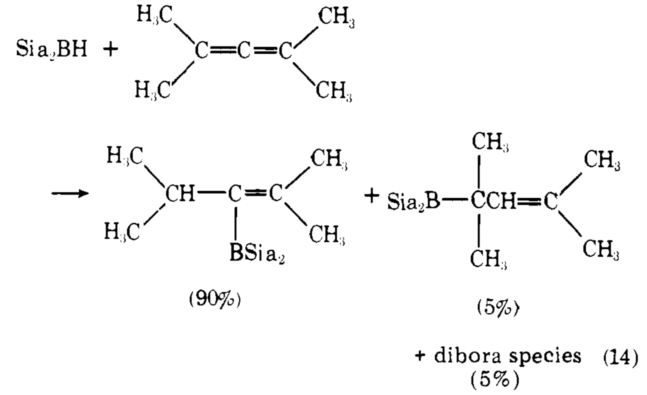
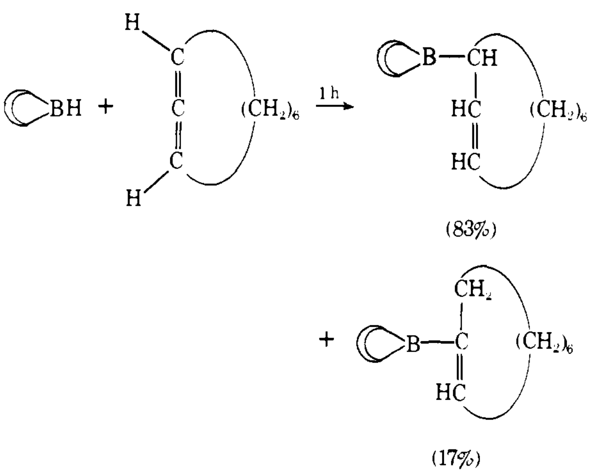


The 9-BBN hydroboration of tetramethylallene (eq 13) was quite slow under our standard conditions, requiring 108 h for 86% utilization of the allene. The allylborane product of this reaction failed to react with acetone under the usual conditions. It was, however, converted to the allylic alcohol upon oxidation. No protonolysis was observed on oxidation. The anomalous behavior of this allylborane is undoubtedly due to the steric bulk surrounding the boron atom. This prevents the coordination of the oxygen in the acetone or water which appears necessary for allylboration or protonolysis.[9,10]

Hydroboration of 1,2-cyclononadiene with 9-BBN produced the only significant amount of vinylborane in our study (eq 15).



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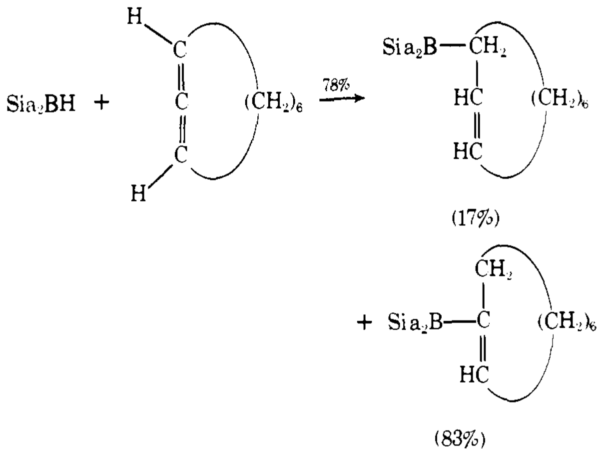
The major product is still the allylborane. Again the 9-BBN result strongly contrasts with the hydroboration of the same allene with disiamylborane (eq 16). The regiochemistry is totally reversed, and the major product is the vinylborane.[18] While the reversal in regiochemistry on going from 9-BBN to disiamylborane is consistent with other internal allene results, the presence of a significant amount of vinylborane in the 9-BBN hydroboration is anomalous. It is possible that the strain in the cumulated double bonds of this allene is reponsible for this occurrence. Since 1,2-cyclononadiene is the smallest stable (room temperature) allene, its allene linkage is probably bent. This lack of linearity may be enough to alter the delicate electronic effects that govern the regiochemistry in the 9-BBN reaction.



(16)

Conclusion

For convenience, the results are summarized in Tables I and II.

The monohydroboration of allenes with 9-BBN provides an unexpectedly simple route to useful *B*-allyl-9-BBN derivatives. In most cases the major product is the allylborane; little if any vinylborane is formed. Minor amounts of side products due to dihydroboration can probably be reduced by using excess allene, but for many purposes their presence should not present problems. Notable exceptions to the above generalization are propadiene, which undergoes exclusive dihydroboration, and 1,2-cyclononadiene, which forms a significant amount of the vinylborane.

The results of allene hydroboration with 9-BBN strongly contrast with those using other dialkylborane reagents. In the case of terminal allenes, disiamylborane produces mixtures of allyl- and vinylboranes. With internal allenes, the preference for attack by both disiamyl- and dicyclohexylborane is at the internal carbon of the allenic chain giving vinylboranes.

The *B*-allyl-9-BBN derivatives formed by the hydroboration of allenes may be utilized for addition of the allyl group to the carbonyl moiety of aldehydes, ketones, and other carbonyl derivatives (allylboration). Since allenes are rather easily prepared from the corresponding olefins,[21,22] the route olefin-allene-allylborane-carbonyl addition product appears to be a general allylation procedure which can serve as a viable alternative to Grignard-based sequences for the syntheses of complex structures.

