Organoboranes. 20. The Facile Allylboration of Representative Carbonyl Compounds with *B*-Allyl Derivatives of 9-Borabicyclo[3.3.1]nonane[1]

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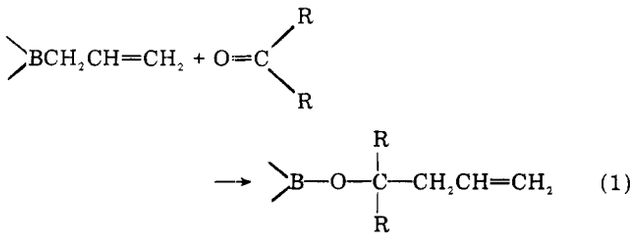
Received December 21, 1976

The reaction of *B*-allyl derivatives of 9-borabicyclo[3.3.1]nonane with representative organic compounds containing carbonyl groups occurs cleanly in the common organometallic manner with the allyl undergoing transfer to the carbonyl carbon and the boron moiety to the carbonyl oxygen. This process evidently proceeds with total rearrangement of the allyl moiety; thus, the *B*-crotyl derivative yields α-methallyl products exclusively. Aldehydes and ketones react in a 1:1 stoichiometry, while acid chlorides, esters, and *N,N*-dimethylamides react with 2 equiv of the allylborane; acid anhydrides utilize 4 equiv. Simple protonolysis of the borinic esters thus formed, conveniently accomplished via transesterification with ethanolamine, affords excellent yields of the corresponding homoallylic alcohols. In many instances, this allylboration reaction competes favorably with the familiar Grignard allylations; however, for the higher *B*-allyl homologues, many of which are easily prepared via hydroboration, the hydroboration–allylboration sequence offers significant advantages.

The chemistry of unsaturated organoboranes often differs markedly from that of their saturated analogues. Both vinyl- and allylboranes react readily with many substrates toward which trialkylboranes are inert.[2] Over the past decade Mikhailov and his co-workers have extensively examined the chemistry of the simple triallylboranes.[3-5] They have reported that such allylboranes add smoothly to various carbonyl derivatives in the usual organometallic fashion, transferring an allyl group to the carbonyl carbon with boron going to the oxygen (eq 1). Such allylborations of aldehydes and ketones



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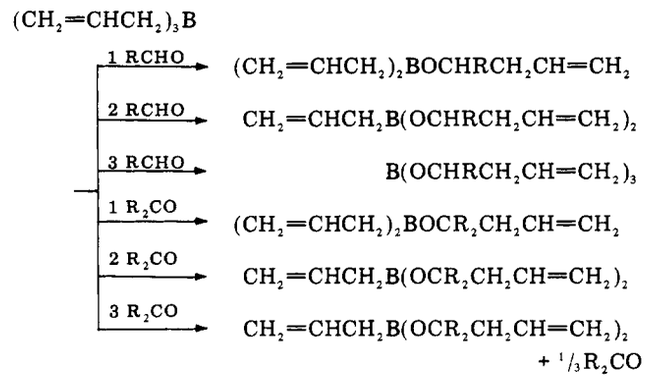
proceed simply, utilizing all three allyl groups in the former case, but only two allyl moieties in the latter. Hydrolysis of the borate ester products affords the corresponding homoallylic alcohols. The allylborations of other carbonyl derivatives, such as nitriles and quinones, are not as straightforward, being accompanied by subsequent reactions of the initial products.[3,4]

Recent studies have shown that the *B*-alkyl derivatives of 9-borabicyclo[3.3.1]nonane (9-BBN) possess unique advantages over simple trialkylboranes in many synthetic applications.[6,7] Consequently, we undertook to study the chemistry of the *B*-allyl derivatives of 9-BBN. We recently reported simple preparations and described some of the basic chemistry of these derivatives.[8] In the present article, we report the results of our investigation into the reactions of the *B*-allyl derivatives of 9-BBN with carbonyl compounds.

Results and Discussion

Allylboration of Aldehydes and Ketones. It was initially reported that treatment of aldehydes with triallylborane leads to mixtures of products containing cyclohexadiene.[9] Mikhailov has established that these early reports are incorrect. Triallylborane reacts with aldehydes to form esters of diallylborinic, allylboronic, or boric acids, depending on the stoichiometry of the reactants. Similarly, ketones afford esters of either diallylborinic or allylboronic acids. The third allyl moiety fails to react with ketones, presumably a result of the severe steric crowding around boron atom (Scheme I).[4] These

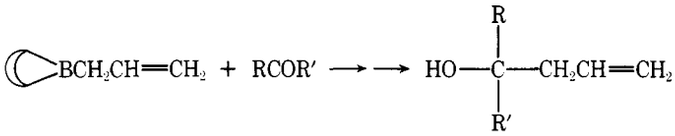
Scheme I



borate esters are easily hydrolyzed. Consequently, the allylboration sequence provides a synthetically useful alternative to the familiar Grignard synthesis of homoallylic alcohols. The allylboration reaction appears to possess synthetically valuable characteristics, and Mikhailov has provided several examples of such applications. However, not much is known about the full range of applicability and possible limitations of this reaction. The ready availability of *B*-allyl derivatives of 9-BBN suggested an examination of their utility in such allylborations. Preliminary results revealed some significant advantages of these reagents. Accordingly, a detailed study of the full scope and possible limitations of the reaction of *B*-allyl derivatives of 9-BBN with representative organic compounds containing carbonyl groups was undertaken.

Analysis of the homoallylic alcohols is considerably easier than analysis of their borinate ester precursors. Therefore, effort was devoted in the initial stages of this study to achieve a simple protonolysis procedure to convert the initial borinate ester product into the corresponding alcohol. In his original work, Mikhailov used triethanolamine to protonolyze the borate esters produced in his allylborations. When this reagent is used with the borinate esters of 9-BBN, the protonolysis is readily achieved, but the homoallylic alcohol is difficult to extract from the thick, sticky, air-sensitive, boron-containing by-product. Hydrolysis may also be effected readily with aqueous sodium hydroxide. Unfortunately, it is again difficult to extract the homoallylic alcohol free of boron-containing materials. Fortunately, ethanolamine solved the problem. Treatment of a pentane solution of a borinate ester of 9-BBN with 1 equiv of ethanolamine results in the rapid formation of a fluffy, white precipitate. VPC analysis of the supernatant liquid reveals a quantitative yield of the corresponding alcohol with no traces of boron-containing materials. The white pre-

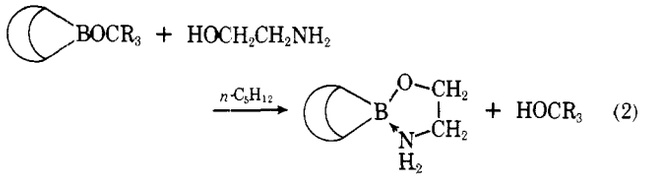
Table I. Allylboration of Aldehydes and Ketones with *B*-Allyl-9-BBN[26]



