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# Allylboranes—molecular design

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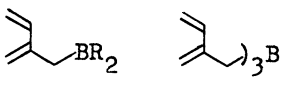
Abstract - Some aspects of the construction of cyclic, cage, and acyclic organic and organoboron systems with the use of triallylborane and various new allylic boranes 1-7 are presented. All known allylborane reactions are classified into six patterns, and principles of their reacting are formulated. Now one can predict the courses of many "new" reactions of this type of compounds.

Allylboranes are useful and, in certain cases, unique tools available for the creation of C-C bonds, cyclization, and functionalization of various organic compounds (1-3). Over the last two decades, allylboranes have been widely used in the synthesis, and at present the scope of their application is expanding penetrating into new fields of organic chemistry. This has been prompted by the exclusive reactivity of these compounds compared to other organoboranes stipulated by the specificity of their structures (β,γ-unsaturated compounds).

This paper describes some aspects of the construction of cyclic, cage, and acyclic unsaturated systems using triallylborane and a series of new type boranes 1-8.

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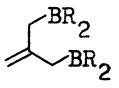
1a

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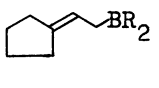


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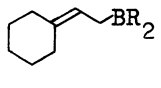


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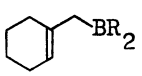


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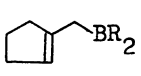


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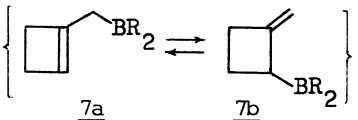
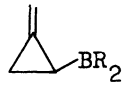



7a 7b




8

Also, the systematization of all so far known reactions of allylic boranes, being of a predictable character, is depicted.

## GENERAL PATTERNS OF ALLYLBORANE REACTIONS

Over 30 various reactions of allylboranes have been described to date (1-3), and we succeeded in dividing them into several general types depending on the centre at which the reaction takes place.

Allylboranes contain four reaction centres: the boron atom, B-C, $C_\alpha$-H, and C=C bonds (A). However, the peculiarities of these compounds are manifested in those reactions which involve the allyl-boron system as a whole (B).

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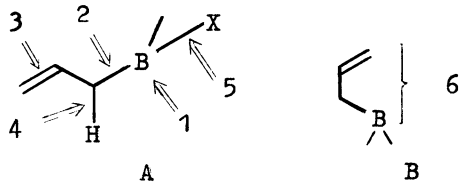
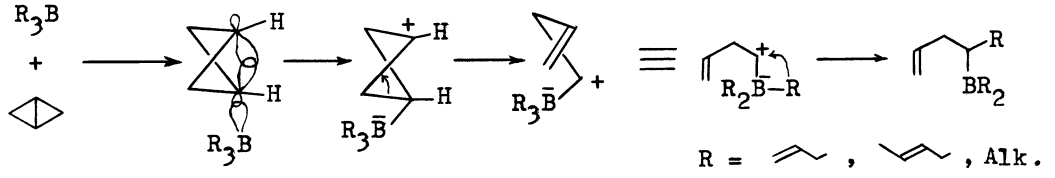
This paper is dedicated to Professor B.M. Mikhailov's memory (1906-1984).




A B

1. The boron atom - electrophilic centre of the molecule. This centre is responsible for coordination with bases ($R^-$, $RO^-$, $R_3N$ etc.). The complexing ability of allylboranes is higher than that of their alkyl analogues due to the influence of the double bond.Complexation is the crucial step in reactions of the types 2 and 6 (see below).

2. The B-C bond. The calculated energy of B-C bond in allylboranes is ca. 68 kcal/mol (4) while in alkylboranes it is ca. 82 kcal/mol. At present only 5 reactions of allylboranes are known to occur by direct rupture of the B-C bond (with retention of configuration): with $H_2O_2$-$OH^-$(5,6), $N_2CH_2COOEt$ (7), cyclopropenes (cleavage of $C_2$-$C_3$ bond)(8,9), bicyclo[1.1.0]butane (10), and $Cl_2CHLi$ (11a). These reactions involve migration of $R^-$ from the negatively charged boron to the neighbouring centre with positive charge in the adduct formed initially. Alkylboranes react with these compounds similarly.

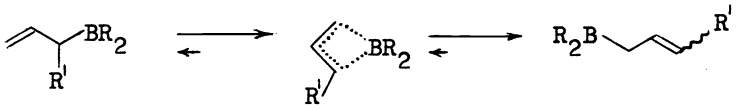



3. The double bond. The presence of double bond enables allylboranes to undergo polymerization, hydrogenation, addition of RSH, $R_3SiH$, $R_3GeH$, and boranes (1,2) as well as diene condensation (12). According to $^{13}C$ NMR, the C=C bond in allylboranes is more polarized as compared to alkenes (13,14).

4. The $C_\alpha$-H bond activated by boron. Under the action of 1-lithium-2,2,6,6-tetramethylpyridine, α-metallation takes place (15,16).

