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Title REACTIONS OF ORGANOBORANES

Abstract approved Redacted for Privacy  
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An examination was made of some reactions involving a transfer of carbon from boron to carbon. In the case of the reaction of a  $C_n$  alkylorganoborane with dichlorocarbene the intermediate was a  $C_{n+1}$  chloroalkylorganoborane. Oxidation of this intermediate yielded an homologous acid (33%) and the usual alcohol (66%). The results of several other transfer studies are presented, and the role of ethereal solvents discussed.

REACTIONS OF ORGANOBORANES

by

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A THESIS

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the requirements for the  
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Assistant Professor of Chemistry  
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Chairman of Department of Chemistry

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Dean of Graduate School

Date thesis is presented October 14, 1966

Typed by Opal Grossnicklaus

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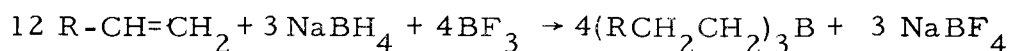
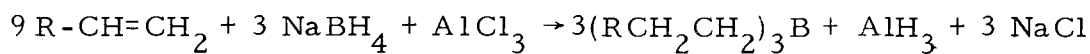
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## REACTIONS OF ORGANOBORANES

### INTRODUCTION

The hydroboration of olefins is a relatively recent introduction to the field of organic chemistry which has proven to be a most fruitful area for exploration. The first example of the conversion of olefins to organoboranes under mild laboratory conditions was reported by Herbert C. Brown in 1956 (4). Since that time progress in this field has been quite rapid with the general hydroboration reaction becoming a very important tool for use in organic syntheses. Brown showed (13) that diborane ( $B_2H_6$ ) adds rapidly and quantitatively to carbon-carbon double and triple bonds, carbon-oxygen double bonds, and carbon-nitrogen double and triple bonds. The current methods for generation and reaction of diborane involve the use of metal hydrides such as sodium borohydride and Lewis bases such as aluminum chloride and boron trifluoride (4, 12, 13).

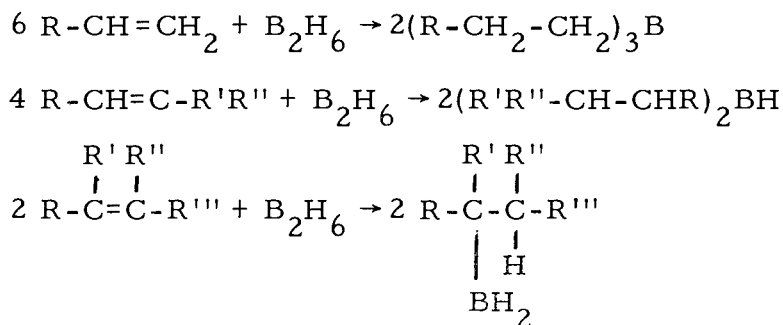


Before Brown, the principal methods of hydroboration had been those involving organozinc (7) or organomagnesium (35) compounds and the boron halide or ester. Early workers also concluded that the reaction of diborane with olefins was a very slow

one requiring elevated temperatures and long reaction periods (31).

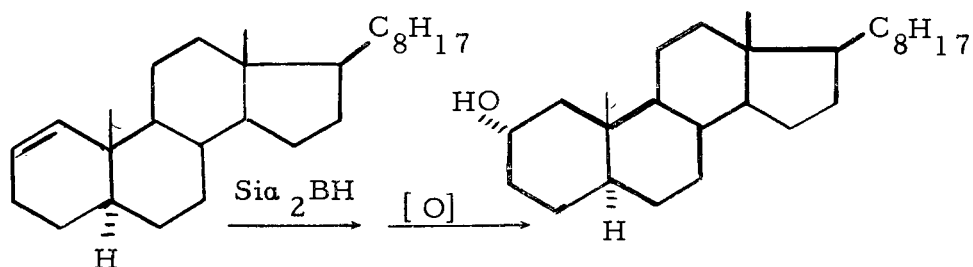
Upon more extensive investigation Brown found these reactions were indeed slow, but were catalyzed by ether solvents such as diglyme, the dimethyl ether of diethylene glycol (D.G.), tetrahydrofuran (THF), or ethyl ether (EE) (7, 10).

It should be noted that with unhindered olefins the stoichiometry used in hydroborating dictates the organoborane produced. A large excess of diborane, the actual hydroborating agent, produces a monoorganoborane ( $\text{RBH}_2$ ) while a large excess of the olefin insures the production of a triorganoborane ( $\text{R}_3\text{B}$ ) (8). Hindered olefins, on the other hand, appear to react rapidly only to the dialkylborane or monoalkylborane stages depending upon the degree of steric



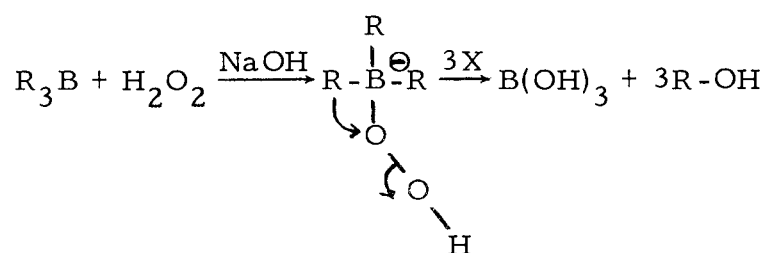
hindrance (7). These species ( $\text{R}_2\text{BH}$  and  $\text{RBH}_2$ ), however, can be used quite successfully as selective hydroborating agents. One such example is disiamylborane (bis(3-methyl-2-butyl)borane) (7).



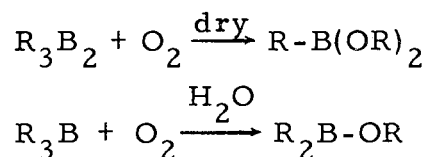


Predominantly: a

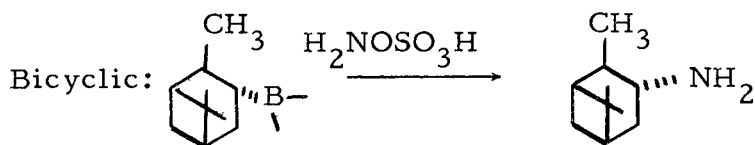
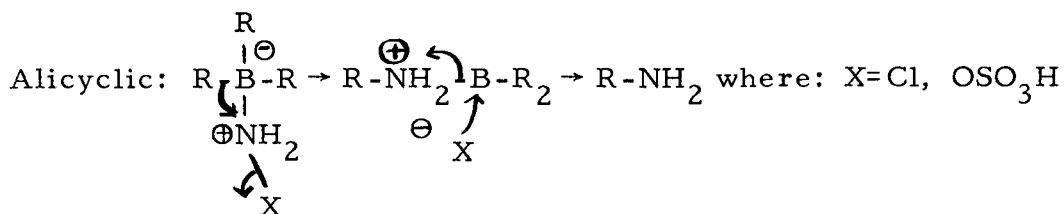
Some of the most interesting and potentially most productive reactions of organoboranes are those which involve an alkyl or aryl group transfer, the so-called migration reactions, which result in a rearranged product. The most useful example to date involves the migration of an R (alkyl or aryl) group from boron to oxygen as is exemplified by the alkaline hydrogen peroxide conversion of boranes to alcohols (33, 38).



A further example of a migration to oxygen was elucidated by Brown in 1962 (7). In this case the reaction varies, dependent upon the amount of moisture present.



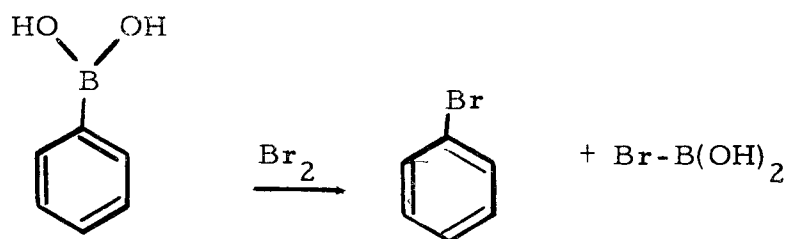
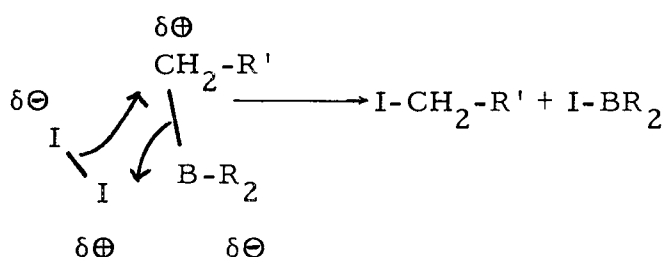
The migration of an R group from boron to nitrogen was used by H. C. Brown in 1964 (14) as a facile synthesis of alicyclic amines. It has since been shown that such migrations are of a much more general nature and apply equally well to bicyclic systems (44). It should be noted that due to variations in nucleophilicity and stereochemistry, the number of alkyl groups undergoing transfer changes from reaction to reaction. In the alicyclic example cited, Brown reports amine yields of ca. 65% implying a two group transfer out



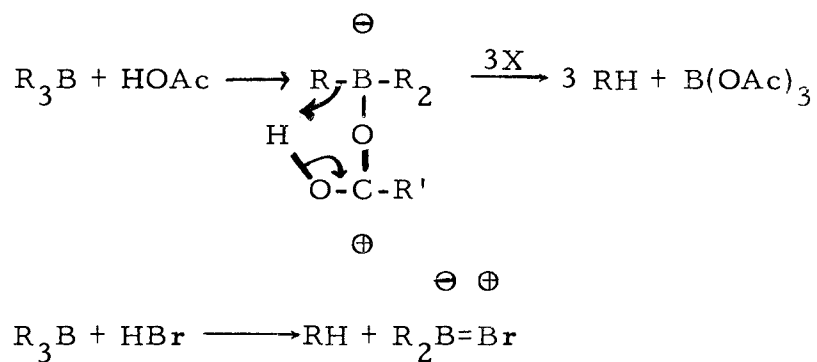
of the possible three. Brown found the stoichiometry of the bicyclic case to show solvent dependency.