R	R'	Product $n^{20}D$	% yield (GLC)[a]	Registry no.
n-C_5	H	1.4409	92	35192-73-5
t-Bu	H	1.4379	97	19550-89-1
Ph	H	1.5322	96	936-58-3
$CH_3CH=CH$	H	1.4535	91	5638-26-6
Me	Me	1.4271	99	624-97-5
Me	*t*-Bu	1.4467	101	1185-08-6
Me	Ph	1.5271	101	4743-74-2
Ph	Ph	1.5875	100	4165-79-1
i-Pr	*i*-Pr	1.4567	98	36971-15-0
t-Bu	*n*-Pr	1.4551	97	61967-23-5
t-Bu	*i*-Pr	1.4591	74[b]	61967-24-6
t-Bu	Ph	1.5178	82[c]	38400-74-7
t-Bu	*t*-Bu	1.4663	<25[d]	754-56-3
Cyclopentanone		1.4676	102	36399-21-0
Cyclohexanone		1.4772	100	1123-34-8
Cycloheptanone		1.4855	94	49564-90-1
4-*tert*-Butylcyclohexanone		1.4756	100[e]	42437-24-1 (cis) 42437-23-0 (trans)
Norcamphor		1.4955	100[f]	61967-25-7 (endo) 61967-26-8 (exo)
Bicyclo[3.3.1]nonan-9-one		41.5–42[g]	85	61967-27-9
$H_2C=CH$	Me	1.4478	94	5903-40-2
$CH_3CH=CH$	Me	1.4578	96	919-98-2
$(CH_3)_2C=CH$	Me	1.4616	94	926-20-5

[a] Unless otherwise stated, the reaction mixtures were allowed to stir for 2 h at 25°C before workup even though the allylborations were generally complete in a few minutes. [b] Stirred for 1 week at 25 °C. [c] Stirred for 4 h at 25 °C. [d] Stirred for 5 days in refluxing *n*-octane. [e] 54.8:45.2 axial:equatorial alcohol. [f] 95.8:4.2 endo:exo alcohol. Anal. Calcd for $C_{10}H_{16}O$ (152.238): C, 78.90; H, 10.59. Found: C, 79.05; H, 10.87. *m/e* M^+ calcd for $^{12}C_{10}{}^{1}H_{16}{}^{16}O$: 152.1201. Found: 152.1210. ^{13}C NMR (C_3D_6O) δ 135.3 (d), 117.4 (t), 78.5 (s), 47.3 (t), 47.1 (d), 45.2 (t), 32.8 (t), 37.6 (d), 28.9 (t), 22.5 (t). [g] Melting point.

cipitate is virtually insoluble in pentane, stable to air, and readily removed by simple filtration or centrifugation–decantation. This solid, mp 202–203.5 °C (with decomposition), was isolated and characterized by spectroscopy and elemental analyses as the ethanolamine ester of 9-BBN (1) (eq 2).[10]



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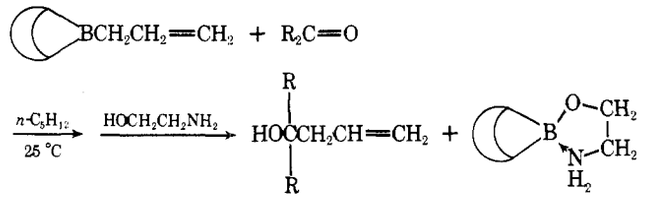
The stoichiometry of the allylborations of aldehydes and ketones with *B*-allyl-9-BBN is 1:1. No secondary addition reactions, such as those which sometimes accompany Grignard allylations,[11] were detected under our conditions. Representative aldehydes and ketones were allylborated with *B*-allyl-9-BBN. The results (Table I) reveal the significant characteristics of this reaction (eq 3). First, the reaction is extremely



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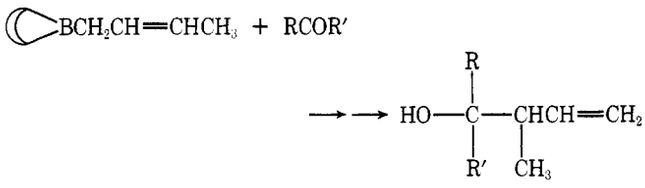
clean. After transesterification with ethanolamine, the only material left in solution is the homoallylic alcohol. In nearly every case studied, the yield of homoallylic alcohol is essentially quantitative. The allylboration of aldehydes and unhindered ketones is usually a very rapid process, being complete in a matter of minutes at room temperature. However, as the steric crowding around the carbonyl group becomes greater, the reaction rate decreases. For example, moderately hindered ketones such as diisopropyl ketone or *tert*-butyl *n*-propyl ketone react readily, but the reaction with pivaloylphenone is only 82% complete in 4 h. In the case of *tert*-butyl isopropyl ketone, the allyboration is only 74% complete after 1 week at room temperature, while di-*tert*-butyl ketone affords less than 25% of the expected product even after 5 days in refluxing *n*-octane. The steric sensitivity of these allylborations is in sharp contrast with the corresponding allylations utilizing Grignard reagents.[12] Even di-*tert*-butyl ketone is completely allylated by allylmagnesium bromide within 6 h in refluxing ether.

Unlike simple trialkylboranes, which add in a 1,4 manner to α,β-unsaturated carbonyl compounds,[13] allylboranes add exclusively in a 1,2 fashion to these substrates.[4] The *B*-allyl derivatives of 9-BBN behave similarly; in all cases, only the products arising from 1,2-addition were detected. It should be noted that allyl Grignard reagents also add exclusively in a 1,2 manner to carbonyl derivatives containing conjugated double bonds.[12]

The allylboration of 4-*tert*-butylcyclohexanone with *B*-allyl-9-BBN produces a 54.8:45.2 mixture of the axial and equatorial homoallylic alcohols. This product distribution is almost identical with that realized in the allylation of this ketone with allylmagnesium bromide in refluxing ether.[14] Similarly, the allylboration of norcamphor afforded a mixture of homoallylic alcohols with an endo:exo alcohol ratio of

Table II. Allylboration of Aldehydes and Ketones with *B*-Crotyl-9-BBN[26]



R	R′	Product n^{20}D	% yield (GLC)[a]	Registry no.
H	H	1.4272	88	4516-90-9
n-C_5	H	1.4436	89[b]	52922-27-7 (threo) 52922-22-2 (erythro)
Ph	H	1.5251	87	25201-44-9
Me	Me	1.4358	100	19781-52-3
Ph	Me	1.5250	97	61967-11-1
Ph	Ph	51–52[c]	96	61967-12-2

[a] Reaction mixture allowed to stir for 2 h at 25 °C before workup, even though the allylboration was generally complete in a few minutes. [b] Threo:erythro = 60:40. [c] Melting point.