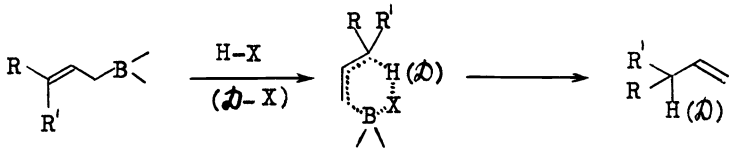
5. The exchange of groups X in $R_2BX$ and $RBX_2$ (R= allylic group) is also common for all types of organoboron compounds.

6. The boron-allyl system as a whole. The specificity of the system is manifested in permanent allylic rearrangement (1,2) and in a tendency of α-substituted allylboranes to convert into more thermodynamically stable isomers with boron on the less substituted carbon atom.

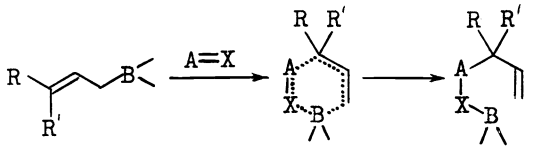


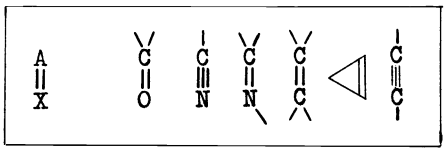

The following reactions proceed with the participation of the boron-allyl system, with all of them involving allylic rearrangement:

a) protolysis with water, alcohols, amines etc.,
b) allylation of aldehydes, ketones, esters, quinones, imines, nitriles, vinyl ethers,cyclopropenes, acetylenes, and allenes (1-3). The addition of triallylborane to aldehydes and ketones was the first reaction of this type (17).



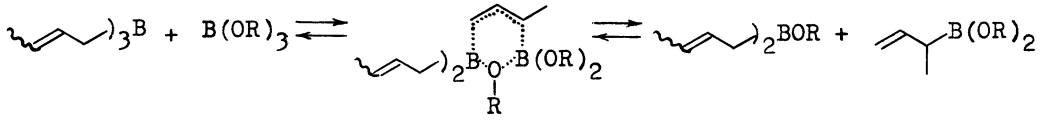

HX = H-OH, H-OR, H-OCOR etc.





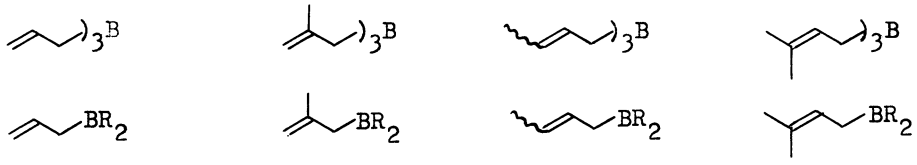
The more the multiple bond in A=X is polarized or strained the easier the allylboration occurs, with the boron atom locating exclusively at the nucleophilic centre of the bond and the allylic group at the electrophilic one. In all cases a bond newly formed is stronger than B-$C_{All}$ bond. Hence, these reactions are thermodynamically favoured (alkylboranes do not add to A=X).

c) exchange reactions with $BX_3$ (X= Hal, OR, SR) and intermolecular allylic rearrangement (18).

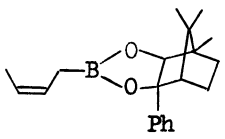


The above systematization allows to predict definitely in most cases and in some cases with great certainty whether that or another "novel" reaction will proceed with or without the rearrangement. Thus, reactions of allylboranes with $R_3NO$, ylides, $RN_3$, and RSCl which were not studied to date should be expected to occur without allylic rearrangement and to proceed via the intramolecular 1,2-migration processes in the corresponding adducts formed instantly (direct cleavage of B-C bond, the type 2).

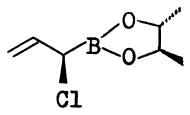
The following rule for allylborane reacting may be offered: "If an allylborane reacts with a reagent by the same mechanism as alkylboranes do, the reaction takes place without allylic rearrangement. Those reactions of allylboranes which are not specific for their alkyl analogues occur with the rearrangement". A formal exception from the rule is protolysis leading to hydrocarbons both in case of allyl- and alkylboranes, but the reaction mechanisms are different. Another exception is the exchange of X in $RBX_2$ and $R_2BX$ (the type 5). We have formulated these regularities (19) as a result of studies on properties of the simplest allyl, methallyl, crotyl, and (partially) prenyl boron derivatives.



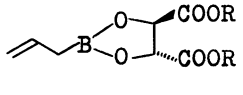
Since the late 1970's, various aspects of allylborane chemistry have been studied by R.W.Hoffmann (20), Y.Yamamoto (21), H.C.Brown (22), W.R.Roush (23), M.Schlosser (6,24), P.G.M.Wuts (25), D.S.Matteson (11), R.Köster (26a), and others. Methods for the preparation of pure Z- and E-crotylboranes (20a,c;24) and a number of functionalized esters of the type $XCH{=}CH{-}CH_2B(OR)_2$ (23) were elaborated. The most important achievement of the latest years has been the synthesis of chiral allylboranes (11c), e.g.



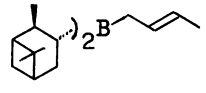
(Ref.20c,d)



(Ref.20b)



(Ref.23a)



(Ref.22a)

These configurationally pure and chiral allylboranes were mainly used for allylboration of aldehydes and ketones as well as imines (21 and refs. therein) and sulfenylimines (25b), but to a less degree.