It has been shown that the boron atom is quite effective in transferring both alkyl (39, 40) and aryl (42) groups to halogen molecules. In such reactions the second halogen atom is usually

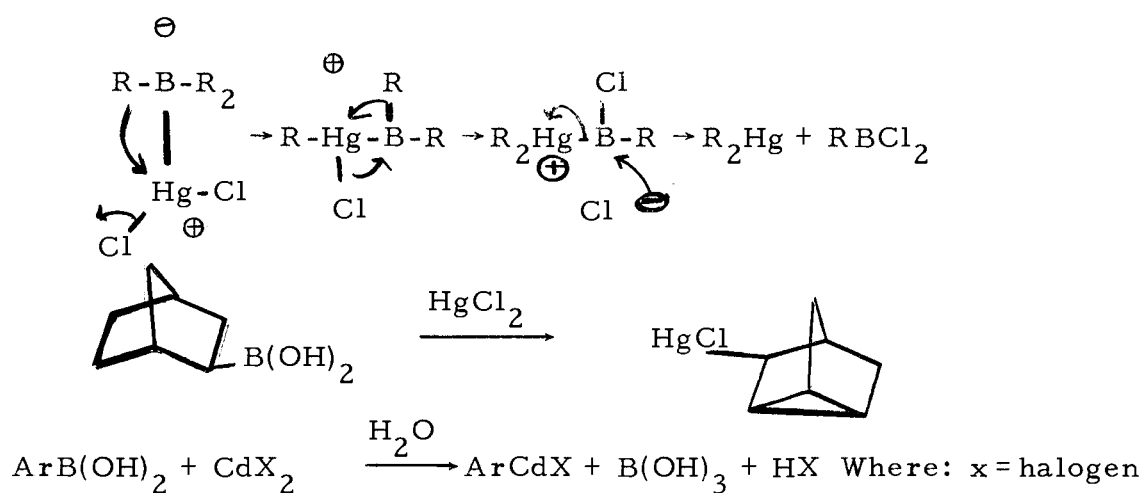
transferred to boron.



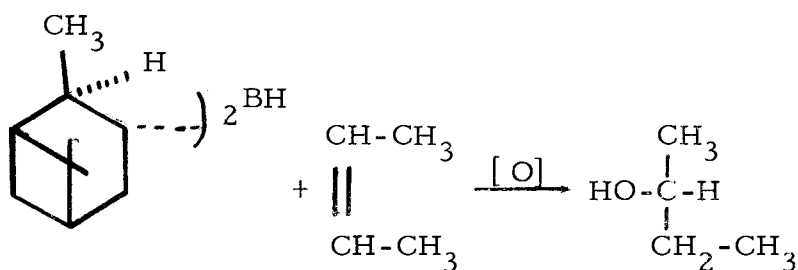
The so-called protonolysis reaction (3, 52) can be cited as another example of the boron transfer of an alkyl group in this case to the hydrogen ion of an organic acid. Transfers to hydrogen have also been observed in reactions involving halogen acids (32). This provides a route to alkanes from olefins which alleviates the necessity of a hydrogenation apparatus.



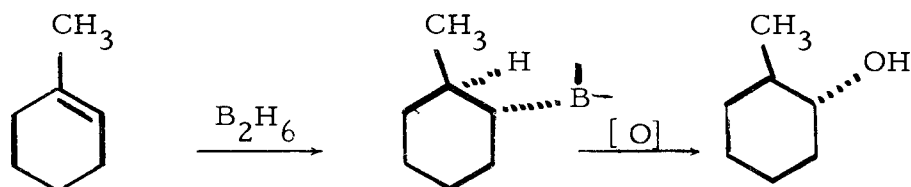
The transfer of an alkyl or an aryl group from boron to some other atom has provided a new route to some otherwise complex syntheses of organometallic compounds. Honeycutt and Riddle (30) have used tri-n-hexylborane to synthesize di-n-hexylmercury and Matteson (41) has synthesized 2-norbornylmercuric chloride. This general reaction has also been applied to aromatic systems by Kuivila (38).



Brown showed that diborane could be used very effectively to accomplish the creation of new asymmetric centers (9). For example, using diisopinocampheylborane as the hydroborating agent followed by oxidation, *cis*-2-butene is converted to optically active 2-butanol in 80% yield and 87% optical purity.



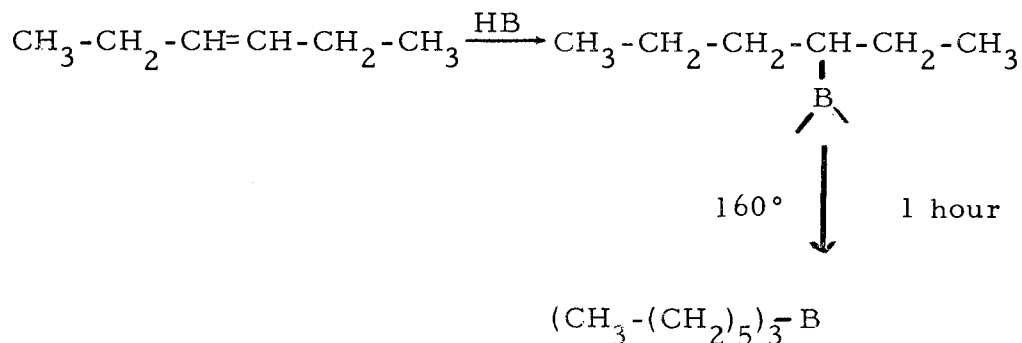
Brown has also been able to use the stereochemical requirements of diborane addition to carry out stereospecific syntheses of alcohols from numerous hindered olefins (5). Thus the hydroboration of 1-methylcyclohexene, followed by the usual oxidation with alkaline hydrogen peroxide, produces exclusively the trans-2-methylcyclohexanol. Since the product isolated in all such cases



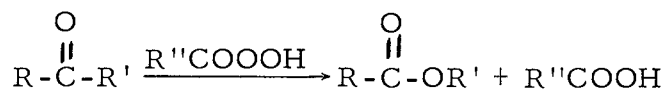
is trans and since the peroxide step proceeds with retention of configuration (7) it is concluded that the stereochemistry of diborane addition is cis (5, 11).

One further general reaction of organoboranes is of particular interest. When internally hydroborated olefins are heated to elevated temperatures for short periods of time (1-2 hours), it is observed that these compounds undergo a thermal isomerization to place the boron atom at the least hindered position of the available

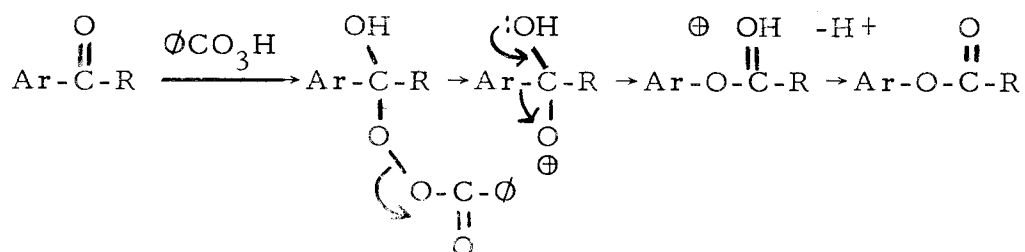
alkyl groups (12, 26).



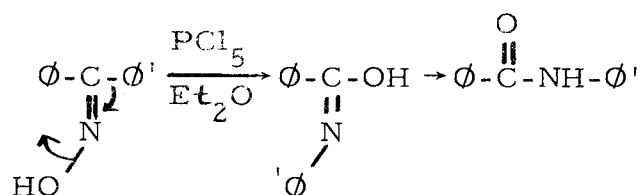
Migrations, such as those mentioned above, are certainly not new to organic chemistry. The Baeyer-Villiger reaction (23, 49) has long been used for this purpose. This transfer involves the reaction of peracids, commonly perbenzoic or peracetic, with ketones, and results in ester formation. Of the two groups bonded



to the carbonyl, that which is best able to bear a positive charge will be transferred to the oxygen. In the example below the most efficient migratory group is the aryl group as it is able to delocalize the positive charge incurred during migration. The Beckmann rearrangement

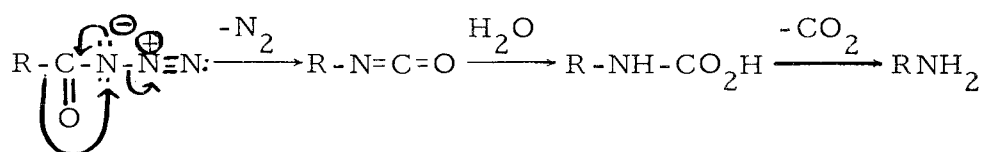


(2) offers a further example of a similar rearrangement. In this case the transfer is from carbon to nitrogen and the migratory aptitude determined by the stereochemistry of the reactant. During the process of the reaction an oxime is formed with the hydroxyl group anti to the most sterically hindered group. It is then the group which is anti that is set up for transfer. The result is the



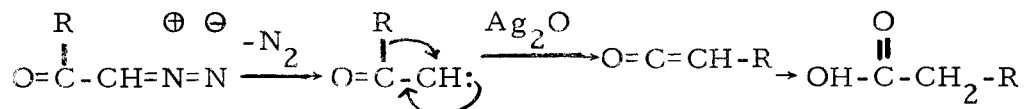
conversion of a ketone to an amide.

Migrations to nitrogen have also been used to synthesize amines directly from carbonyl compounds. In the Curtius rearrangement (19, 50), the attacking species is the azide ion and the rearrangement is accomplished with loss of molecular nitrogen. The addition of water and subsequent loss of carbon dioxide gives the desired amine.



The last step of the Arndt-Eistert rearrangement (1, 22) likewise involves the loss of nitrogen. However, in this case the transfer is from carbon to carbon and results in homologation of a

carboxylic acid. Diazomethane upon heating reacts with the acid chloride followed by loss of  $N_2$  to give what is postulated as a carbenoid species. The resultant rearrangement is accomplished in the presence of aqueous silver oxide.