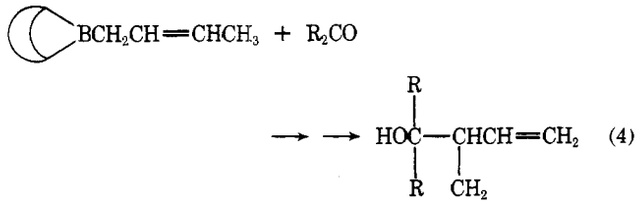
Table III. Allylboration of Acetone with *B*-Allyl-9-BBN Derivatives[26]

B-Allyl-9-BBN derivative	Product	n^{20}D	% yield (GLC)[a]
Allyl	2-Methyl-4-penten-2-ol	1.4271	99
2-Methylallyl	2,4-Dimethyl-4-penten-2-ol	1.4384	95
Crotyl	2,3-Dimethyl-4-penten-2-ol	1.4385	100
3,3-Dimethylallyl	2,3,3-Trimethyl-4-penten-2-ol	1.4490	93
3,3-Dimethyl-1-isopropylallyl	2,3,3,6-Tetramethyl-4-hepten-2-ol	1.4520	85[b]
2-Cyclohexen-1-yl	2-(2-Cyclohexenyl)-2-propanol	1.4833	86

[a] Reaction mixture allowed to stir for 2 h at 25 °C before workup, even though the allylboration was generally complete in a few minutes. [b] Largely the trans isomer.

95.8:4.2. Allylation of norcamphor with ethereal allylmagnesium bromide at reflux produced the same mixture of homoallylic alcohols (endo:exo 99:1).

Allylborations with the parent compound, *B*-allyl-9-BBN, cannot detect one very important feature of this reaction: the complete allylic rearrangement of the allyl moiety during the allylation.[4] However, the *B*-crotyl derivative shows this nicely (eq 4). No evidence was obtained through GLC, ^{13}C NMR, or



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^{1}H NMR examination of any unrearranged products (Table II). Two products were detected in the allylborations of aldehydes with *B*-crotyl-9-BBN; however, these proved to be diastereomers, not positional isomers. One interesting difference between the 9-BBN and the parent borane derivatives was observed. *B*-Crotyl-9-BBN reacts with monomeric formaldehyde to give only the rearranged alcohol, 2-methyl-3-buten-1-ol, after protonolysis. On the other hand, Mikhailov has reported that treatment of tricrotylborane with monomeric formaldehyde gives only 15% of this alcohol accompanied by 85% of the unrearranged alcohol.[17]

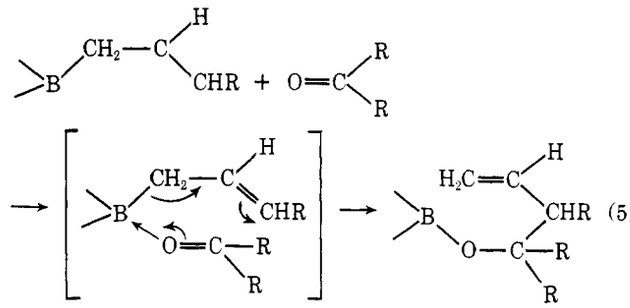
Table IV. In Situ Hydroboration–Allylboration Sequence with Acetone[26]

Diene[a]	Product	% yield (GLC)[b]
1,3-Cyclohexadiene	2-(2-Cyclohexenyl)-2-propanol	68
3-Methyl-1,2-butadiene	2,3,3-Trimethyl-4-penten-2-ol	80
2,5-Dimethyl-2,4-hexadiene	2,3,3,6-Tetramethyl-4-hepten-2-ol	80

[a] Diene was hydroborated with 9-BBN (1:1 stoichiometry) for 24 h at 25 °C in pentane; then 1 equiv of acetone was added, and the mixture allowed to stir for 2 h at 25 °C before workup.

Several other *B*-allyl derivatives of 9-BBN were treated with 1 equiv of acetone. Unsymmetrical allylboranes gave only the rearranged homoallylic alcohol (Table III). In several of these cases, the allylboranes can be prepared directly via hydroboration of the appropriate allene or conjugated diene. In order to demonstrate the synthetic utility of this hydroboration–allylboration sequence, these allylboranes were prepared with 9-BBN and the appropriate diene and then treated in situ with acetone. The results (Table IV) show that the desired homoallylic alcohols are produced in good yield. Consequently, the allylboration sequence offers a very simple method for preparing relatively complex homoallylic alcohols.

The formation of rearranged homoallylic alcohols from unsymmetrical allylboranes has been accounted for by Mikhailov in terms of a six-centered transition state mechanism (eq 5).[4] The possibility of the six-centered mechanism, along



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with the enhanced Lewis acidity of the allylboranes, may account for their ability to add easily to carbonyl derivatives, whereas normal trialkylboranes do not.[18]

The allylboration sequence offers certain advantages over the more familiar Grignard route for the preparation of homoallylic alcohols. First, certain functional groups are better tolerated by the allylboration reaction. For example, the presence of halide substituents in the substrate should offer no difficulties, since the allylboration can be carried out in carbon tetrachloride or chloroform without difficulty. In addition, as pointed out later, the reactions with unhindered aldehydes and ketones are far faster than those with esters and amides. The former groups are readily allylborated in the presence of the latter. Secondly, the intermediate boronic ester is not strongly basic, as are the intermediates in the lithium or magnesium allylations. Thirdly, the workup conditions are extremely mild. Acidic hydrolysis agents are not required, and there are no problems with gels, emulsions, or extractions from

Table V. Allylboration of Carbonyl Derivatives with *B*-Allyl- and *B*-Crotyl-9-BBN

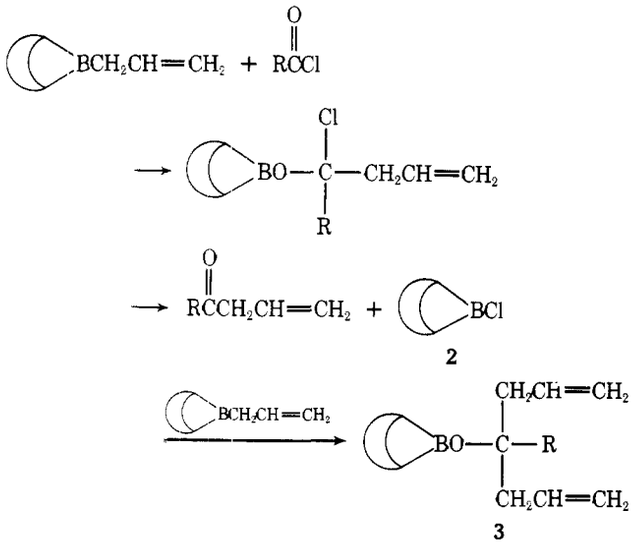
B-R-9-BBN, R	Substrate	Stoichiometry[a]	Product[b]	% yield (GLC)[c]
Allyl	Acetyl chloride	2:1	A	95
	Benzoyl chloride	2:1	B	89
	Acetic anhydride	4:1	A	95
	Benzoic anhydride	4:1	B	82
	Ethyl acetate	2:1	A	90
	Ethyl benzoate	2:1	B	50[d]
	N,N-Dimethylacetamide	2:1	A	50–57
	N,N-Dimethylbenzamide	2:1	B	91[e]
	B-Acetoxy-9-BBN	2:1	A	84
Crotyl	Acetyl chloride	2:1	C	93
	Acetic anhydride	4:1	C	97

[a] Allylborane to substrate. [b] A = 4-methyl-1,6-heptadien-4-ol, n^{20}D 1.4518; B = 4-phenyl-1,6-heptadien-4-ol, n^{20}D 1.5290; C = 3,4,5-trimethyl-1,6-heptadien-4-ol (mixture of diastereomers), n^{20}D 1.4594. [c] Unless noted otherwise, the reaction mixture was stirred for 2 h at 25 °C before workup, even though the allylboration was generally complete in a few minutes. [d] After 50 h in refluxing *n*-hexane. [e] After 3 h at 25 °C.

aqueous hydrolysis media. Finally, the greater sensitivity to the steric environment should make possible more selective reactions.