Reactions with aldehydes proved to occur not only regio-, but also stereoselectively (20a,d). Diastereo- and enantioselective methods for the preparation of homoallylic alcohols were also developed. The allylboration was used as one of stages in the synthesis of stegobinone (20f), D-fucose derivatives (23d), antibiotic X-14547A (23e), artemisia alcohol (22b,24), components of

the red bollworm moth pheromone (11b), and other natural substances (20g,25c).

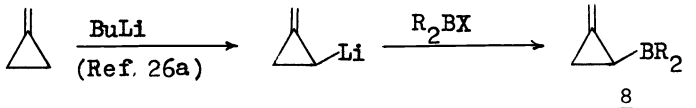
## NOVEL ALLYLBORANES

Recently we have begun a study on the allylboranes 1-8 with the aim of developing new approaches to acyclic and cyclic compounds.

### Synthesis

The allylboranes 1-8 were obtained by three methods with the use of respective hydrocarbons, allylic bromides, and allenes as starting compounds. The choice of a method was determined chiefly by an availability of the allylating agent.

A. From olefins, via lithium and potassium derivatives:

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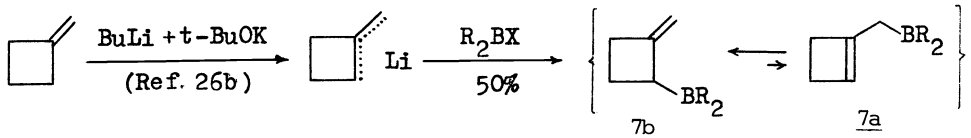
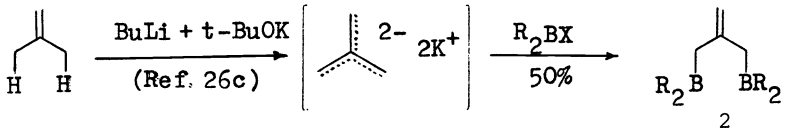


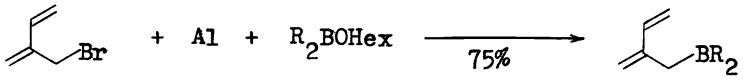

7b 7a

(Ref.27)

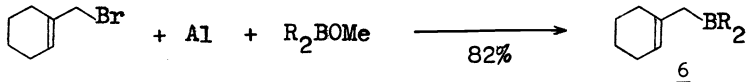



2 (Ref.28)

B. From respective allylic bromides, via sesqui-allylaluminum bromides:

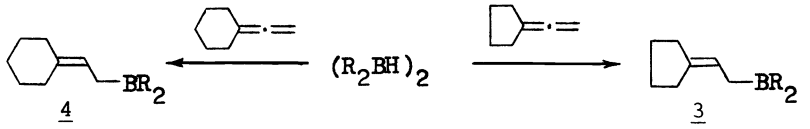



1 (Ref.29)




6 (Ref.30)

C. By hydroboration of allenes:




4 3 (Ref.31)

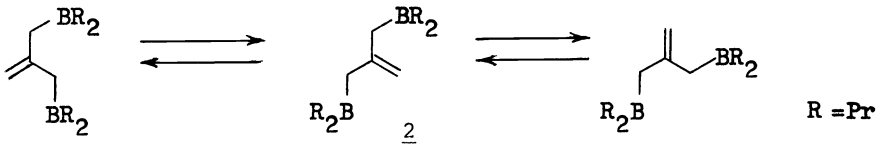
Tetraalkyldiboranes and 9-BBN were used as hydroborating reagents.

### Properties

The boranes 1-7 (see Table) are stable in an inert atmosphere; they are readily hydrolyzed and oxidized when exposed to air.

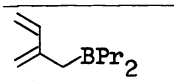
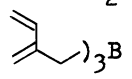
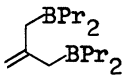
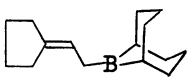
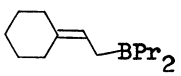
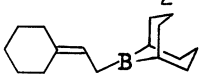
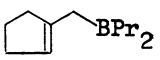
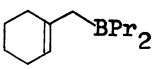
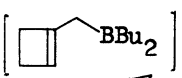
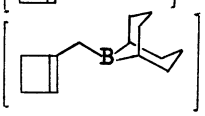
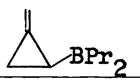
Permanent allylic rearrangement (PAR). NMR data show boranes 1-8 to undergo PAR the rate of which is determined by their structures. In boranes 1,1a,3-6, PAR proceeds slowly at room temperature, which is evident from a slight broadening of proton signals of $B-CH_2$. In borane 2, PAR proceeds at a

great rate even at room temperature.




Signals of protons of four propyl groups are only observed in $^{1}H$ NMR spectrum of compound 2, with the proton signals of $CH_2$=C and B-$CH_2$-C= being broadened considerably.