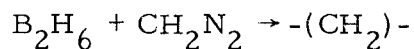


In nearly all the rearrangements discussed above, the ultimate object is, or was, homologation; reactions which extend the carbon chain of the reactant (45). It should be noted that reactions which result in the creation of new carbon carbon bonds are relatively few in organic chemistry and thus the elucidation of new pathways becomes an extremely important endeavor.

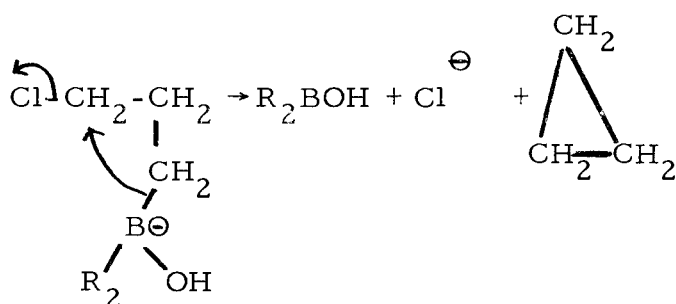
By far the potentially most important uses of boron transfers are those which would allow the formation of new carbon-carbon bonds. At this date the number of successful applications of such a reaction is noticeably small, but a great deal of recent effort has been devoted to this particular area of endeavor. One of the first reports of a successful attempt to increase the carbon chain was that of G. H. von Dorion in 1964 (21). From the reaction of diazomethane ( $\text{CH}_2\text{N}_2$ ) with diborane, he was able to isolate methylene polymers of various lengths. Also using diazomethane, Davies et al. (20) found that boron halides or esters produced no chain



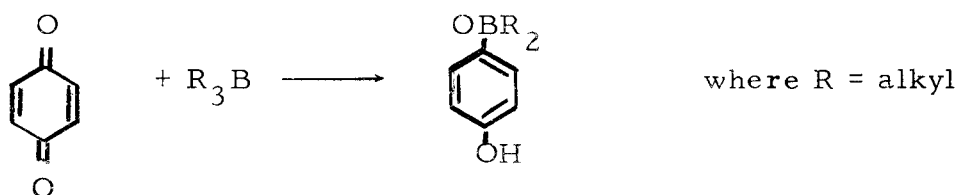
extended products. Alkyboranes (or arylboranes) were found to



give some methylenation product and boronic anhydrides a more synthetically useful yield of methylenation product. Hawthorne and Dupont (24) have reported a boron to carbon transfer which results in the formation of a cyclopropane ring. The reaction requires basic conditions and chloride ion is the leaving group.

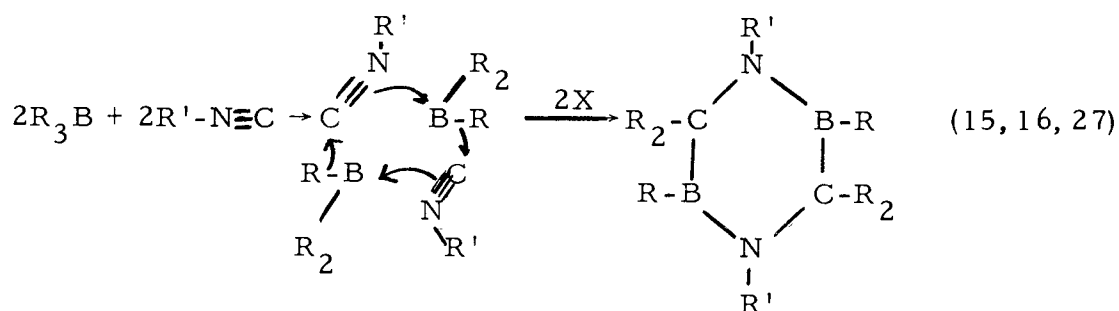
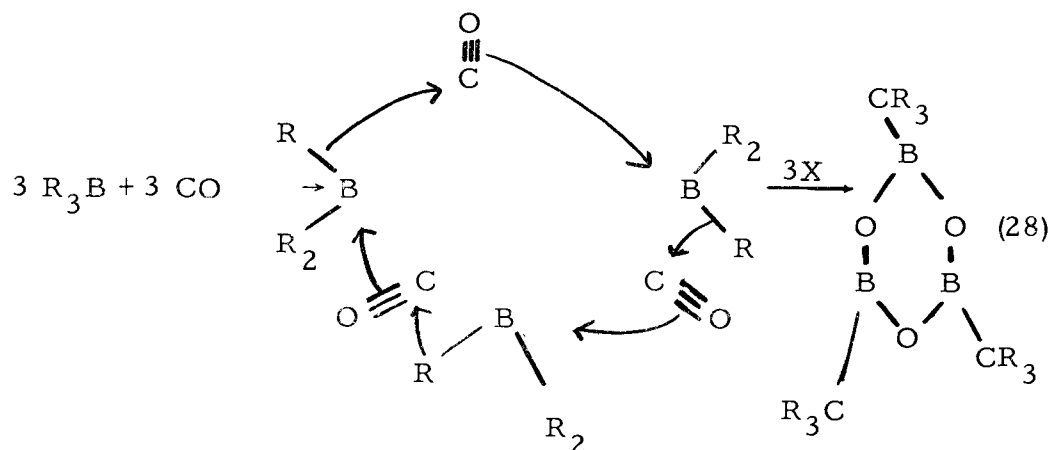


Another example in the recent literature provides a method for alkylating quinones (25).



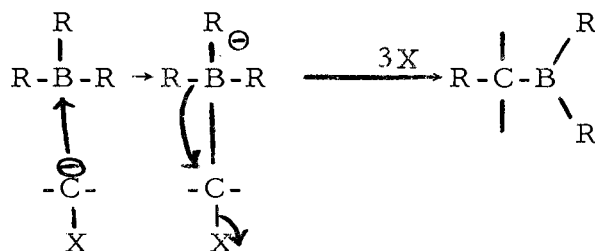
Transfer reactions to form heterocyclic ring systems have received extensive investigation recently with two of the more

interesting examples shown below. Note that migration of carbon from boron to carbon is involved in both.

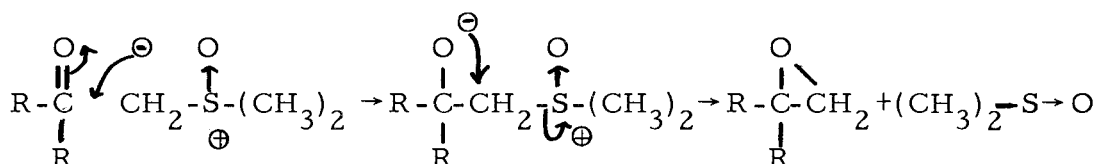


With the ready availability of organoboranes and the potential, synthetic significance of migrations of carbon from boron to carbon, it was decided to seek general reactions of this type. That is, it was desired to affect rearrangements resulting in the formation of new carbon-carbon bonds via the organoborane as a transfer agent. In general the type of reaction proposed for investigation was one in which some nucleophilic species would be coordinated with the electron deficient boron atom of an alkyl (or aryl) borane followed by the

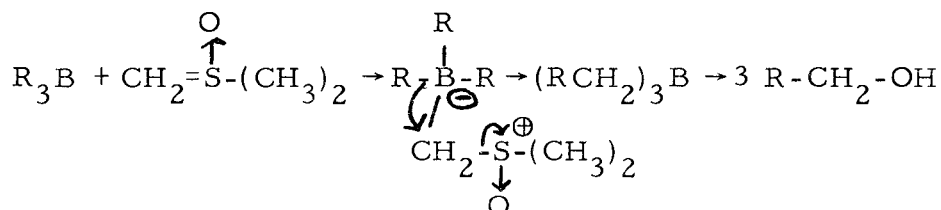
migration of one or more of these alkyl groups to the coordinating species. If one were able to procure the proper carbenoid nucleophiles then transfers would result in the formation of carbon-carbon bonds.



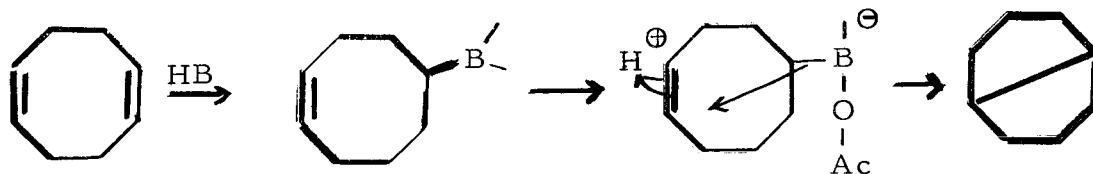
In 1964-65 Corey published a series of two papers (17, 18) on the reactions of sulfonium and sulfoxonium ylides. Corey used these compounds as nucleophilic species for reactions with ketones to



form epoxides (18). It was felt that if ylides would attack carbonyl groups, it might be possible to cause them to coordinate with organoborane followed by a rearrangement which upon oxidation would yield a homologous alcohol.

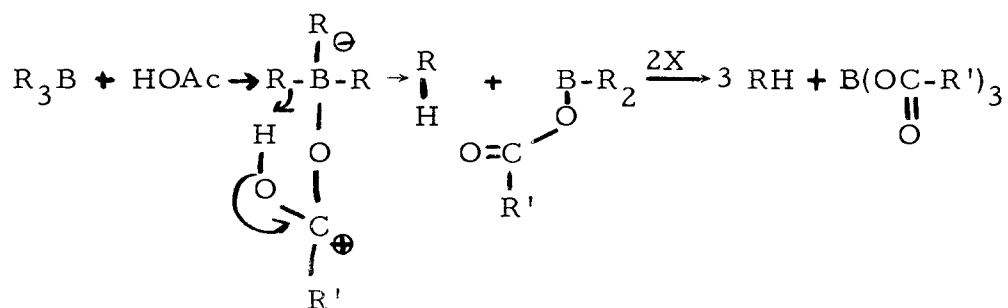


The protonolysis reaction discussed previously (3) provides a transfer to hydrogen. It was decided to see whether one could induce the migration to proceed from carbon to carbon as well, by using a cyclic system such as 1,5-cyclooctadiene. This could be considered somewhat analagous to the formation of the cyclopropane ring mentioned earlier. Here, however, the reaction would involve a transannular carbon migration resulting in a bicyclic ring system. It should be noted that the stereochemistry of the cyclooctadiene ring is such that the chance for such transannular reaction is quite favorable.