Experimental Section

General Comments. The techniques described in Chapter 9 of ref 12 were used extensively. All glassware was dried at 140 °C for at least 4 h, assembled hot, and allowed to cool under a purge of prepurified nitrogen. All reactions were carried out under a static pressure of prepurified 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.[12] Gases were delivered using gas-tight syringes.

Materials. The *n*-alkanes (Phillips) employed as GC internal standards were used as received. Technical grade pentane was stirred over concentrated sulfuric acid, washed with aqueous base, dried over anhydrous magnesium sulfate, and distilled under nitrogen from lithium aluminum hydride. THF was distilled under nitrogen from lithium aluminum hydride and stored in large ampules with Teflon stopcock controlled septum inlets. Acetone (Mallinckrodt SpectAR) was distilled under nitrogen and the heart cut stored in similar ampules. 9-BBN solutions (0.5 M in active hydride) were prepared according to reported procedures.[3,4,12] Solid 9-BBN was recrystallized twice from THF and washed with ice-cold pentane, followed by vacuum drying (mp 151–153 °C). The following allenes were obtained from Chemical Samples Co. and were used as received after checking their purity by refractive index and GC (12 ft × 1/8 in. o.d., 10% SE-30, and 6 ft × 1/4 in. o.d., 10% XE-60): 1,2-pentadiene, 2,3-pentadiene, 3-methyl-1,2-butadiene, 4-methyl-2,3-pentadiene, and 2,4-dimethyl-2,3-pentadiene. 1,2-Butadiene (Columbia Carbon Co.) was used after checking its ^1H and ^{13}C NMR spectra. Propadiene (Peninsular Chem-Research) was used as received after checking its purity by ^1H NMR and GC (36 ft × 1/8 in. o.d., 10% UC-W-98). Phenylpropadiene, *p*-anisylpropadiene, 1,2-cyclononadiene, and 3-phenyl-1,2-butadiene were prepared according to published procedures.[21,22] These were used after establishing their purity by ^1H NMR, IR, and GC.

Analyses. IR spectra were recorded on a Perkin-Elmer 137 spectrometer from film samples held between salt plates. ^1H 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 obtained on a Varian CFT-20 (20 MHz) instrument. GC analyses were carried out on a Varian 1200 flame ionization chromatograph using 1/8 in. o.d. columns or a Hewlett-Packard 5752 B thermal conductivity chromatograph using 1/14 in. o.d. columns. Both chromatographs were equipped with strip chart recorders and Disc mechanical integrators for determining peak areas. Analyses were done by the internal standard method using correction factors determined from authentic samples. For analyses on mixtures containing organoboranes, a tetrahydroxyethylethylenediamine (THEED) stripper column was used to prevent contamination of the analytical column with organoborane.[23] This THEED column was prepared by packing the 1/4 in. injection port liner with 20% THEED on Chromosorb W and was connected in series with the analytical column. Analyses for diol products was carried out on their bis-Me_3Si derivatives as described previously.[6] Preparative GC was carried out on a modified Wilkens A-100 chromatograph using 5 ft × 1/2 in. columns filled with 10–20% loaded packing on AW DMCS 60/80 Chromosorb W. The following liquid phases were used: SE-30, XE-60, DC-710, and DEGS. In certain cases analyses were carried out on a Perkin-Elmer 226 capillary chromatograph using a 150 ft × 0.01 in. Golay column coated with OS-138 PPE.

Hydroboration of Allenes. General Procedure. An oven-dried, nitrogen-flushed 100-mL flask fitted with a septum inlet and a magnetic stirring bar was connected to a water-cooled condenser topped with a connecting tube leading to a mercury bubbler.[24] To the 100-mL flask were added 20.0 mL of 0.5 M 9-BBN in THF (10.0 mmol) and 2.5 mmol of *n*-alkane (GC internal standard). Stirring was begun, and the allene (10.0 mmol) was added via syringe. The progress of the reaction was monitored by GC. When the amount of residual allene remained constant, 0.75 mL of acetone (10.0 mmol) was added. A slightly exothermic reaction was often noted at this point. After 1 h, the mixture was oxidized in the usual manner using 3.0 mL of 3 M sodium hydroxide and 3.0 mL of 30% hydrogen peroxide.[12] About 6 g of anhydrous potassium carbonate was added to saturate the aqueous layer, and the organic layer was separated. The aqueous phase was extracted with THF (3 × 15 mL), and the extracts were combined with the organic phase. The organic mixture was first dried over anhydrous magnesium sulfate and then crushed 3Å molecular sieves. Analyses were carried out by GC. In several cases samples of the products were available commercially or from previous studies. In these cases product identity was established by the spiked injection technique using at least two GC columns of differing polarity (usually SE-30, Carbowax 20M, and XE-60). In other cases the products were collected and purified by preparative GC. Their structures were confirmed by ^1H NMR and IR prior to their use in establishing GC correction factors. In certain cases a portion of the dried organic mixture was subjected to Me_3Si derivatization, and analyses for diol derivatives were carried out on the capillary GC.

Hydroborations with disiamylborane and dicyclohexylborane were carried out in essentially the same manner except that these dialkylboranes were prepared in situ according to the procedures in ref 25.

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