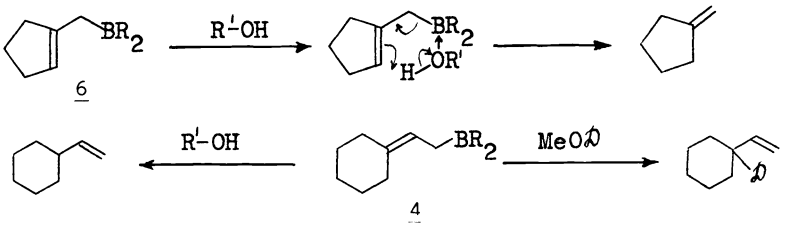
Borane 7 represents a unique borotropic system. $^{1}H$ and $^{13}C$ NMR spectra evidence the exchange 7a ⇄ 7b to take place at ca 30°C, whereas 7b only exists at -60°C. This is the first instance for a boron-allyl system where boron is bonded to the secondary and not to primary carbon atom.

| Compound | Synthetic method | Yield (isolated) % | B.p. °C(mm Hg) | $n_D^{20}$ | $\delta^{11}B$ ppm | $\nu$C=CH $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|
|  | B | 75 | 40(1.5) | 1.4569 | 86.58 | 1590<br>3090 | 1635 |
|  | B | 32 | 80 (1) | | | 1590<br>3085 | 1630 |
|  | A | 40 | 98 (1) | 1.4495 | 85.75 | 1634 | 3075 |
|  | C | 77 | 118(1) | 1.5173 | 84.00 | 1665 | 3030 |
|  | C | 50 | 76 (2) | 1.4551 | | 3062 | |
|  | C | 82 | 132 (1)<br>116(0.1) | 1.5180 | 83.74 | 1645<br>3040 | 1670 |
|  | B | 79 | 43 (1) | 1.4542<br>(23.5°) | 85.3 | 1649 | 3042 |
|  | B | 70 | 50 (1) | 1.4583<br>(23.5°) | 86.3 | 1667 | 3042 |
|  | A | 51 | 50 (1) | 1.4495 | 82.7 | 1630<br>3043 | 1650<br>3079 |
|  | A | 62 | 74 (1) | 1.5104 | 81.3 | 1628<br>3045 | 1650<br>3078 |
|  | A | 48 | 71(18) | | 80.05 | 1731 | 3080 |

*) Compound readily polymerizes

Protolytic cleavage. The B-$C_{All}$ bond in boranes 1-8 is easily cleaved under the action of water, alcohols, and amines, the protolysis proceeding with rearrangement of the allyl moiety.

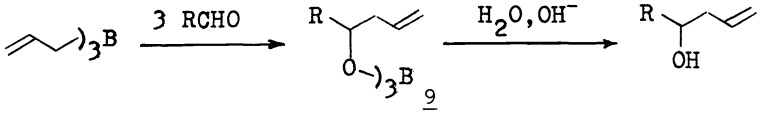
Borane 1 (R= Pr) reacts with water and alcohols to lead to isoprene and $R_2BOR'$ (29) while boranes 6 and 5 give methylenecyclopentane and methylenecyclohexane, respectively (30).



The protolytic cleavage of compounds 4 afforded vinylcyclohexane, and the reaction with MeOD gave 1-vinyl-1-deuterocyclohexane.

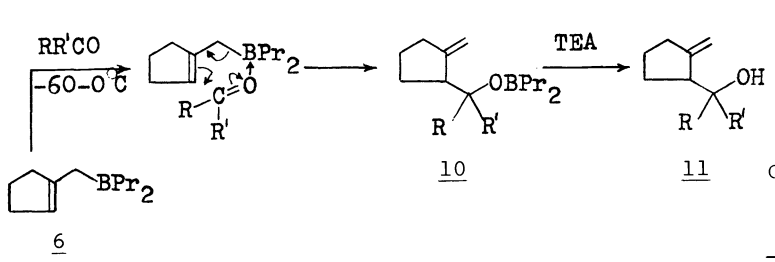
**Allylboration of carbonyl compounds**

It was shown in 1964 (17) that triallylborane adds to aldehydes and ketones with the formation of the boron esters 9 which are hydrolyzed to yield the corresponding homoallyl alcohols.

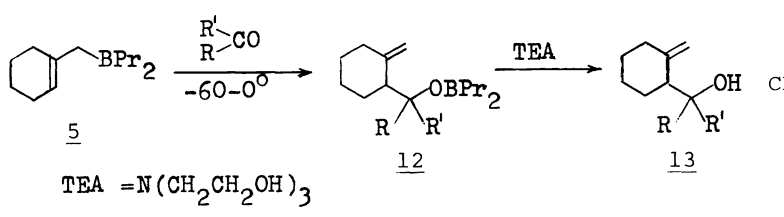


The allylboration of carbonyl compounds was later on studied widely and in detail.

Using a set of original allylboranes, we have developed new approaches to a variety of homoallylic alcohols, 2-substituted methylenecyclanes, gem-substituted vinylcycloalkanes, 1,5-diols, and other compounds. The addition of boranes 5 and 6 to carbonyl compounds occurs with allylic rearrangement to give rise to boron esters 10 and 12. The reactions proceed under mild conditions with a good yield. The corresponding carbinol 11 or 13 is distilled off directly from the reaction mixture in vacuo after adding triethanolamine (30).