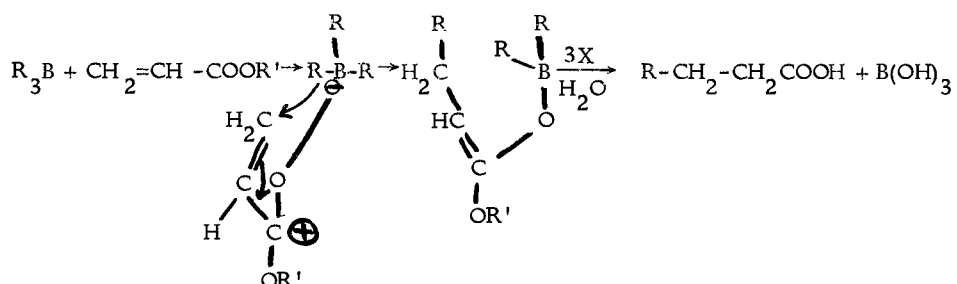


As another analogy to the protonolysis reaction, one speculated as to the possibility of accomplishing a boron-carbon transfer by creating a situation in which the reaction could easily proceed via a six member transition state. Such an example would be the coordination of ethyl acrylate with a trialkylborane. The reaction, if successful, would provide the means by which a three carbon unit could be added to an alkyl (or aryl) group.

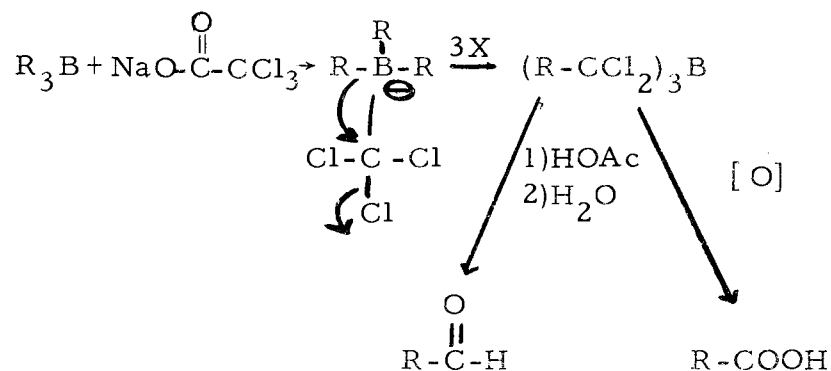
Protonolysis:



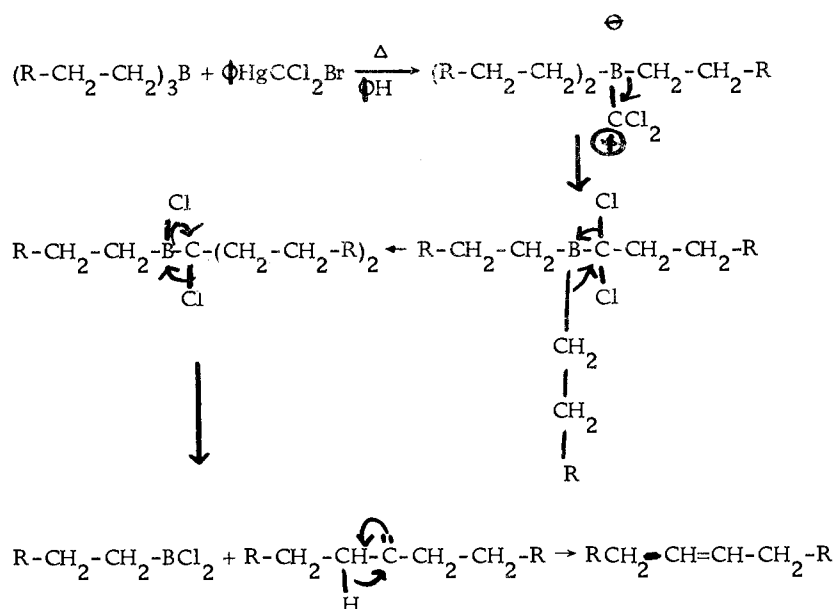
Acrylate:



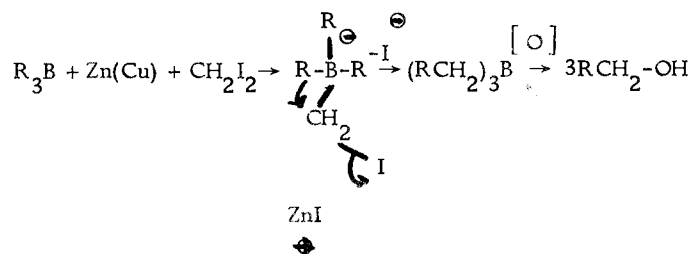
Sodium trichloroacetate ( $NaOC(O)CCl_3$ ) decomposes first to give  ${}^{\ominus}CCl_3$  which undergoes further decomposition to yield  $Cl^{\ominus}$  and  $:CCl_2$  (dichlorocarbene) (53). It was proposed that either or both of these species ( ${}^{\ominus}CCl_3$  or  $:CCl_2$ ) might be induced to coordinate with an organoborane and effect a migration. Again the result would be chain elongation. During the course of the investigation Seyferth



published a paper describing the reaction of  $R_3B$  with phenyl(tri-halomethyl) mercury ( $\phi HgCX_3$ ) compounds. He found the decomposition of the mercury compound gives  $:CX_2$  directly and that in benzene the product isolated from reaction with  $R_3B$  is a  $2_{n+1}$  olefin from an  $n$  carbon  $R$  group. The following mechanism was proposed.



One further initial proposal was made. It was decided to attempt homologation by means of a reagent known to add a methylene unit to a multiple bond. It was hoped that the Simmons-Smith reagent ( $I-Zn-CH_2-I$ ) (51) would coordinate with a trialkylborane and like the  $^{\ominus}CCl_3$  case would result in an homologous organoborane.

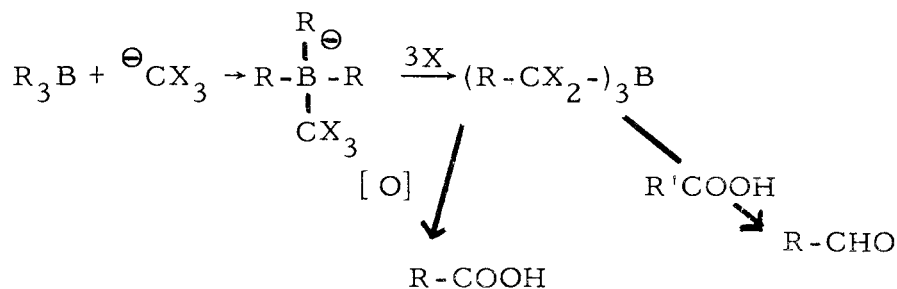


## DISCUSSION

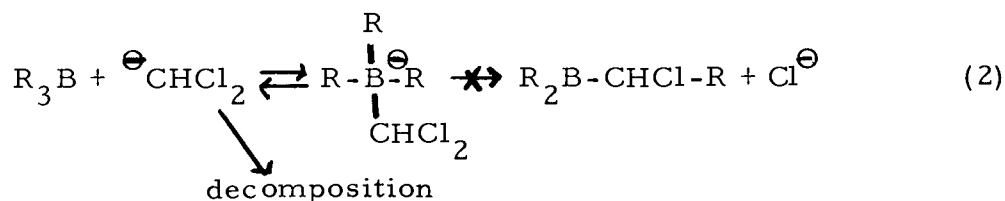
The organoboranes utilized in this investigation were usually synthesized by two routes. The syntheses in the early part of this work were accomplished by passing externally generated diborane (from  $\text{NaBH}_4$  and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) into the flask containing the olefin (4). In later hydroborations, a standard solution of diborane (see experimental) in tetrahydrofuran was added dropwise to the olefin. This somewhat easier procedure accorded the same result. As previously discussed, an excess of the olefin was used to insure production of a tri-alkylborane, while the monoalkylated borane was produced by excess  $\text{B}_2\text{H}_6$ .

Reactions of Organoboranes with  $^{\ominus}\text{CX}_3$

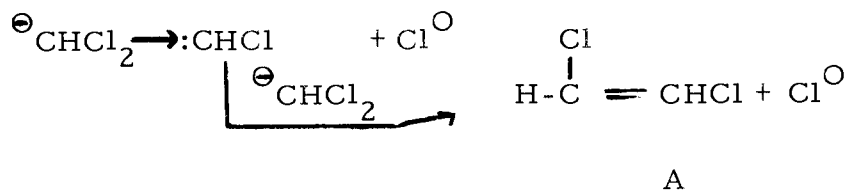
Initial experiments in this investigation involved the consideration of possible reactions between organoboranes and  $^{\ominus}\text{CX}_3$  (where  $\text{X}=\text{H}$ ;  $\text{X}=\text{halogen}$ ).



Dichloromethyl-lithium ( $\text{LiCHCl}_2$ ) and trichloromethyl-lithium ( $\text{LiCCl}_3$ ), as synthesized by Köbrich et al. (34) provide a route to nucleophiles of the general type  $^{\ominus}\text{CX}_3$ . Since the reaction conditions for  $\text{LiCHCl}_2$  ( $T = -70^\circ$ ) were more easily obtainable than those for  $\text{LiCCl}_3$  ( $T = -100^\circ$ ) this compound was used. During the course of the reaction of  $\text{R}_3\text{B}$  with  $^{\ominus}\text{CHCl}_2$ , the formation of a solid was observed. Upon heating (ca.  $80^\circ$ ) however, this solid disappeared and when the reaction was worked up no rearranged product was found. Presumably an equilibrium was established, but rearrangement did not occur. Upon heating, the anion decomposed by an alternative route. Compounds such as  $^{\ominus}\text{CX}_3$  are known to undergo further



decomposition to produce carbenoid species (47) which upon recombination produce compounds such as A. This was probably the case



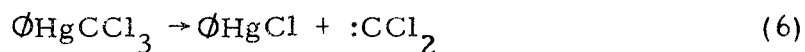
in this reaction, although no attempt was made to identify the side products.