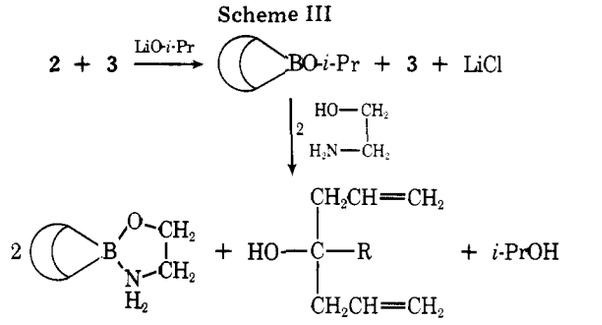
Allylboration of Acid Chlorides. *B*-Allyl-9-BBN reacts vigorously with acid chlorides. The stoichiometry of the reaction is two allylboranes to one acid chloride. The products of this reaction are 1 equiv each of *B*-chloro-9-BBN (**2**) and the 9-BBN borinic ester of the alkyldiallylcarbinol (**3**) (Scheme II).

Scheme II

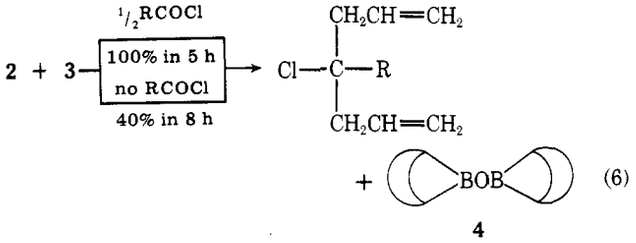


The presence of the chloroborane (**2**) necessitates a slight modification of the usual protonolysis procedure (eq 2). If 2 equiv of ethanolamine is added to the mixture of **2** and **3**, the protonolysis is incomplete, and the boron-containing products form a sticky gel. This is probably due to the formation of hydrogen chloride from the protonolysis of the chloroborane (**2**). To circumvent this difficulty, it is only necessary to add 1 equiv of lithium isopropoxide before adding the 2 equiv of ethanolamine. The lithium isopropoxide, chosen because it is soluble in hexane, reacts with the chloroborane forming lithium chloride and the isopropyl ester of 9-BBN borinic acid. The 2 equiv of ethanolamine then transesterifies both borinic esters liberating the alkyldiallylcarbinol and 2-propanol (Scheme III) (Table V).

Scheme III

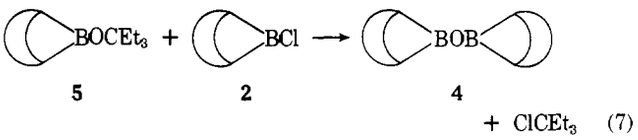


If the mixture of products from Scheme II is not worked up immediately after the reaction is complete, or if excess acid chloride is used, an interesting side reaction occurs (eq 6). It



should be emphasized that this side reaction can be entirely avoided by short reaction times and use of the exact stoichiometry.

Since the side reaction occurs only after long reaction times, it is probably due to a reaction between the products of the allylboration reaction (**2** and **3**). This was confirmed by the formation of triethylcarbinyl chloride from the reaction of **2** and **5** (eq 7). This reaction appears to be catalyzed by the acid

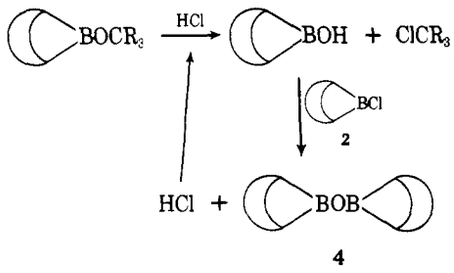


chloride, for when **2** and **5** are mixed, no reaction occurs even after 30 h. However, when 1 equiv of acetyl chloride is added, the formation of the tertiary chloride is complete in a few hours. Analyses by infrared and ^{1}H NMR show that the acetyl chloride is not consumed to any significant extent during the reaction. Furthermore, the chloride formation is only observed when the borinate ester is tertiary. When similar experiments were carried out with the *n*-butyl or *sec*-butyl esters of 9-BBN borinic acid, no *n*-butyl chloride or *sec*-butyl chloride were detected even after 15 days.

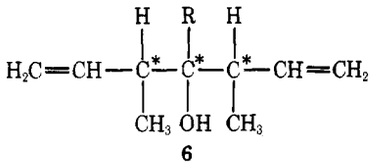
Although we did not carry out a detailed study of the tertiary chloride formation, it is probably produced by the cleavage of the borinate ester with hydrogen chloride formed by trace hydrolysis of the acid chloride or chloroborane. Lappert and Gerrard have shown that tertiary and benzylic borinate esters undergo carbon–oxygen cleavage with hydrogen halides, whereas secondary and primary borinate esters do not react under anhydrous conditions.[20] In the present case, such a cleavage can be a chain process (Scheme IV).

B-Crotyl-9-BBN reacts with acid chlorides in the same fashion as the parent *B*-allyl derivative. As noted earlier for aldehydes and ketones, complete allylic rearrangement of the crotyl moieties occur in the reaction with the acid chloride. GLC analyses of the products after protonolysis revealed a

Scheme IV



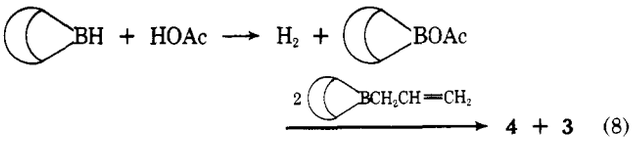
mixture. Fortunately, it was possible to isolate separately two of the major components by preparative GLC. ^{1}H NMR showed them to be diastereomers due to the juxtaposition of three asymmetric centers (**6**), not positional isomers.



Some preliminary attempts were made to stop the allylboration following the addition of but one allyl group. Unfortunately, these attempts failed. Even with reaction at low temperature with a 1:1 stoichiometry, only the diallylated product was observed.

Allylboration of Acid Anhydrides. *B*-Allyl-9-BBN reacts vigorously with acid anhydrides. The stoichiometry of the reaction is four allylboranes to one anhydride. The products, determined by ^{11}B NMR, ^{1}H NMR, and GLC, are 1 equiv of oxybis-9-BBN (**4**) and 2 equiv of the 9-BBN borinic ester of the alkyldiallylcarbinol (**3**). A possible reaction path leading to these products is outlined in Scheme V. Transesterification with 4 equiv of ethanolamine results in the formation of high yields of the corresponding alkyldiallylcarbinols (Table V). *B*-Crotyl-9-BBN reacts similarly; here again the addition occurs with complete allylic rearrangement of the crotyl moieties.