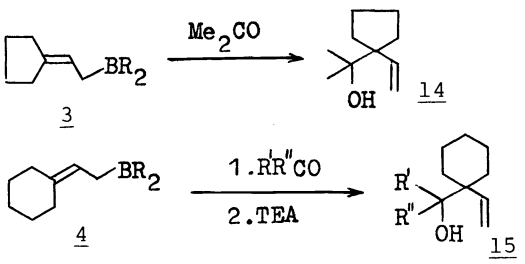
| R | R' | Yield % |
|---|---|---|
| H | H | 50 |
| Me | H | 70 |
| Me | Me | 87 |
| $CH_2$=CH | Me | 75 |
|  | H | 40 |



| | | |
|---|---|---|
| H | H | 91 |
| Me | H | 74 |
| $CH_2$=CH | Me | 69 |
| $(CH_2)_4$ | | 53 |

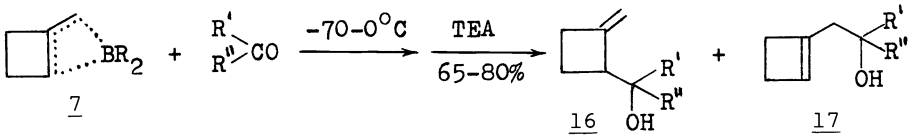
TEA = $N(CH_2CH_2OH)_3$

The cycloalkylidene boron derivatives 3 and 4 react in a usual manner, i.e. with total rearrangement of the allyl moiety (31).



| R' | R'' | Yield,% |
|---|---|---|
| Me | H | 55 |
| Me | Me | 63 |
| $(CH_2)_4$ | | 68 |
| $(CH_2)_5$ | | 50 |

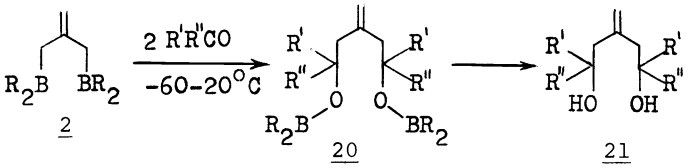
It is noteworthy that boranes 3-6 react with α,β-unsaturated carbonyl compounds only via 1,2-addition to the C=O group, conjugated 1,4-addition being never observed. Reactions of boranes 7 with many ketones proceed selectively to lead exclusively or essentially to the methylene compounds.




| | | |
|---|---|---|
| acetone | 100% | 0% |
| cyclopentanone | 100% | 0% |
| cycloheptanone | 98% | 2% |
| camphor | 100% | 0% |
| cyclohexanone | 90% | 10% |
| benzaldehyde | 60% | 40% |
| acetaldehyde | 53% | 47% |

At the same time, aldehydes and cyclohexanone give a mixture of methylene 16 and cyclobutene carbinols.

A number of interesting structures were prepared using diboron compound 2 as an allylating agent. Its reactions with carbonyl compounds (1:2) result in diboron esters 20, hydrolysis of which yields substituted 1,5-diols 21.



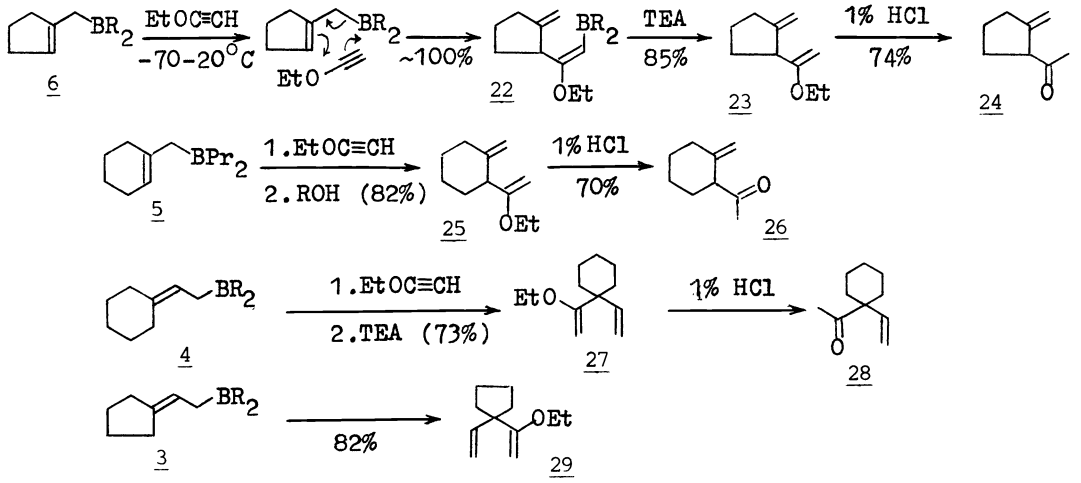

| R' | R'' | Yield,% |
|---|---|---|
| Me | H | 80 |
| Me | Me | 75 |
| Ph | H | 83 |
| $(CH_2)_6$ | | 78 |

Reactions of 2 with R'R''CO in a ratio of 1:1 lead to mixtures of mono and disubstituted products.