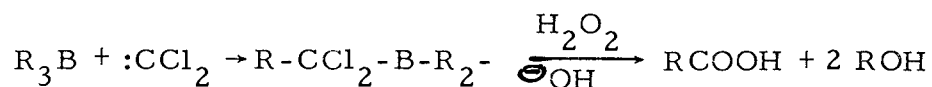


intermediate.

The next series of reactions was carried out using the thermal decomposition of phenyl (trichloromethyl) mercury. Seyferth has postulated (47) that this compound decomposes directly to  $\text{:CCl}_2$  without intervention of the  $^{\ominus}\text{CCl}_3$  anion. These reactions were also



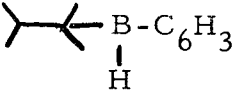
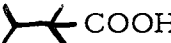

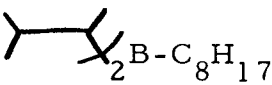


carried out in glyme solvents. The intermediate was subjected to alkaline hydrogen peroxide oxidation, the basic layer extracted with ether, and then acidified. Quite surprisingly, these reactions were successful since in each case oxidation afforded the homologous carboxylic acid. The organoboranes studied and the results



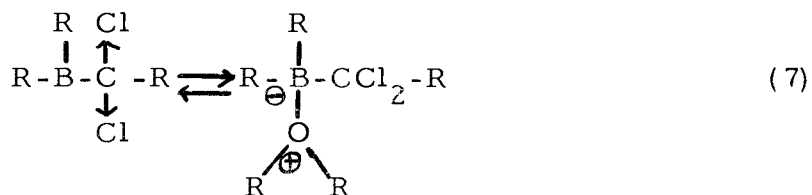
obtained are given in Table 1.

It will be noted that whether  $\text{R}_3\text{B}$  or  $\text{RBH}_2$  was employed, that the maximum yield of acid was 33%. Presumably, whatever the inserting species ( $^{\ominus}\text{CCl}_3$  or  $\text{CCl}_2$ ), the product  $\text{R-CCl}_2\text{-BR}_2$  is resistant to further attack. This can be explained on either steric or electronic grounds assuming that attack at boron is required. Possibly the chlorine atoms are large enough to shield the boron

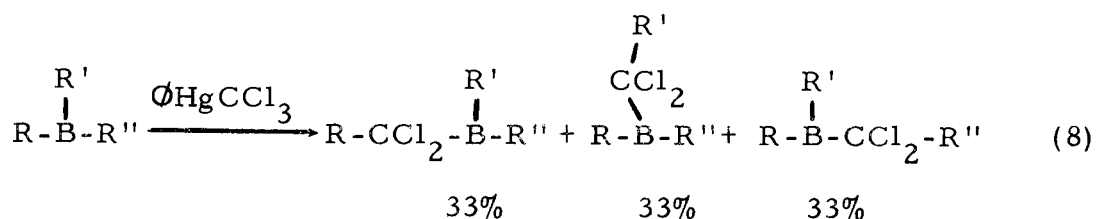
Table 1. Products from reaction of  $R_3B$  with  $\phi HgCCl_3$ 

	$R_3B$	Acid (yield)	Other products
1.	$(C_6H_{13})_3B$	$C_6H_{13}COOH$ (32%)	$C_6H_{13}-OH$
2.	$C_6H_{13}-BH_2$	$C_6H_{13}COOH$ (31%)	$C_6H_{13}-OH$
3.	$(C_8H_{17})_3B$	$C_8H_{17}COOH$ (33%)	$C_8H_{17}-OH$
4.	$C_8H_{17}B-H_2$	$C_8H_{17}COOH$ (32%)	$C_8H_{17}-OH$
5.		$C_6H_{13}COOH$ (17%)  (15%)	 $C_6H_{13}-OH$
6.		$C_8H_{17}COOH$ (10%)  (21%)	 $C_8H_{17}OH$

atom from further attack. A more likely explanation can be given on electronic grounds. The strong electron demands of the chlorines would so increase the electrophilicity of the boron that further attack would be prevented by the tight coordination with the ether solvent. This quite obviously limits the synthetic utility of the reaction.

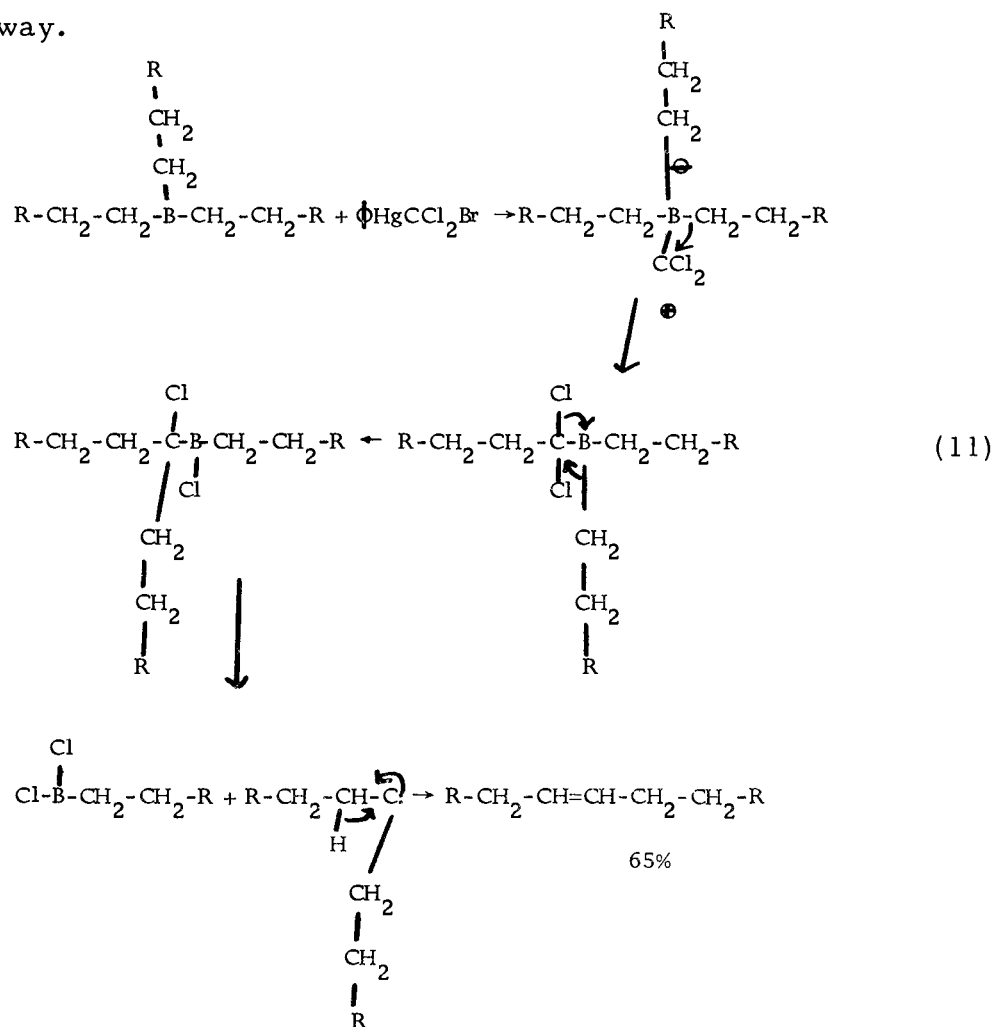


It can also be seen from Table 1 that no migratory preference was noted in the reaction.



to exhibit some migratory preference. That is, one would expect the extent of migration to depend upon the degree of branching in the alkyl group (tert. > sec. > prim.). Since this preference was not observed, this pathway seems unlikely.

As mentioned in the introduction, a reaction between  $R_3B$  and  $\phi HgCCl_2Br$  was reported during the course of this work (48). Seyferth found an olefin to be formed, and proposed the following pathway.



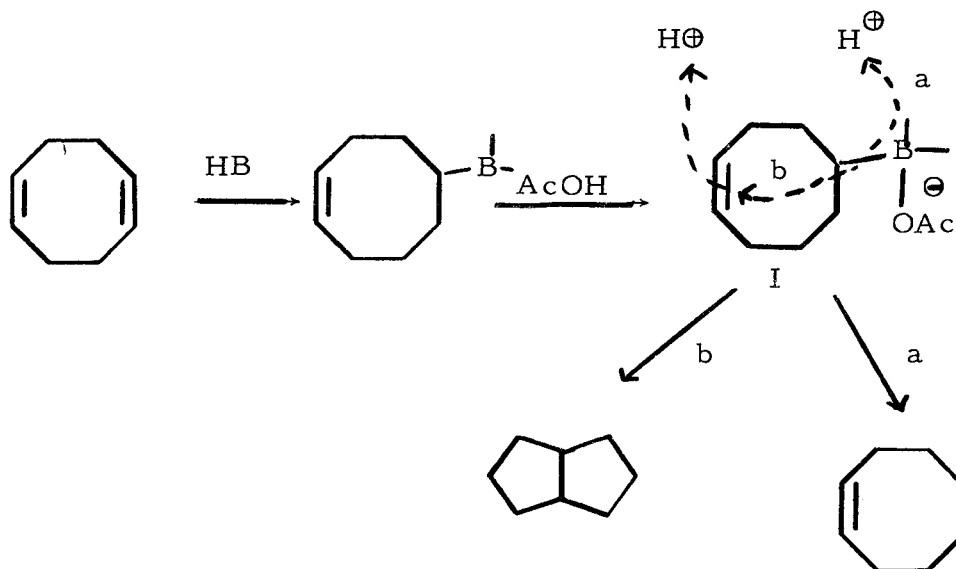
Our attempts to repeat Seyferth's work using  $\text{ØHgCCl}_3$  proved unsuccessful. When the intermediate ( $\text{R-CCl}_2\text{-BR}_2$ ) was either made in glyme and the reaction continued in benzene, or when the entire reaction was run in benzene, there was no evidence of further rearrangement. The results are the same as those reported in Table 1. We are unable to explain the discrepancy in these two studies. Unfortunately, no experimental conditions are given in Seyferth's work, but it would appear that the only difference in this work and that of Seyferth was the use of  $\text{ØHgCCl}_3$  in our work and  $\text{ØHgCCl}_2\text{Br}$  in his.

