

## Organoborane–Carbon Monoxide Reactions. A New Versatile Approach to the Synthesis of Carbon Structures

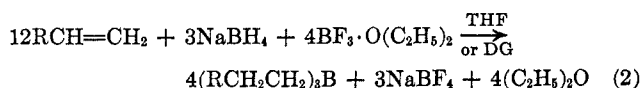
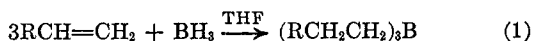
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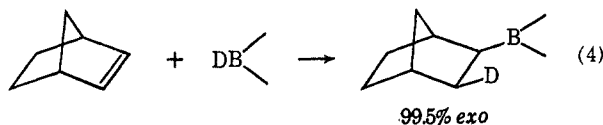
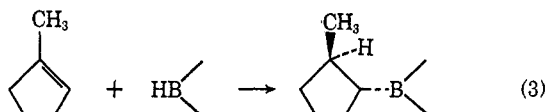
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### Hydroboration

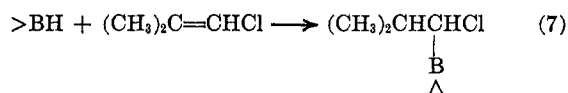
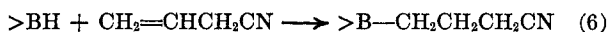
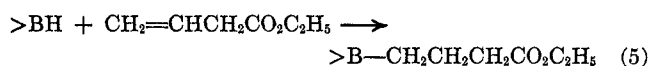
The discovery that diborane in ether solvents reacts practically instantaneously and quantitatively with alkenes and related unsaturated carbon compounds to convert them into the corresponding organoboranes made these intermediates readily available for the first time<sup>1</sup> (1, 2). The characteristics of this reaction,



hydroboration, are highly favorable for synthetic work.<sup>2</sup> Not only is the reaction very fast and essentially quantitative, but practically all unsaturated compounds, with very rare exceptions,<sup>3</sup> undergo the reaction. Rearrangements of the carbon structure are practically unknown. The reaction appears to involve an anti-Markovnikov *cis* addition from the less hindered side of the double bond (3, 4).



Of equally great significance is the fact that many functional groups are readily accommodated without difficulty<sup>4</sup> (5–7). Thus the organic chemist has at his



disposal for the first time a relatively reactive organo-metallic capable of bearing many different functional groups in the organic radical.

### The Organoboranes as Synthetic Intermediates

These developments have created intense interest in the discovery of new reactions of organoboranes of utility in organic synthesis. Among the more interesting possibilities to which attention should be called are: isomerization,<sup>2</sup> displacement,<sup>2</sup> contrathermodynamic isomerization of olefins,<sup>2</sup> cyclization,<sup>5a,b</sup> protonolysis,<sup>2</sup> oxidation to alcohols (alkaline hydrogen peroxide),<sup>2</sup> oxidation to ketones (chromic acid),<sup>5c</sup> amination,<sup>5d</sup> metallation,<sup>5e</sup> coupling with alkaline silver nitrate,<sup>5f,g</sup> 1,4 addition to  $\alpha,\beta$ -unsaturated aldehydes,<sup>5h,i</sup> ketones,<sup>5j</sup> and Mannich bases,<sup>5k</sup> reaction with ylides<sup>5l</sup> or with  $\alpha$ -halo carbanions,<sup>5m,n</sup> and carbonylation<sup>6</sup> to tertiary alcohols, secondary alcohols, ketones, methylol derivatives, aldehydes, ring ketones, and polycyclics.