**Allylboration of ethoxyacetylene**

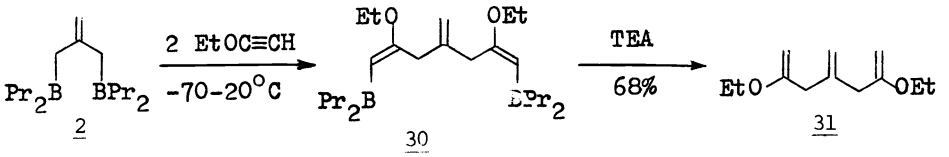
The simple allylic triorganoboranes react with monosubstituted acetylenes via cis-addition of the boron-allyl fragment to the triple bond, alkoxyacetylenes being the most active in these electrocyclic reactions (1,2).

Boranes 2-7 also add to ethoxyacetylene at -60 - 0°C to form E-2-ethoxyvinylboranes of the type 22. These cis-allylboration reactions occur instantly after mixing the reagents.



The deboronation of adducts 22 presents no difficulties. The B-$C_{sp^2}$ bond in these compounds is cleaved under the action of alcohols at 0 -20°C, and the yield of dienes 23,25,27,29 is usually above 70% calculated on the starting allylborane.

The controlled hydrolysis of 2-ethoxy-1,4-dienes with 1% HCl resulted in the formation of unsaturated ketones 24,26, and 28. In the use of the above reactions for the synthesis of dienes 23,25,27, and 29, isolation of the boron adduct 22 in the pure state is not necessary. In these cases, after adding ethoxyacetylene to the corresponding allylborane (1:1) at -60 - 0°C, the reaction mixture is allowed to warm to room temperature, afterwards 1.2 mol of triethanolamine or another high boiling alcohol is added followed by distilling off the respective diene directly from the reaction mixture in vacuo. A similar reaction of 2 with ethoxyacetylene (1:2) led to the diboron adduct 30 which was deboronated to produce the triene 31 (28).

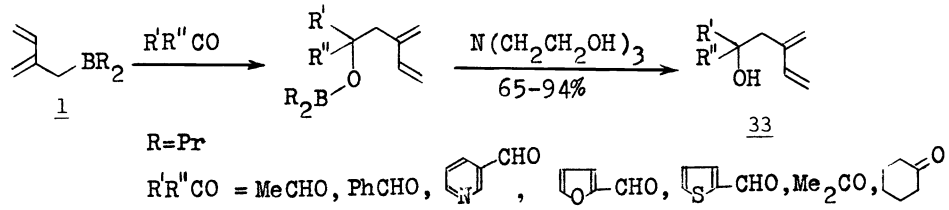



2 30 31

**Isoprenylation**

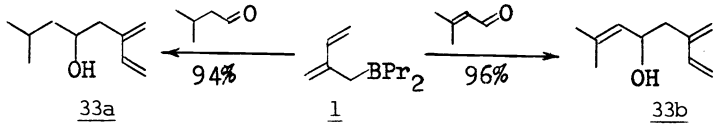
The compounds 1 are the boron derivatives of isoprene. They show high reactivity and represent the excellent "$C_5$-synthons" which were successfully used for the isoprenylation of various organic compounds. It should be pointed out that the development of convenient methods for introducing the isoprene fragment is one of the urgent tasks in organic synthesis since different isoprene derivatives occur widely in Nature.

The borane 1 (R= Pr) adds to ketones at -70 - 0°C (29), and this reaction is apparently the most convenient method for the preparation of the diene alcohols 33.



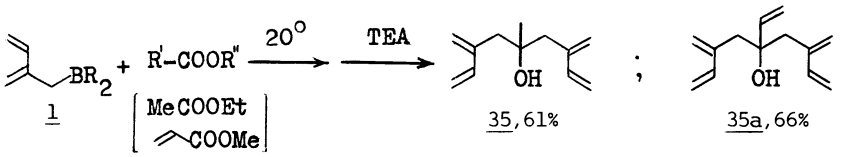

1 33

Of the carbinols 33, two terpenoid compounds, ipsenol 33a and ipsdienol 33b, which are principal components of the aggregational pheromones of Ips confusus and Pityocteines, are of interest.These carbinols were synthesized by interaction between 1 and isovaleric aldehyde or 3,3-dimethylacrolein, respectively.




33a 1 33b

Carboxylic esters undergo diisoprenylation under the action of boranes 1. Thus, the tetraene carbinol 35 was synthesized from ethyl acetate, and pentaene carbinol 35a from methyl acrylate:

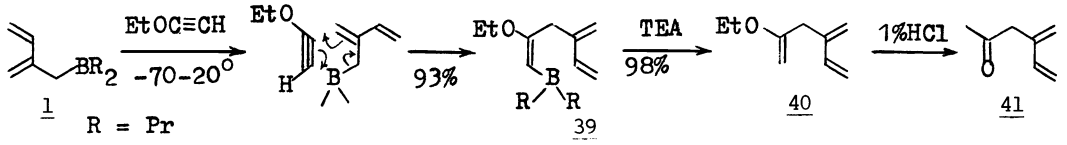



1 35,61% 35a,66%

Allylboration of esters with triallyl-, diallyl(alkyl)-, and allyl(dialkyl)-boranes proceeds similarly (32).

The borane 1 (R= Pr) readily adds to ethoxyacetylene (-70 - 0°C) with the formation of boron triene 39 (93%). This reaction represents the first instan-

ce for the isoprenylation of acetylene compounds. On action of alcohols on 39 2-ethoxy-4-methylene-1,5-hexadiene 40 is obtained.