It can be seen that the reactions of organoboranes with the Seyferth type reagents are somewhat complex. Solvent effects are obviously important, but a more detailed study will be required before definitive conclusions can be reached. Assuming that  $:\text{CCl}_2$  is the reacting species one can conclude that the  $\text{ØHgCCl}_3$  and  $\text{NaOCOCCl}_3$  precursors are definitely not producing a carbene of the same reactivity, since no reaction was observed with the latter reagent.

### Protonolysis Studies

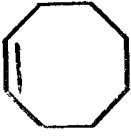
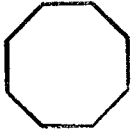
As mentioned in the introduction section it was also of interest to investigate the possibility of a transannular carbon-carbon bond formation. The cyclooctane ring system was chosen for this study.

Monohydroboration of 1,5-cyclooctadiene was carried out under conditions chosen to give a maximum yield of monoproduct (I).

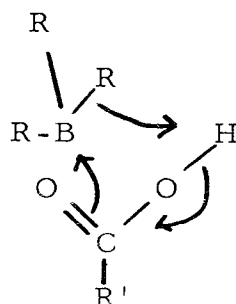


In all cases some starting material and some hydroborated product material was obtained, complicating the product analysis. The decomposition of I with organic acids has been shown by Dessy (52) to involve electrophilic cleavage of the C-B bond assisted by nucleophilic participation at boron. In the cyclooctadiene case, decomposition in the normal manner would give cyclooctene (path a), whereas transannular reaction (path b) would give bicyclo [ 3.3.0 ] octane. The reaction was carried out using three different acids, acetic ( $\text{R}' = \text{Me}$ ), propionic ( $\text{R}' = \text{Et}$ ), and pivalic ( $\text{R}' = \text{t-butyl}$ ) and the results are shown in Table 2.

Table 2. Results of protonolysis studies

Acid			Other
acetic	ca. 20%	ca. 70%	10
propionic	25%	65%	10
pivalic	50%	40%	10

This failure to observe transannular reaction in the protonolysis steps adds support to the proposal that the reaction is concerted proceeding through a six membered transition state. The

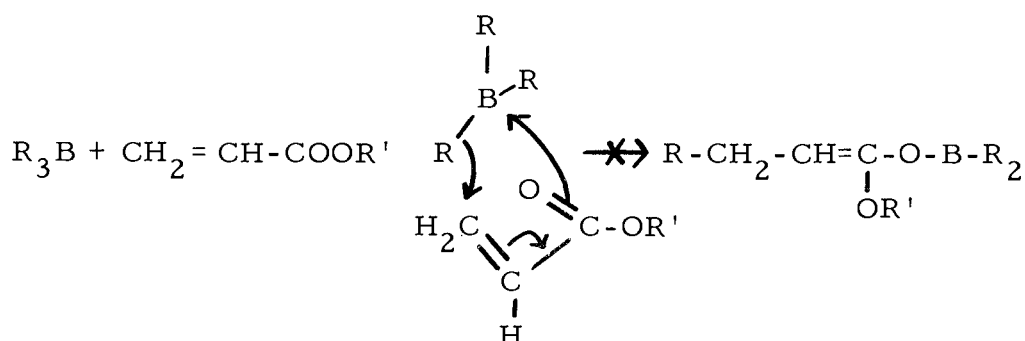


analogous transition state leading to bicyclo [3.3.0] octane would require a large ring intermediate of lower stability. One possible way of overcoming this problem which was not investigated would

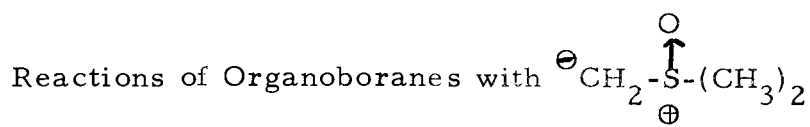


be to carry out the protonolysis in the presence of a strong external nucleophile.

It was of interest to investigate the possibility of attaining homologation through a protonolysis type reaction. When an organoborane was reacted with ethyl acrylate, however, the major product (other than alcohol) was a polymeric material which showed the presence of only carbon, hydrogen and oxygen. In this case, the reaction

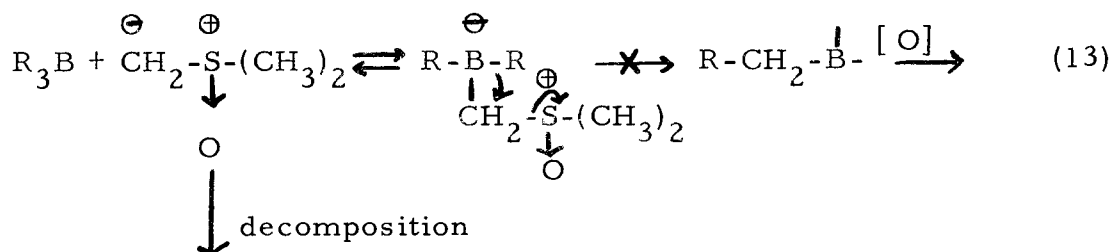


could proceed through a six membered transition step, but no such evidence was observed.



It was also of interest to explore the reaction of organoboranes with a nucleophilic species ( $\ominus CH_2-\overset{\oplus}{S}(O)(CH_3)_2$ ) synthesized by Corey (17). When Corey reacted dimethyloxosulfonium methyllide with carbonyl containing compounds, the nucleophilic nature of the

compound ( $\ominus\text{CH}_2-\overset{\text{O}}{\overset{\uparrow}{\text{S}}}^{\oplus}(\text{CH}_3)_2$ ) produced, as described in the introduction, an epoxide. The result of the reaction of this ylide with an organoborane would be, upon oxidation, an homologous alcohol. The ylide was prepared and its concentration determined by titration (see



experimental). Reactions were run at  $0^\circ$ , room temperature, and in refluxing tetrahydrofuran ( $64^\circ$ ) and the concentration of ylide followed by titration. Longer reaction periods were necessary to attain decomposition of the ylide at lower temperatures, but in all cases the only product (upon oxidation) was the alcohol ( $\text{R}-\text{OH}$ ). Here as in the sodium trichloroacetate reactions, the formation of a solid was observed during the course of the reaction but at temperatures evidently required for rearrangement, any coordination step was reversed.

#### Reactions of Organoboranes with Simmons-Smith Reagent

The final reaction studied in this investigation was another attempt to produce an homologous alcohol. In this case it was of



been formed. Further investigation involving a different method of addition would seem to be indicated.

One final comment should be made concerning the choice of solvents for attempted migrations from boron. As has been previously mentioned, the solvents used in this investigation were usually ethereal since these are the most desirable for work with alkylboranes. One attempt to enhance the chance for ionic coordination by use of a higher dielectric solvent (dimethyl sulfoxide) provided increased difficulty in work-up procedures. The possibility of using non-Lewis acid solvents such as benzene, suggested by Seyferth's work (48), was briefly investigated as mentioned with the  $\text{ØHgCCl}_3$  studies. The ambiguous nature of our results kept us from a further investigation of this possibility. It is obvious, however, that the migrations from boron to nitrogen or oxygen which occur readily in aqueous or ethereal solutions do not carry over readily to systems involving carbon.

## EXPERIMENTAL

All proton n.m.r. spectra were run in either carbon tetrachloride or deuteriochloroform and are reported as chemical shifts in parts per million ( $\delta$ ) from tetramethylsilane. The infrared spectra were obtained using a Beckman IR-8 spectrometer. All melting points were taken on a Fischer-Jones melting point apparatus and are corrected. G. L. C. chromatograms were obtained on various columns in an Aerograph A-90.

Trihexylborane<sup>4</sup>

Into a dry 300-ml. three-necked flask fitted with a magnetic stirrer, reflux condenser, dropping funnel, and dry nitrogen source was placed 25.2g (0.30 mole) of 1-hexene in 60 ml. of tetrahydrofuran. After cooling in an ice bath for ten minutes, 30 ml. of a 1 M solution of diborane in tetrahydrofuran was added dropwise over a period of 45 minutes. The reaction mixture was allowed to come to room temperature over a period of two to three hours. The tetrahydrofuran and excess 1-hexene were then removed in vacuo at aspirator pressure and the desired reaction solvent introduced. The solution obtained is a mixture of products, approximately 94% addition to the primary carbon and 6% addition to the secondary position.

#### Trioctylborane<sup>4</sup>

Into a dry 200-ml. three-necked flask fitted with a magnetic stirrer, pressure equalized dropping funnel, dry nitrogen source, and gas inlet tube was placed 1.28 g. (0.042 mole) of sodium borohydride in 100 ml. of dry diglyme. To this was added 6.39 g. (0.045 mole) of boron trifluoride etherate over a half hour period. The diborane generated (0.022 mole theoretical) was passed into a solution of 22.4 g. (0.20 mole) of 1-octene in 100 ml. of tetrahydrofuran. The solution flask was cooled in an ice bath for approximately one hour and then allowed to come to room temperature. Removal of the tetrahydrofuran and excess olefin was again accomplished in vacuo (at aspiration pressure) and the desired reaction solvent introduced.