One step in our reaction mechanism (Scheme V) involves the allylboration of *B*-acetoxy-9-BBN (**7**). We tested this proposal by preparing this material (**7**) by an independent route, and then treated it with *B*-allyl-9-BBN in a 1:2 stoichiometry. The products anticipated were formed rapidly (eq 8). Attempts to stop the addition to acid anhydrides at the monoaddition stage were unsuccessful.



(8)

Allylboration of Carboxylic Acid Esters. *B*-Allyl-9-BBN reacts much more slowly with carboxylic acid esters than with the carbonyl derivatives discussed earlier. The stoichiometry is two allylboranes per ester. The products are 1 equiv each of the alkyldiallylcarbinyl ester of 9-BBN borinic acid (**3**) and the *B*-alkoxy-9-BBN ester (**8**) (Scheme VI). The usual transesterification with 2 equiv of ethanolamine affords good yields of the corresponding alcohols. The allylboration reaction is quite sluggish for aromatic carboxylic esters. For example, the allylboration of ethyl benzoate is incomplete even after 6 days at room temperature. In refluxing hexane, the reaction is 50% complete in 50 h. At higher temperatures, in *n*-nonane at reflux, the allylborane is consumed in 3 h. Unfortunately, side reactions occur, and the yield of the homoallylic alcohol, following transesterification, is only 28%. Attempts to stop the allylboration at the monoaddition stage were not successful.

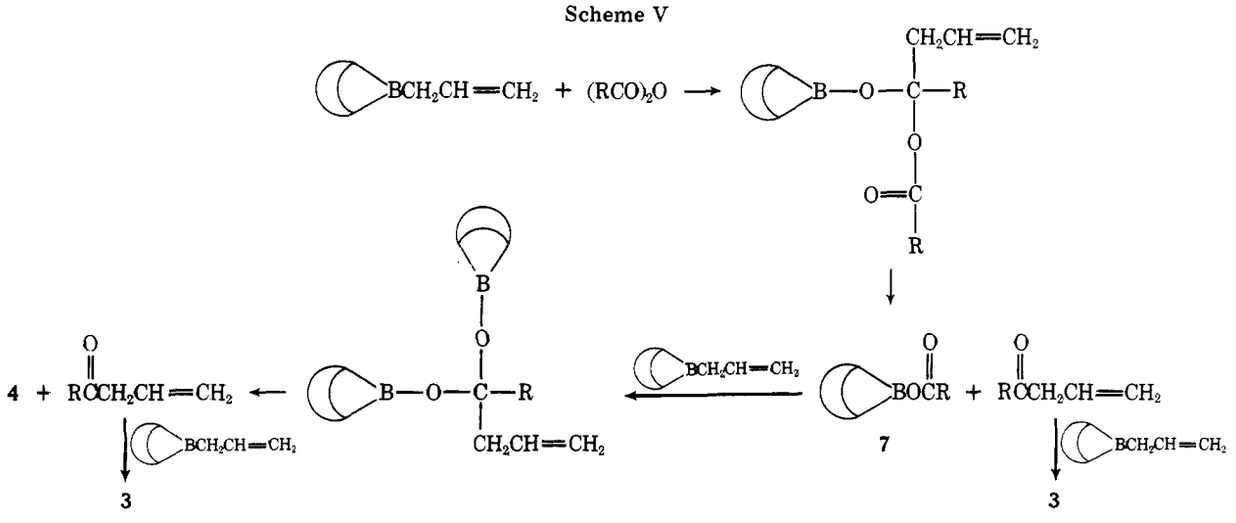
Allylboration of *N,N*-Dimethylamides. *B*-Allyl-9-BBN reacts slowly with *N,N*-dimethylbenzamide in a 2:1 stoichiometry. The products, as identified by ^{11}B NMR, ^{1}H NMR, and GLC, are 1 equiv each of *B*-*N,N*-dimethylamino-9-BBN (**9**) and the diallylphenylcarbinyl ester of 9-BBN borinic acid (Scheme VII). Transesterification wth ethanolamine produces the corresponding homoallylic alcohol and dimethylamine.

In contrast to the straightforward allylboration of *N,N*-dimethylbenzamide, the reaction with *N,N*-dimethylacetamide is complex. The stoichiometry appears to be two allylboranes to one amide. Analysis of the reaction mixture by ^{1}H NMR shows evidence of several competing reactions. The exact nature of these reactions, as well as the identities of all of the products, is not known at present. Transesterification of the reaction mixture affords only a 50% yield of the expected diallylmethylcarbinol.

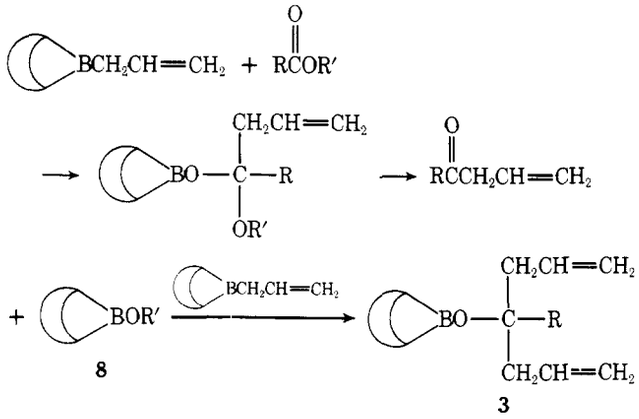
Summary

The allylborations of carbonyl compounds with *B*-allyl derivatives of 9-BBN, followed by transesterification with ethanolamine, provides a simple, convenient method for the synthesis of homoallylic alcohols. Unsymmetrical allylboranes show complete allylic rearrangement of the allyl moiety during addition. The tolerance of the allylboration reaction to certain functional groups, as well as its very mild reaction and workup conditions, make it competitive with the more familiar Gri-

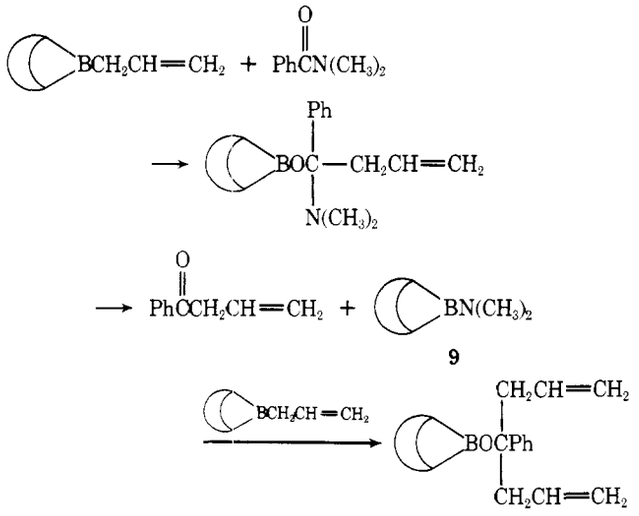
Scheme V



Scheme VI



Scheme VII



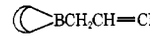
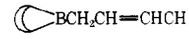
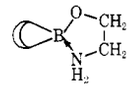
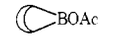
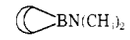
gnard allylations. Since many *B*-allyl derivatives of 9-BBN may be readily prepared via hydroboration of the appropriate allenes or conjugated dienes, the in situ hydroboration–allylboration sequence provides a simple, one-pot synthesis of many complex homoallylic alcohols.