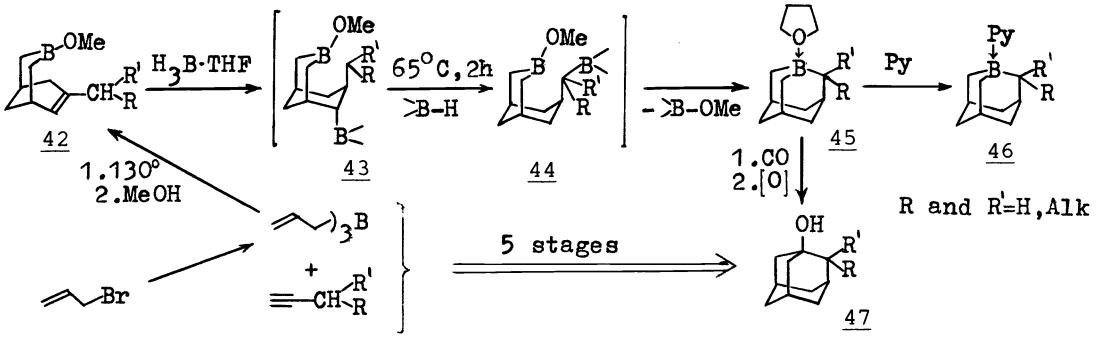

1 39 40 41

All the reactions of boranes 1 studied proceed under mild conditions without a catalyst and are not complicated by side processes.

## ALLYLBORON–ACETYLENE CONDENSATION

We have also continued studies on the allylboron-acetylene condensation (ABAC) and have worked out new approaches to hardly accessible cyclic and cage compounds, both organic and organoboronic.

ABAC was discovered in 1965 (33) and, in our opinion, it is the most interesting and important reaction of allylboranes due to its simplicity and selectivity (1,2,19). Heating triallylborane with monosubstituted acetylenes (130°, 2-3 h) affords high yields (75-98%) of 7-substituted 3-allyl-3-borabicyclo [3.3.1]non-6-enes. On treatment of the latter with alcohols, the respective bicyclic esters 42 form in over 90% yield serving as key compounds for the preparation of 2-substituted 1-boraadamantanes and 1-adamantanols (34-38). The diboron compounds 43 formed on hydroboration of 42 with the $BH_3$·THF complex (2:1) are converted to tetrahydrofuran complexes of 1-boraadamantane (R=R'=H) and 2-alkyl- or 2,2-dialkyl-1-boraadamantane 45.

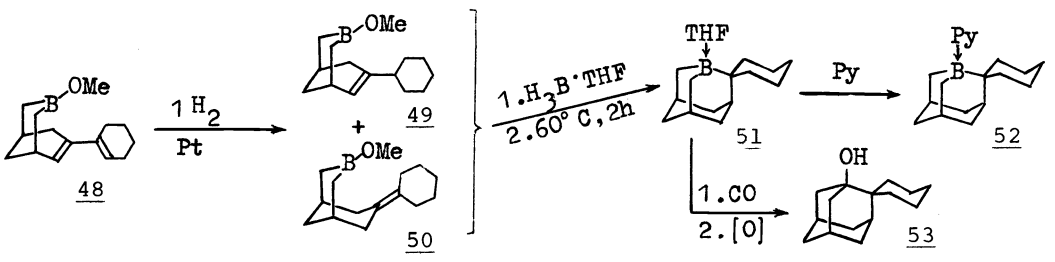



42 43 44 45 46 47

The isomerization of 43 to 44 (migration of boron to the α-carbon atom of the side chain) and subsequent closure to 1-boraadamantane system proceed under unusually mild conditions. This is explained by the specificity of the bicyclic system. Compound 42 having an alkyl group of any length in the 7 position (n-Pr,n-Bu etc.) affords respective 2-alkyl-1-boraadamantane compounds only. Further migration of the boron along the chain does not take place. Stable to air complexes 46 were prepared by the action of pyridine on 45.

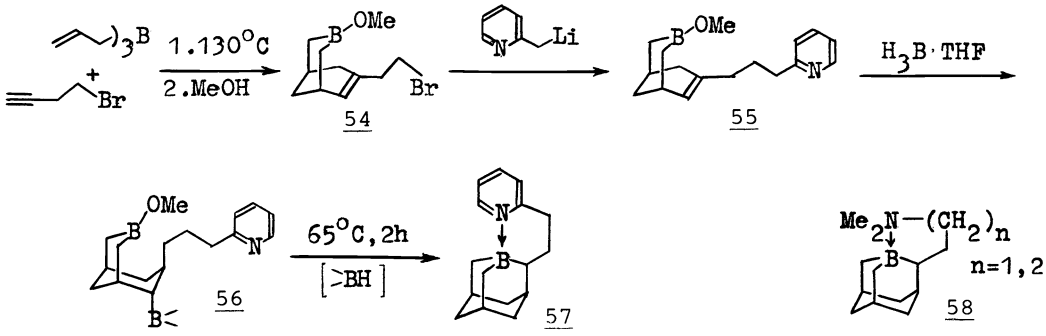
The carbonylation of complexes 45 followed by oxidation gave 2-substituted 1-adamantanols 47. The combination of the above reactions appears to be one of the best accesses to these cage carbinols because it requires only six simple stages starting with allyl bromide and the corresponding acetylene.