#### Bis(3-methyl-2-butyl)borane<sup>6</sup>

To a solution of 4.7 g (0.066 mole) of 2-methyl-2-butene in 50 ml. of tetrahydrofuran at 0° was added 16.7 ml. (0.0167 mole) of a diborane in tetrahydrofuran solution (1 M). The reaction was kept under dry nitrogen during the course of the reaction. The solution was stirred at 0° for an additional hour and used immediately. The diborane ( $B_2H_6$ ) concentration in tetrahydrofuran solutions used in these reactions was measured by standard hydrogen

gas evolution displacement of water. One ml. of the diborane solution when injected into a flask containing diethylene glycol, was found to produce 135 ml. of hydrogen gas measurable by water displacement. This corresponds to a 1 M solution.

Bis(3-methyl-2-butyl)octylborane

Into a dry 300-ml. three-necked flask fitted with a pressure equalized dropping funnel, reflux condenser, magnetic stirrer, and dry nitrogen source was placed a solution of 0.33 moles of bis(3-methyl-2-butyl)borane (disiamyl borane) in 50 ml. of dry tetrahydrofuran. After cooling the flask in an ice bath, a solution of 3.7 g (0.033 mole) of 1-octene in 25 ml. of dry tetrahydrofuran was added over a 45 minute period. The reaction was stirred an additional hour at 0° and then allowed to come to room temperature. The tetrahydrofuran was removed in vacuo (at aspirator pressure) and the solvent for further reaction introduced.

Bis(exo-bicyclo[2.2.1]-2-heptyl) borane

Into a dry 300-ml. three necked flask fitted with a magnetic stirrer, pressure equalized dropping funnel, reflux condenser, and dry nitrogen source was placed a solution of 4.7 g. (0.05 mole) of bicyclo[2.2.1] hept-2-ene in 50 ml. of tetrahydrofuran.

The flask was cooled to 0° in an ice bath and allowed to stand 15 minutes. A 1 M diborane solution (12.5 ml., 0.0125 mole) in tetrahydrofuran was added via the dropping funnel over 30 minutes. The flask was allowed to come to room temperature and the solvent removed in vacuo at aspirator pressure. The desired solvent for further reaction was then introduced.

#### 2,3-dimethyl-2-butylhexylborane

To a solution of 3.36 g. (0.04 mole) of 1-hexene in 50 ml. of tetrahydrofuran under dry nitrogen and in an ice bath was added dropwise, 30 ml. of 1.28 M solution of 2,3-dimethyl-2-butylborane. The stirred flask was allowed to come to room temperature over a two hour period. Again, the tetrahydrofuran was removed in vacuo at aspirator pressure and the solvent for further reaction introduced.

#### Octylborane

A 1 M solution of diborane in tetrahydrofuran (75 ml., 50% excess) was added via a dropping funnel to a solution of 11.2 g. (0.10 mole) of 1-octene in 50 ml. of dry tetrahydrofuran at 0° C. over the period of 45 minutes. The entire system was kept under dry nitrogen and allowed to stir until the reaction flask reached room temperature. In vacuo (aspirator pressure) removal of the



tetrahydrofuran provided the desired organoborane.

### Hexylborane

Into a dry 300-ml. three-necked flask fitted with pressure equalized dropping funnel, magnetic stirrer, condenser, and dry nitrogen source, was placed 8.4 g. (0.100 mole) of 1-hexene in 50 ml. of dry tetrahydrofuran. The flask was cooled to 0° C. and 75 ml. of a 1 M solution of diborane in tetrahydrofuran (50% excess) was added over a period of 45 minutes. The flask was allowed to come to room temperature and the solvent removed in vacuo at aspirator pressure. The desired solvent for further reaction was then added to the organoborane.

### Synthesis of ethyl trichloroacetate

Trichloroacetic acid (454 g., 3.0 mole) was added to 1600 ml. of absolute ethanol and heated under reflux overnight. The ethanol-water azeotrope (95:5) which boils at 79.2° was distilled until the temperature began to rise above 80°. At this time, the remaining liquid (ca. 400 ml.) was transferred to a smaller flask and fractionated. The fraction boiling between 168-172° was collected (300 g., 53%) and used immediately.

Phenyl (trichloromethyl) mercury<sup>47</sup>

A mixture of 240 g. (1.80 moles) of ethyl trichloroacetate, 132 g. (0.37 mole) of phenylmercuric bromide, and 2000 ml. of anhydrous benzene was placed in a 3000-ml. three-necked flask fitted with a mechanical stirrer, reflux condenser, and a dry nitrogen source. The solution was stirred at 0° C. for ca. 15 minutes and 84.0 g. (1.54 moles) of freshly prepared sodium methoxide added in one portion. The reaction was stirred for 1.5 hours at 0° C. and two liters of water added. The residual solid was filtered and the benzene phase separated from the aqueous phase. The aqueous portion was extracted with 2-500 ml. portions of benzene and the extracts combined with the benzene layer. The benzene solution was dried with magnesium sulfate and the benzene removed in vacuo at aspirator pressure. The yellowish white solid which remained (120 g., 81%) was recrystallized from chloroform hexane producing 100 g. (68%) of a white solid, m. p. 113-114° [lit. 46, p. 851, m.p. 114-115°]. It should be noted that mercury containing compounds are extremely hazardous and very careful handling of such compounds is mandatory. This compound caused skin blistering.

Reaction of trioctylborane with  
phenyl (trichloromethyl) mercury

To a solution of 0.02 moles of trioctylborane in 150 ml. of dry diglyme at 80° was added 70.0 g. (0.175 mole) of phenyl (trichloromethyl) mercury over a 48 hour period. The system was kept under dry nitrogen at all times. After cooling to room temperature the reaction was placed in an ice bath at 0° C., and 20 ml. of 3 N sodium hydroxide added. This was followed by the addition of 20 ml. of 30% hydrogen peroxide. The reaction was stirred several hours and then filtered to remove the solid formed during reaction (phenylmercuric chloride). The basic solution was extracted with ethyl ether, washed with a saturated sodium chloride solution, dried over magnesium sulfate, and the solvent removed in vacuo at aspirator pressure. The product remaining (5.8 g.) was found to contain 5.2 g. (66.7%) of 1-octanol, identifiable by comparison of its infrared spectrum and G. L. C. retention times with an authentic sample. The column used for analysis was a 5 ft.  $\times$  1/4 in. -10% Apiezon K packed on firebrick at 100° and 60 mls/min., conditions which were shown to separate 1-octanol, 2-octanol, and 1-nonanol. The basic layer from above was acidified (Hydrochloric acid) and worked up as above. The product was found to consist of 2.98 g. (32%) of nonanoic acid identifiable by its infrared

and n.m.r. spectra, and amide formation.

The nuclear magnetic resonance spectrum of the acid shows an acidic hydrogen at  $\delta = 9.45$ , a methylene triplet at  $\delta = 2.33$ , a methylene multiplet at  $\delta = 1.35$  and a single methyl peak at  $\delta = 0.93$ .

#### Preparation of nonamide

The acid (0.100 g.) was added to ca. one milliliter of thionyl chloride and the mixture refluxed for one half hour. The solution was then poured into three milliliters of cold concentrated (28%) ammonia. Yellowish crystals separated and were recrystallized from ethanol giving fine, white needles, m.p.  $95-96^{\circ}$  [lit. 29, p. 984, m.p.  $96-97^{\circ}$ ].

#### Heptanoic acid

Into a dry 300-ml. three-necked flask fitted with a mechanical stirrer and a dry nitrogen source was placed 0.033 mole of tri-n-hexylborane. The temperature was raised to  $80^{\circ}\text{C}$ . and 39.6 g. (0.100 mole) of phenyl (trichloromethyl) mercury was added over a 48 hour period. The flask was allowed to cool to room temperature, placed in an ice bath, and 40 ml. of 3 N sodium hydroxide was added followed by the addition of 40 ml. of 30% hydrogen peroxide. After stirring for several hours, the

solid formed during the reaction (phenylmercuric chloride) was filtered and the basic layer extracted with ethyl ether, washed with saturated sodium chloride, dried over magnesium sulfate, and the solvent removed in vacuo at aspirator pressure. The product isolated (14.4 g., 62%) was found to have a G. L. C. retention time and an infrared spectrum identical to 1-hexanol. The aqueous layer was acidified and worked up as above, yielding 8.7 g. (31%) of heptanoic acid identifiable by its infrared spectra.

The infrared spectrum showed significant bands at  $1720\text{ cm}^{-1}$  attributed to the carbonyl group, and the typically broad carboxyl group absorption at from  $3600\text{ cm}^{-1}$  to  $2800\text{ cm}^{-1}$ .

Reaction of phenyl(trichloromethyl) mercury  
with (2, 3-dimethyl-2-butyl)hexylborane

To a solution of 6.67 g. (0.038 mole) of (2, 3-dimethyl-2-butyl) hexylborane in 100 ml. of dry diglyme at  $80^{\circ}$  was added 79.2 g. (0.200 mole) of phenyl(trichloromethyl) mercury over a 48 hour period. To the cooled reaction flask was added 25 ml. of 3 N sodium hydroxide followed by 25 ml. of 30% hydrogen peroxide. The reaction was stirred for ca. five hours and the precipitate formed (phenylmercuric chloride) was filtered. The (basic) solution was extracted with ethyl ether. The extract was then washed with a cold saturated salt solution to remove diglyme,

dried over magnesium sulfate, and the ether removed in vacuo at aspirator pressure. The residue, 1.6 g. (20%) was an equimolar mixture of the two expected alcohols, 1-hexanol and 2,3-dimethyl-2-butanol. Hexanol-1 was identified by its infrared spectra and by coinjection with an authentic sample on a 5 ft.  $\times$  1/4 in. -10% Apiezon K gas chromatography column at 100° and 60 ml/min. The 2,3-dimethyl-2-butanol was identified by an examination of its collected n.m.r. spectra.

The basic layer was acidified and worked up as above. The product consisted of 4.0 g. (40%) of what was presumably an equimolar mixture of heptanoic acid and 2,2,3-trimethylbutanoic acid.