Experimental Section

General Comments. The techniques described in Chapter 9 of ref 7 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. The reaction flasks were fitted with side arms capped with rubber septa and were flamed out under a nitrogen purge immediately before use. All reactions were carried out under a static pressure of prepurified nitrogen. The transfers of liquids and solutions of organometallics were done either with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles or by the double-ended needle technique.[7] All reactions were stirred magnetically using oven-dried, Teflon-coated stirring bars.

Materials. The solvents, allylboranes, and other organoboron derivatives used as standard samples for identification purposes were prepared as described previously.[8] Most of the aldehydes and ketones used in this study were commercial materials. All were purified by distillation, recrystallization and vacuum drying, or preparative GLC prior to use. The bicyclo[3.3.1]nonan-9-one was prepared as previously described.[21] Acetyl chloride, *N,N*-dimethylacetamide, ethyl acetate, and benzoyl chloride were distilled under nitrogen from calcium hydride. Acetic anhydride and ethyl benzoate were distilled under nitrogen from phosphorus pentoxide. The *N,N*-dimethylbenzamide was recrystallized from pentane. Benzoic anhydride, triethanolamine, and ethanolamine were used without purification. The simple *B*-alkoxy-9-BBN derivatives were prepared by treatment of 1 equiv of 9-BBN with 1 equiv of the corresponding alcohol (dried over 4 Å molecular sieves). Lithium isopropoxide in hexane was prepared by the addition of the calculated quantity of 2-propanol (dried over 3 Å molecular sieves) to a standardized solution of *n*-butyllithium in hexane.

Table VI. ^{11}B NMR Resonances of Pertinent 9-BBN Derivatives

Compd	^{11}B resonance, δ
	−85.6
	−86.0
	−5.7
	−82
	−56 to −52
	−55
	−16.4
	−47.7

Analyses. ^{11}B NMR spectra were recorded on a Varian XL-100-15 spectrometer (32.1 MHz) using a Nicolet 1080 data system. The spectra were recorded in the CW mode using ^{1}H, ^{2}H internal, or ^{19}F external locks; all chemical shifts are relative to $BF_3{\cdot}OEt_2$ (δ 0) with the chemical shifts downfield from $BF_3{\cdot}OEt_2$ assigned as negative (Table VI). ^{1}H NMR spectra were recorded on Varian T-60 (60 MHz) or Perkin-Elmer R-32 (90 MHz) machines, while ^{13}C NMR spectra were obtained on a Varian CFT-20 (20 MHz FT) spectrometer. Both the ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane (δ 0).

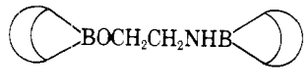
GLC analyses were generally carried out on a Hewlett-Packard 5752B chromatograph fitted with a Disc integrator using 6 ft × 0.25 in. stainless steel columns filled with 10% loaded packing on AW DMCS 60/80 Chromosorb W. Apiezon L and SE-30 were used for the analyses of the organoboranes, while Carbowax 20M, XE-60, SE-30, and DC-710 were used for the analyses of most of the homoallylic alcohols. The isomeric alcohols from the allylboration of 4-*tert*-butylcyclohexanone were analyzed on either DEGS or QF-1 columns, while the diastereomeric α-methallyl products were analyzed on DEGS or Carbowax 1540. The GLC analyses for the endo and exo norbornyl derivatives were carried out on a Perkin-Elmer 226 capillary chromatograph fitted with a 150 ft × 0.01 in. Golay column coated with DEGS. Quantitation of all GLC analyses was done by the internal standard method using appropriate normal hydrocarbons (usually *n*-octane or *n*-decane) as standards. Preparative GLC was carried out on a modified Wilkins A-100 instrument using 5 ft × 0.5 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.

Mass spectra were obtained from Hitachi Perkin-Elmer RMU6-D (low resolution) or CEC 21-110 (high resolution) spectrometers. Exact mass determinations were done by peak matching technique using PFK standard.

In general the homoallylic alcohols products were identified either by comparison of their GLC retention times (on at least two columns of differing polarities) with those of commercial samples or samples prepared by the Grignard allylation of the corresponding ketone, or by isolation and characterization through their infrared, ^{1}H NMR, ^{13}C NMR, and mass spectra. The identification of the isomeric alcohols from the allylboration of 4-*tert*-butylcyclohexanone, as well as the threo and erythro products from the crotylboration of aldehydes, is based on the GLC retention time data of Abenhaim.[16] The assignments of the exo and endo homoallylic alcohols from norcamphor were established as follows. The allylboration product was compared by GLC retention times (spiked injection) with the product from the Grignard allylation. It was assumed that the Grignard reaction would give almost exclusively the endo alcohol.[22] The ^{13}C NMR spectra of the allylboration product, and the Grignard allylation product, were identical and were consistent with the spectra expected for a single isomer. A sample of the exo alcohol was prepared from the endo alcohol by conversion to the tertiary chloride followed by solvolysis in an aqueous buffer.[23]

Isolation and Characterization of 1. The white solid remaining after transesterification of a ketone allylboration was dissolved in THF, then reprecipitated by the addition of cold pentane. The solid

was filtered, washed twice with cold pentane, recrystallized from pentane–THF, and vacuum dried at 25 °C (15 mm) for 6 h (mp 202–203.5 °C with decomposition in a sealed evacuated capillary). Anal. Calcd for $C_{10}H_{20}BNO$ (181.092): C, 66.32; H, 11.13. Found: C, 66.25; H, 11.19. ^{11}B NMR (THF) δ −5.7. ^1H NMR (C_3D_6O) δ 4.9 (broad, ~2), 3.75 (t, 2, J = 6 Hz), 3.0 (m, 2), 1.77 (methylene envelope, ~12), 0.51 (m, ~2, bridgehead hydrogens). *m/e* M^+. Calcd for $^{12}C_{10}{}^1H_{20}{}^{11}B^{14}N^{16}O$: 181.1638. Found: 181.1644. This material underwent a partial reaction in the mass spectrometer: evidently two molecules of 1 combine with the elimination of ethanolamine to form



which gives high mass ions containing two boron atoms. M^+ calcd for $^{12}C_{18}{}^1H_{33}{}^{14}N^{16}O^{11}B_2$: 301.2748. Found: 301.2723. Calcd for $^{12}C_{18}{}^1H_{33}{}^{14}N^{16}O^{11}B^{10}B$: 300.2785. Found: 300.2762.