When hydrogenated over Pt or Pd catalysts, the diene compound 48 (2) absorbs 1 mol of hydrogen. In this case a mixture (1:1) of 1,2- and 1,4-addition products 49 and 50 is obtained. Hydroboration of the mixture led to the spiro-compound 51 which was converted to the pyridinate 52 and the carbinol 53 (34-36).




48 49 50 51 52 53

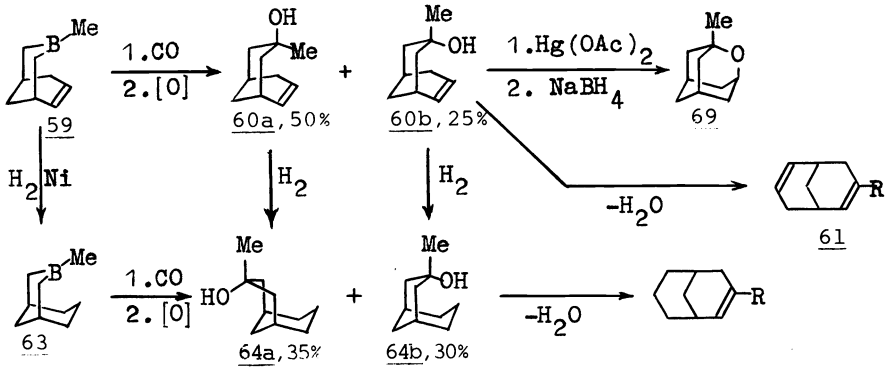
Starting from bicyclic bromide 54, we succeeded in synthesizing the intramolecular 1-boraadamantane complex 57 (37,38).



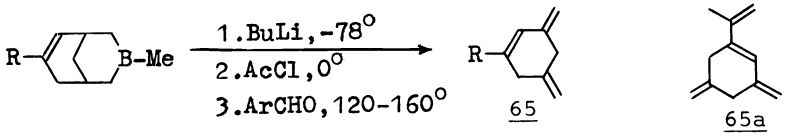

The pyridine fragment was introduced into the side chain by the action of α-picolyllithium on the bromide 54. Subsequent hydroboration of compound 55 followed by heating under reflux in a THF solution led to the target boraadamantane 57.

The intramolecular complexes, 2-(ω-dimethylaminoalkyl)-1-boraadamantanes 58, were synthesized from the corresponding homologues of the bromide 54 (37,38). The preparation of 2-trimethylsilylmethyl-1-boraadamantane pyridinate was also reported (39).

Carbonylation-oxidation of the B-methyl compound 59 affords a mixture (ca. 2:1) of bicyclic epimeric carbinols 60a and 60b. Both carbinols were isolated in the pure state by column chromatography on $Al_2O_3$. Dehydration of 60a and 60b by heating with $H_2SO_4$ or $H_3BO_3$ results in the formation of 3-methylbicyclo[3.3.1]nona-2,6-diene 61 with an admixture of its 2,7-isomer (ca. 20%). Starting from 3α-hydroxy-3β-methylbicyclo[3.3.1]non-6-ene 60b, 1-methyl-2-oxaadamantane was prepared in two stages (40).



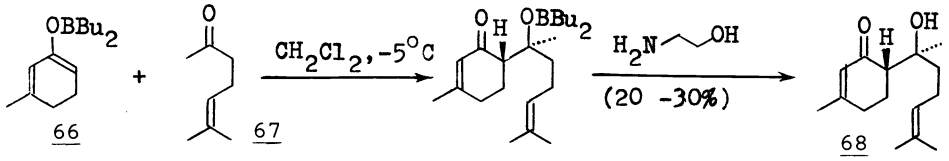

Similar reactions were carried out with 63. The α-methyl carbinol 64a has the preferential chair-boat while its β-methyl isomer the chair-chair conformation ($^{13}C$ NMR and $^{1}H$ NMR, 360 MHz) (40). In above reactions, the system of 3-borabicyclo[3.3.1]non-6-ene compounds was used with maximum efficiency. Another type of the bicycle conversions consists of their deboronation. Based on two types of β-hydride abstraction reaction (41,42) (dehydroboration), we obtained a series of 3,5-dimethylene compounds 65, of which the tetraene hydrocarbon 65a containing a system of isolated and conjugated double bonds is the most interesting (34,36).




R = H, Me, $CH_2$=C(Me)-

**Hernandulcin**

Finally, our synthesis of (±)-hernandulcin 68 should be mentioned in which the dienyloxyborane 66 (43), an oxygen analogue of allylboranes, was used as the key substance.




66 67 68

The reaction of 66 with 67 is the "boronic" version of aldol condensation and proceeds stereospecifically. Hernandulcin, a sesquiterpene of the bisabolene series, was recently isolated from Lippia dulcis (44). This substance is $10^3$ times as sweet as sugar.

## CONCLUSION

Only some aspects of modern allylborane chemistry have been considered in this paper. However, data cited here show clearly enough that the allyl derivatives of boron are extremely convenient and useful substances in the construction of very diverse organic systems. There is no doubt that the further development of this fruitful direction will enrich organic chemistry with new synthetic methods.

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