The n.m.r. spectra of 2,3-dimethyl-2-butanol shows a multiplet at  $\delta = 1.60$  ascribed to the tertiary hydrogen, a singlet at  $\delta = 1.11$  ascribed to the methyl groups adjacent to the hydroxyl, and a doublet at  $\delta = 0.89$  assigned to the remaining two methyl groups.

Reaction of phenyl (trichloromethyl) mercury  
with bis-(3-methyl-2-butyl)octylborane

To a solution of 8.6 g. (0.033 mole) of bis-(3-methyl-2-butyl) octylborane in 100 ml. of dry diglyme at 80° C. was added 39.6 g. (0.100 mole) of phenyl(trichloromethyl) mercury over a 48 hour

period. The solution was cooled, placed in an ice bath, and 30-ml. of 3 N sodium hydroxide added, followed by the addition of 30 ml. of 30% hydrogen peroxide. The reaction was stirred for several hours and the precipitate formed during decomposition (phenylmercuric chloride) was filtered. The basic solution was extracted with ethyl ether, the extract washed with a cold saturated salt solution, dried over magnesium sulfate and the solvent removed in vacuo at aspirator pressure. The alcohol isolated (4.0 g., ca. 66%) was, upon G. L. C. analysis found to contain 67% 3-methyl-2-butanol and 33% n-octanol. The water phase was acidified and worked up as above to yield 3.2 g. (32%) of material which showed typical carboxyl absorption in the infrared. Based upon the percent alcohols obtained, the acids should be 33% heptanoic and 67% 2,3-dimethylbutanoic acid.

The column used for G. L. C. analysis was a 5 ft.  $\times$  1/4 in. - 10% Apiezon K on firebrick under conditions which affect complete separation of low molecular weight alcohols, 80° and 45 ml./min.

Attempted synthesis of 6-undecene  
via hydroboration<sup>48</sup>

To trihexylborane (0.05 mole) placed in 100 ml. of dry benzene was added 19.8 g. (0.05 mole) of phenyl(trichloromethyl) mercury. With stirring the temperature of the suspension was slowly raised

to 80° at which time the solid had gone into solution. After ca. one hour a white precipitate ( $\text{ØHgCl}$ ) began forming and the reaction was kept at 80° for another seven hours to insure complete decomposition. The solution was cooled and the solid filtered (10 g.). The benzene solution was washed with water, dried over magnesium sulfate, and the benzene distilled off. The residue consisted of some solid (more  $\text{ØHgCl}$ ) and 6.5 grams of a liquid which has only C-H and C-B absorption in the infrared. This liquid was oxidized with alkaline hydrogen peroxide to yield 4.1 g. of n-hexanol and 2.8 g. of heptanoic acid. The identification of hexanol and heptanoic acid was made by a comparison of their infrared spectra with those of authentic samples.

#### Protonolysis of cyclooctene

To a stirred solution of 11.0 g. (0.10 mole) of cyclooctene and 1.06 g. (0.028 mole) of sodium borohydride in 55 ml. of dry triglyme was added 5.36 g. (0.038 mole) of boron trifluoride etherate over the period of one and one half hours. Propionic acid (11.1 g., 0.15 mole) was then introduced, a distillation column connected, and the temperature of the system raised slowly to 135° C. under aspiration vacuum. A fraction (12.5 g.) was taken between ca. 50° and 70° at which time the temperature dropped markedly. The product (9.98 g.) was then washed with five percent sodium bicarbonate and



analyzed by G. L. C. The analysis shows 6.8 g. (62%) of cyclooctane and 3.1 g. (28.5%) of cyclooctene by comparison with authentic compounds. In this experiment the G. L. C. Analysis was carried out on an 18 ft.  $\times$  1/4 in. -15% XF-1150 column under conditions which affect separation of cyclooctane and cyclooctene.

Protonolysis studies with  
1.5 cyclooctadiene

To a stirred solution (under a nitrogen atmosphere) of 10.8 g. (0.10 mole) of 1,5-cyclooctadiene and 1.89 g. (0.05 mole) of sodium borohydride in 50 ml. of dry tetrahydrofuran was added 9.35 g. (0.066 mole) of boron tri-fluoride etherate over a one hour period. The reaction was stirred an additional hour and the tetrahydrofuran removed in vacuo at aspirator pressure. Propionic acid (62.2 g., 0.84 mole) was then introduced and the reaction heated under reflux (ca. 140° C.) overnight. The reaction was cooled and extracted with ethyl ether, the extract was washed with 5% sodium bicarbonate to remove any acid, and dried over magnesium sulfate. The ether was removed in vacuo at aspirator pressure and the residue (7.0 g.) subjected to a G. L. C. analysis. The analysis shows a mixture of essentially two components: cyclooctane (65%) and cyclooctene (25%). It should be noted that in both protonolyses some polymeric boron-hydrocarbon was isolated. Attempted analyses proved unfruitful.

Attempted addition of ethyl  
acrylate to trihexylborane

Into a dry 200-ml, three-necked flask fitted with a dropping funnel, stirrer, condenser, and dry nitrogen source was placed 0.06 mole of trihexylborane in 50 g. (0.50 mole) of ethyl acrylate. The reaction was heated under reflux for several hours, cooled, and water added. The solution was made basic and extracted with ethyl ether. The ether extract was washed with a saturated salt solution, dried over magnesium sulfate, and the ether removed in vacuo at aspirator pressure. The residue (10.1 g.) was a very viscous white solid which seemed to contain some hexanol but appeared to be mostly an acrylate polymer. The aqueous layer from above was acidified and worked up in like manner yielding 3.9 g. of a material which appeared to be acidic from infrared data but not the desired nonanoic acid. It was decided that this reaction was rendered unacceptable by the degree of polymerization incurred.

Preparation of trimethyloxosulfonium iodide

A solution of 96 g. (1.23 moles) of dimethylsulfoxide and 180 ml. of methyl iodide was heated under reflux under nitrogen for three days. The yellowish precipitate was collected (145 g., 53.6%) and recrystallized from water yielding white needles, which were

crushed and dried over phosphorous pentoxide.

#### Preparation of trimethyloxosulfonium chloride

Trimethyloxosulfonium iodide (30 g., 1.36 mole) was dissolved in 300 ml. of distilled water at 50° and chlorine gas bubbled in until no more iodine was observed to precipitate. The liquid was decanted and washed with ethyl ether to remove any iodine. The water was evaporated and the residue recrystallized from a methanol-benzene (1:1) solution. The white solid remaining after recrystallization (14 g., 80%) had a m.p. 221-222° dec. [lit. 17, p. 1357 m.p. 220-222° dec.] .

#### Preparation of dimethyloxosulfonium methyllide

A weighted amount of sodium hydride (12.0 g., 0.50 mole) was placed in a 500-ml. three-necked flask and washed with light pet. ether three times. The pet. ether was removed and the system placed under nitrogen, followed by the addition of 62 g. (0.49 mole) of trimethyloxosulfonium chloride and 250 ml. of dry tetrahydrofuran. The flask (with stirring) was allowed to reflux until no more hydrogen gas was evolved (ca. 6-8 hrs.). The solution was then cooled, filtered through celite, and stored under nitrogen. Titration of the solution with hydrochloric acid to the phenolphthalein end point showed the production of 0.125 moles of the ylide. The

ylide can be stored (under nitrogen) at 0° for several weeks.

Attempted reaction of  $R_3B$  with  
dimethyloxosulfonium methylide

To a stirred solution of 0.125 moles of dimethyloxosulfonium methylide in 200 ml. of dry tetrahydrofuran at 0° C. was added 0.012 moles of trioctylborane. The reaction was stirred, under nitrogen at 0° C. for two to three hours and then overnight at room temperature. Sodium hydroxide (25 ml., 3 N) was then added followed by hydrogen peroxide (25 ml., 38%). After stirring for several more hours the reaction was cooled and extracted with ethyl ether.. The ether extract was washed with a saturated salt solution, dried over magnesium sulfate, and the ether removed in vacuo at aspirator pressure. A G.L.C. analysis of the residue (4.0 g., 91%) showed the only products to be a mixture of 1-octanol (85%) and 2-octanol (6%). The methylide used in this reaction was synthesized and the concentration determined using the method of E. J. Corey and Michael Chaykovsky (17). It was found that 10.0 ml. of the ylide required 124.0 ml. of 0.10 N hydrochloric acid to reach the phenolphthalein end point implying that the solution of dimethyloxosulfonium methylide was 1.25 N. G.L.C. analysis of products from this reaction was carried out on a 5 ft.  $\times$  1/4 in. - 10% Apiezon K on firebrick column at 100° and 60 ml./min.

Attempted addition of Simmons-Smith  
reagent to trioctylborane

A zinc-copper couple (0.20 mole) (51) was placed in a 500-ml three-necked flask fitted with a mechanical stirrer, reflux condenser, dropping funnel and dry nitrogen source. Dry tetrahydrofuran (75 ml.) and a crystal of iodine were introduced and the system stirred until the iodine color disappeared. Through the dropping funnel, in three portions, was added a solution of 0.033 moles of trioctylborane and 53.6 g. (0.20 mole) of methylene iodide in 100 ml. of dry tetrahydrofuran. The reaction was kept under reflux overnight, cooled to room temperature, and 40 ml. of 3 N sodium hydroxide added in one portion. Hydrogen peroxide (40 ml., 30%) was then added slowly with cooling when necessary. The solid was filtered and the reddish liquid extracted with ethyl ether. The extract was washed with a saturated solution of sodium bisulfite, dried over magnesium sulfate, and the solvent removed in vacuo at aspirator pressure. A G.L.C. analysis of the residue (13.9 g.) showed it to be a mixture of mainly n-octyliodide (28-30%), n-octanol (50%) and 2-octanol (6%). The infrared spectrum and n.m.r. spectrum of the 30% component are consistent with n-octyliodide.

The n.m.r. spectrum has a triplet of  $\delta = 3.28$  attributed to the methylene adjacent to the iodine, a singlet at  $\delta = 1.75$ , a

multiplet at  $\delta = 1.45$  attributed to the internal methylenes, and a multiplet at  $\delta = 1.00$  assigned to the terminal methyl group.

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