Allylboration of Aldehydes and Ketones. General Procedure (5-mmol Scale). To an oven-dried, nitrogen-flushed, flamed-out, 25-mL flask fitted with a septum inlet, a magnetic stirring bar, and topped with a connecting tube leading to a mercury bubbler, there was added a weighed amount of neat *B*-allyl-9-BBN derivative (~5 mmol). About 15 mL of dry, olefin-free pentane was added and 0.5 mL of the *n*-alkane (GLC internal standard). Stirring was begun, and the calculated amount of the neat carbonyl derivative (1 equiv) was added dropwise from a syringe.[24] The progress of the reaction was monitored by GLC. In most cases the reaction appeared to be complete in a few minutes, but the mixtures were generally allowed to stir for 2 h to ensure completion. One equivalent of neat ethanolamine was added from a syringe.[25] After stirring for about 1 h, the supernatant liquid was analyzed by GLC. The supernatant liquid was then decanted and the precipitate washed (2 × 10 mL) with pentane. The combined extracts were concentrated under a stream of nitrogen, then bulb-to-bulb distilled. The distillate, consisting normally of the homoallylic alcohol and the GLC internal standard, was subjected to a preparative GLC separation. The alcohol fraction, which was generally analytically pure, was used for the determination of spectra and the GLC correction factors. Even with product losses due to the small reaction scale and inefficiencies in the preparative GLC collections, the isolated yields were always over 60%. In preparative reactions, where no GLC internal standard is employed, the products are easily isolated in excellent yield by simple distillation. If the precipitate (1) is carefully removed, the products are normally analytically pure after removal of the pentane.

Allylboration of Pivaldehyde (23.3-mmol Scale). Following the general procedure given above, 3.775 g (23.3 mmol) of *B*-allyl-9-BBN was dissolved in about 25 mL of dry, olefin-free pentane in a 50-mL flask. This flask was immersed in a cold water bath where 2.60 mL (23.3 mmol) of freshly distilled pivaldehyde was added dropwise from a syringe to the stirred solution. The cooling bath was removed when the addition was complete, and the mixture was stirred for 1 h at 25 °C. Neat ethanolamine (1.40 mL, 23.3 mmol) was added dropwise from a syringe. After a few minutes, the thick, white precipitate of 1 had formed. This slurry was stirred for 0.5 h, then the contents of the reaction flask were poured into a 50-mL centrifuge tube. The flask was rinsed into the tube with ~10 mL of pentane. After centrifugation, the supernatant liquid was decanted and ~15 mL of pentane added to the tube. The solid was stirred, then the tube was centrifuged. This washing procedure was repeated three times. The combined extracts were concentrated under a stream of nitrogen and the residual oil subjected to simple vacuum distillation. Only one fraction, 2.53 g (85%), of a clear liquid, bp 55.5–56 °C (19 mm), was collected. GLC analysis of the product ($n^{20}D$ 1.4379) showed it to be 99.9+% pure. The IR and ^1H NMR spectra were consistent with the structure of 2,2-dimethyl-5-hexen-3-ol. The allylic methylene protons are not magnetically equivalent; therefore the α-hydroxy methine hydrogen appears as a doublet. ^1H NMR (CCl_4) δ 0.96 (s, 9, *t*-Bu), 1.97 (s, 1, OH), 2.25 (m, 2, allylic methylenes), 3.28 (dd, 1, J_1 = 8 Hz, J_2 = 2.5 Hz, methine), 5.02, 5.23, 5.9 (m, 3, terminal alkene); IR 3448 (OH), 1642 (C=C), 1381, 1368 (*t*-Bu), 995, 913 cm^{-1} (terminal double bond).

Allylboration of Acid Anhydrides, Esters, and *N,N*-Dimethylamides. General Procedure (5-mmol Scale). These reactions were carried out under essentially the same conditions as described above with the reaction stoichiometries adjusted as necessary. During the addition of the acid anhydrides, it was necessary to cool the reaction flask in a cold water or ice bath to prevent the solvent from boiling.

Allylboration of Acid Chlorides. General Procedure (5-mmol Scale). These reactions were carried out as described above up through the addition of the acid chloride. It was necessary to cool the reaction flask to prevent the solvent from boiling during this addition. The reaction mixture was allowed to stir for 1 h, and then 1 equiv of lithium isopropoxide in hexane was added dropwise from a syringe. After stirring for about 15 min, 2 equiv of ethanolamine was added and the reaction mixture worked up and analyzed in the usual manner.

In Situ Hydroboration–Allylboration Sequence. To an oven-dried, flamed-out, nitrogen-flushed, 25-mL flask fitted with a magnetic stirring bar, septum inlet, and topped with a connecting tube leading to a mercury bubbler, there were added 11.6 mL of 0.43 M 9-BBN in pentane (5.0 mmol), 0.5 mL of the GLC internal standard, and 5.0 mmol of the allene or diene. Stirring was begun and the progress of the hydroboration monitored by GLC. In all cases, the amount of residual diene remained constant after 24 h. Then 0.37 mL (5.0 mmol) of acetone was added. The mixture was worked up either by the usual transesterification procedure with ethanolamine or by the normal oxidative procedure using 3 M aqueous sodium hydroxide and 30% hydrogen peroxide.[7]

Acknowledgment. We thank the National Science Foundation for the support of this work under Grant GP 41169X. We also thank Professor R. A. Benkeser for helpful discussions involving this work.

Registry No.—**1**, 61967-22-4; 1 coordination form, 62059-31-8; *B*-allyl-9-BBN, 53317-08-1; pentanal, 110-62-3; pivaldehyde, 630-19-3; benzaldehyde, 100-52-7; 2-butenal, 4170-30-3; acetone, 67-64-1; 3,3-dimethyl-2-butanone, 75-97-8; 1-phenylethanone, 98-86-2; diphenylmethanone, 119-61-9; 2,4-dimethyl-3-pentanone, 565-80-0; 2,2-dimethyl-3-hexanone, 5405-79-8; 2,2,4-trimethyl-3-pentanone, 5857-36-3; 2,2-dimethyl-1-phenyl-1-propanone, 938-16-9; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; 4-*tert*-butylcyclohexanone, 98-53-3; norcamphor, 497-38-1; bicyclo[3.3.1]nonan-9-one, 17931-55-4; 3-buten-2-one, 78-94-4; 3-penten-2-one, 625-33-2; 4-methyl-3-penten-2-one, 141-79-7; *B*-crotyl-9-BBN, 61967-28-0; formaldehyde, 50-00-0; 2-methylallyl-9-BBN, 61967-13-3; 3,3-dimethylallyl-9-BBN, 55454-18-7; 3,3-dimethyl-1-isopropylallyl-9-BBN, 61967-14-4; 2-cyclohexen-1-yl-9-BBN, 61967-15-5; 2,4-dimethyl-4-penten-2-ol, 19781-53-4; 2,3,3-trimethyl-4-penten-2-ol, 36934-19-7; *trans*-2,3,3,6-tetramethyl-4-hepten-2-ol, 61967-16-6; *cis*-2,3,3,6-tetramethyl-4-hepten-2-ol, 61967-17-7; 2-(2-cyclohexenyl)-2-propanol, 5723-91-1; 1,3-cyclohexadiene, 592-57-4; 3-methyl-1,2-butadiene, 598-25-4; 2,5-dimethyl-2,4-hexadiene, 764-13-6; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; acetic anhydride, 108-24-7; benzoic anhydride, 93-97-0; ethyl acetate, 141-78-6; ethyl benzoate, 93-89-0; *N,N*-dimethylacetamide, 127-19-5; *N,N*-dimethylbenzamide, 611-74-5; *B*-acetoxy-9-BBN, 62015-69-4; 4-methyl-1,6-heptadien-4-ol, 25201-40-5; 4-phenyl-1,6-heptadien-4-ol, 38400-77-0; 3,4,5-trimethyl-1,6-heptadien-4-ol, 756-43-4; BBN-9-ylaminoethoxy-9-BBN, 61967-18-8; ethanolamine, 141-43-5.