The carbonylation reaction appears to be especially

(5) (a) H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *ibid.*, **88**, 1443 (1966); (b) R. Köster, *Angew. Chem. Intern. Ed. Engl.*, **3**, 174 (1964); (c) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2951 (1961); (d) M. W. Rathke, N. Inoue, K. R. Varma, and H. C. Brown, *ibid.*, **88**, 2870 (1966); (e) J. B. Honeycutt, Jr., and J. M. Riddle, *ibid.*, **82**, 3051 (1960); (f) H. C. Brown and C. H. Snyder, *ibid.*, **83**, 1001 (1961); (g) H. C. Brown, C. Verbrugge, and C. H. Snyder, *ibid.*, **83**, 1002 (1961); (h) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); (i) H. C. Brown, G. W. Kabalka, M. W. Rathke, and M. M. Rogić, *ibid.*, **90**, 4165 (1968); (j) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **89**, 5708 (1967); (k) H. C. Brown, M. W. Rathke, G. W. Kabalka, and M. M. Rogić, *ibid.*, **90**, 4166 (1968); (l) J. J. Tufariello, L. T. C. Lee, and P. Wojtkowski, *ibid.*, **89**, 6804 (1967); (m) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818 (1968); (n) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 1911 (1968).

(6) Discussed in detail in this review.

(1) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(3) M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **29**, 1120, 1131 (1964).

(4) H. C. Brown and M. K. Unni, *J. Am. Chem. Soc.*, **90**, 2902 (1968); H. C. Brown and R. M. Gallivan, Jr., *ibid.*, **90**, 2906 (1968); H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

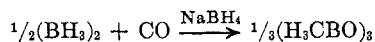
promising in its versatility, and this review will be devoted to a discussion of its utility.

### Early History

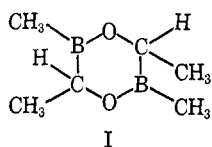
In 1937 Burg and Schlesinger reported that diborane reacts with carbon monoxide in a sealed tube at 100° under 20 atm to give a simple addition compound, borane carbonyl<sup>7</sup> (8). The product is a gas, bp -64°,



which is largely dissociated into its components at atmospheric pressure.<sup>8</sup>



At approximately the same time, Schlesinger and his coworkers studied the reaction of the methyl derivatives of diborane with carbon monoxide.<sup>9</sup> Dimethylborane (dimer) reacted with carbon monoxide at a pressure of 5 atm to produce a number of relatively complex materials. The major product was a liquid with the empirical formula  $[(\text{CH}_3)_2\text{BHCO}]_2$ . However, this compound did not liberate hydrogen when treated with water, indicating the absence of the original boron-hydrogen bond. The authors were unable to assign any structure to this intermediate. However, in view of our own studies with dialkylboranes,<sup>10</sup> it is probably I.



In 1961 a patent was issued to Reppe and Magin for the preparation of compounds of the type  $(\text{R}_3\text{BCO})_n$  by the carbonylation of trialkylboranes under pressure.<sup>11</sup> Typically, a trialkylborane reacted at a temperature of 10 to 20° with carbon monoxide at pressures of 100 to 200 atm to give, after distillation, a mixture of two products. The major component possessed a molecular weight and analysis in agreement with the empirical formula  $(\text{R}_3\text{BCO})_2$ . The minor product corresponded to the empirical formula  $(\text{R}_3\text{BCO})_3$ . No indication was presented of any understanding of the structures of these materials or of the nature of the chemical reaction taking place.

To Hillman belongs the credit for first establishing the nature of this reaction of carbon monoxide and trialkylboranes.<sup>12</sup> He treated the organoborane

(7) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).

(8) Under the catalytic influence of small amounts of sodium borohydride, the reaction between diborane (in tetrahydrofuran) and carbon monoxide proceeds very rapidly at room temperature and atmospheric pressure to yield trimethylboroxine: M. W. Rathke and H. C. Brown, *ibid.*, **88**, 2606 (1966).

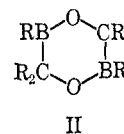
(9) F. L. McKennon, Ph.D. Thesis, The University of Chicago, 1937.

(10) Unpublished research with M. W. Rathke and M. M. Rogić.

(11) W. Reppe and A. Magin, U. S. Patent 3,006,961 (Oct 31, 1961); *Chem. Abstr.*, **55**, 10386i (1961).

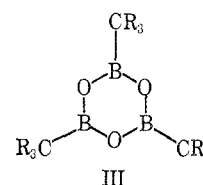
(12) (a) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); (b) *ibid.*, **85**, 982 (1963); (c) *ibid.*, **85**, 1626 (1963).

with carbon monoxide at very high pressures, usually about 10,000 psi, in the presence of water.<sup>12a</sup> He reported that the products from carbonylation at relatively low temperature (50–75°) were 2,5-diboradioxanes (II), corresponding to the dimer of Reppe and

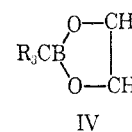


Magin.<sup>11</sup> Oxidation of these materials with alkaline hydrogen peroxide did not produce the expected dialkyl ketones, but rather the corresponding dialkylcarbinols.<sup>13</sup>

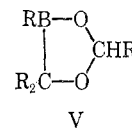
At higher temperatures, generally 150°, the 2,5-diboradioxanes (II) were converted into the corresponding boronic anhydrides (boroxines) (III).



Hillman examined the carbonylation reaction in the presence of various glycols.<sup>12b</sup> He noted that whereas certain glycols led to the formation of polymeric products, the use of ethylene glycol yielded the corresponding cyclic esters (IV) smoothly. Finally, carbonylation



in the presence of aldehydes yielded 4-bora-1,3-dioxalanes<sup>12c</sup> (V).



### Carbonylation at Atmospheric Pressure

Practically all of Hillman's research had been done at very high pressures, generally about 10,000 psi. He had tried some carbonylations at atmospheric pressure but had noted that the reactions were relatively slow and incomplete.<sup>12a</sup>

It was apparent that carbonylation, combined with hydroboration, offered a highly promising synthetic route. However, very few laboratories are equipped to run carbonylations at 10,000 psi. Moreover, even if they were so equipped, the inconvenience of such a procedure would mitigate against the adoption of such a procedure unless there were no simple alternatives available. Consequently, we undertook to see if we

(13) As discussed later, we have found it possible to convert the carbonylation intermediate either to the ketone or to the carbinol, as desired, in excellent yields.

could find means to accomplish such carbonylations at atmospheric pressures.

Initially, our investigation took the form of a search for possible catalysts for the reaction. However, we soon discovered that merely by raising the temperature to 100–125° practically all of the organoboranes of interest reacted essentially quantitatively with carbon monoxide at atmospheric pressure, usually in 1–3 hr, although some of the more hindered derivatives required a longer time. Obviously, this solved the problem of a convenient laboratory procedure, and we undertook a study of the new synthetic entry.

This study was greatly facilitated by our familiarity with the Brown<sup>□</sup> hydrogenator.<sup>14</sup> This instrument, although originally developed for hydrogenations, is a very convenient automatic gas generator. It permits one to follow the rate of absorption of a gas by the system. Thus we have utilized it for hydrochlorinations.<sup>15</sup> In some cases the automatic feature has revealed that a given hydrochlorination is complete in 1 min, with the initial product being very different from that present after 10 min.<sup>16</sup>

As adapted for carbonylation, the apparatus is assembled (Figure 1). In the buret A is placed formic acid. In the generator flask C is placed concentrated sulfuric acid maintained at approximately 100° by a heating mantle. The hydroboration is carried out in the reactor E in the usual manner. The system is flushed with carbon monoxide by injecting formic acid through the serum cap into the generator C. Then the reactor temperature is raised to an appropriate level, depending on the reaction, and stirring is initiated. The mercury in the valve B is sufficient to support the column of formic acid in the buret as long as the pressure in the apparatus is atmospheric. However, as soon as carbon monoxide is absorbed by the organoborane solution in the reactor E, the pressure drops approximately 20 mm below atmospheric, and formic acid is drawn through the mercury seal into the generator. In this way the carbonylation proceeds automatically to completion. At any moment a mere reading of the buret will indicate the progress of the reaction. At the end of the reaction, the reactor vessel is cooled, an appropriate base is added, followed by 30% hydrogen peroxide, and the reaction product is then isolated.