References and Notes

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(10) The remarkable air stability of this material is probably a result of the chelate structure.
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(14) The axial–equatorial ratio of products from the Grignard allylations is dependent on the reaction temperature.[15] It is reported to be 50.3:49.7 at 35 °C;[15] in our study we found it to be 54.3:45.7 in refluxing ether.
(15) M. Cherest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968).
(16) D. Abenhaim, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 4043,

4038 (1969).
(17) B. M. Mikhailov and V. F. Pozdnev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1477 (1967), *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1428 (1967).
(18) It has recently been reported that *B*-vinyl derivatives of 9-BBN add in a 1,2 manner to unhindered aldehydes to give allylic alcohols after hydrolysis.[19] While no mechanism was postulated, it is interesting that the addition occurs with complete retention of the stereochemistry in the vinyl moiety.
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(21) B. A. Carlson and H. C. Brown, *Synthesis*, 776 (1973).
(22) M.-H. Rei, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1967.
(23) E. N. Peters, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1972; E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 265 (1974).
(24) Solid carbonyl compounds were dissolved in the minimum amount of pentane or benzene and added to the reaction mixture.
(25) Excess ethanolamine should be avoided, since it makes the precipitate of **1** sticky and renders more difficult the extraction of the products.
(26) ^{1}H NMR and infrared spectra of all the homoallylic alcohols prepared may be found in the Ph.D. Thesis of G. W. Kramer, Purdue University, 1976.

Selective Transformation of Vicinal-Disubstituted Epoxides into Ketones by Homogeneous Rhodium Catalysts[1]

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Received January 19, 1977

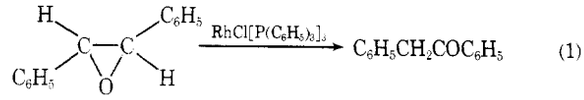
Chlorotris(triphenylphosphine)rhodium has been shown to catalyze the selective rearrangement of many vicinal-disubstituted epoxides to ketones between 150 and 210 °C. Kinetic measurements for various *trans*-1,2-diarylethylene oxides and $RhCl(PAr_3)_3$ catalysts were carried out. The reaction rate was shown to increase by introduction of electron-donating substituents into either the catalyst ligands or the substrate. The catalysis is inferred to proceed in the following order: (a) dissociation of $RhCl(PAr_3)_3$, (b) reversible nucleophilic cis addition of the epoxide to the activated catalyst to give a Rh(III) hydride, (c) intramolecular hydrogen transfer from the rhodium atom to the noncoordinated oxirane carbon, (d) reductive elimination to form the ketone and activated catalyst. The data are compatible with the expression rate = $k_1k_2[S][C]_0/(k_{-1} + k_2 + k_1[S])$ where [S] and $[C]_0$ are substrate and initial catalyst concentration, respectively. Step c is considered rate determining on the basis of kinetic isotope effect measurements. Complexes $RhCl(PAr_3)_3$ have been shown to catalyze also an unusual carbon–carbon bond cleavage in stilbene oxides having potent electron-attracting substituents to yield benzaldehydes and polymers. Epoxides in which one aromatic ring is more electron attracting than the other form aldehydes with the least electronegative groups.

Ring opening of epoxides by acids, bases, and salts has been extensively studied and reviewed.[2] In recent years some transition metal complexes have been shown to cleave catalytically C–O bonds in the oxirane system.[3] However, only in a few cases could the activities of the metal complexes be attributed to other than their acidic properties.

In this paper we present a detailed investigation on the transformation of vicinal-disubstituted ethylene oxides by the nonacidic $RhCl[P(C_6H_5)_3]_3$, including kinetic measurements and mechanistic studies on a selective isomerization of some stilbene oxides to deoxybenzoins. In addition we describe an epoxide system in which the C–C bond is cleaved in addition to the C–O linkage.

Results

Conversion of Epoxides to Ketones. While both acid- and base-catalyzed isomerization of *trans*-stilbene oxide gives usually diphenylacetaldehyde as the main product,[2c,4,5] the $RhCl[P(C_6H_5)_3]_3$-promoted reaction affords 88% deoxybenzoin, simply by heating 1 mol of the epoxide under N_2 with 2×10^{-2} mol of rhodium complex for 2 h at 210 °C. The only by-products in reaction 1 are diphenylmethane (7.9%),



(1)

trans-stilbene (2.8%), *cis*-stilbene (0.3%), and benzene (1.0%). Although $RhCl[P(C_6H_5)_3]_3$ has been assumed to liberate HCl in some other catalyses,[6] we could prove that no such decomposition is taking place in our system. The addition of a weak base to the reaction mixture that is able to remove any HCl that might have been formed, but is refractory toward the rhodium catalyst (e.g., 2,6-di-*tert*-butylpyridine), has no effect whatsoever on the results. On the other hand, addition of minute amounts of gasous hydrogen chloride causes the stilbene oxide to rearrange mainly to diphenylacetaldehyde.[7]

The high selectivity in our catalysis is conditioned by the existence of an absolutely inert atmosphere. Experiments performed under 90% N_2 and 10% O_2 gave no more than 26.5% of the ketone. *cis*-Stilbene oxide, which proved to undergo different transformations than the trans isomer by bases and acids,[5] gives the same yield of deoxybenzoin when the Wilkinson catalyst is employed.

The scope and potential synthetic application of the catalysis for selective conversion of stilbene oxides into the rearranged ketones are demonstrated by the examples listed in Table I.

While stilbene oxides with electron-donating groups give results similar to those with the unsubstituted parent compound, 4-nitrostilbene oxide forms only little of the expected ketone and 3,3′- as well as 4,4′-dinitrostilbene oxide give none at all. The negatively substituted epoxides undergo catalytic C–C bond cleavage which will be discussed below.

When two substituents of different electronic nature are being attached to the phenyl rings (one to each) the C–O bond that is closer to the more electron-donating group is expected to be the weaker one[2b] and to be cleaved preferentially. This is in fact observed in expt 5 and 6 (Table I): *trans*-4-chloro-4′-methylstilbene oxide yields $4\text{-}ClC_6H_4COCH_2C_6H_4\text{-}4\text{-}CH_3$ and $4\text{-}ClC_6H_4CH_2COC_6H_4\text{-}4\text{-}CH_3$ in ratio 7:3, and *trans*-4-