### Tertiary Alcohols<sup>17</sup>

It was observed that a wide variety of organoboranes, readily synthesized *via* hydroboration in diglyme (2), reacted readily with carbon monoxide at temperatures of 100–125°. Oxidation of the intermediates with alkaline hydrogen peroxide provided the corresponding trialkylcarbinols in excellent yield (9). In some cases

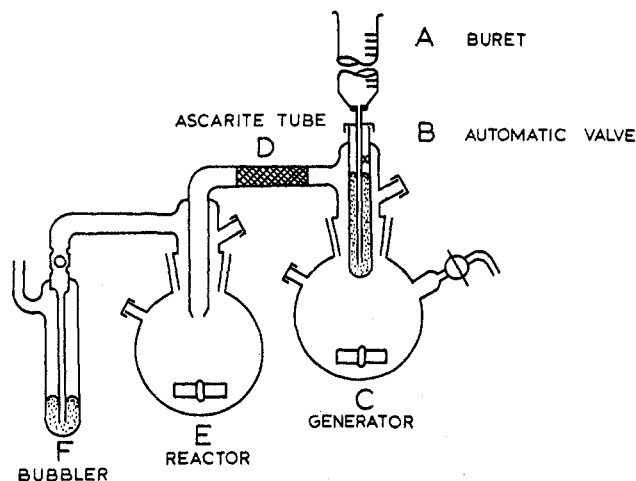
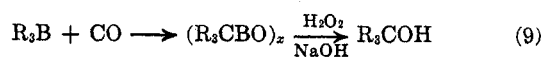
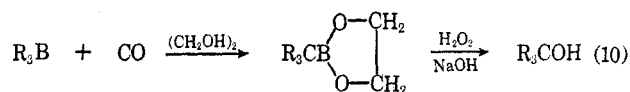


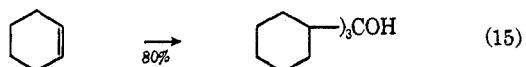
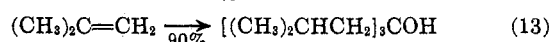
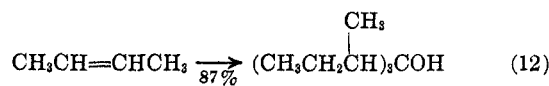
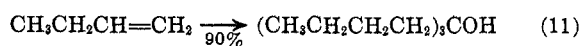
Figure 1. Hydrogenation apparatus modified for generation of carbon monoxide.



the intermediate appeared to be polymeric and difficult to oxidize. However, by carrying out the carbonylation in the presence of ethylene glycol,<sup>12b</sup> this difficulty could be avoided (10).



The synthesis appears to be of wide applicability, as indicated by the following preparations (11–16). This



makes readily available for the first time trialkylcarbinols containing bulky groups. For example, the yield of tricyclohexylcarbinol, through the Grignard reaction, is reported to be only 7%, and this was raised to 19% by use of a special procedure involving sodium.<sup>18</sup> No difficulty was experienced in achieving an isolated yield of 80% with the present procedure.

### Mechanism of the Carbonylation Reaction

Carbonylation of an equimolar mixture of triethylboron and tri-*n*-butylboron gave an equimolar mixture of triethylcarbinol and tri-*n*-butylcarbinol (17). There

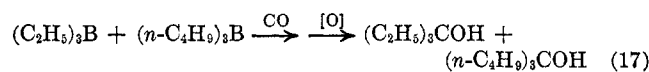
(14) C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 2829 (1962); *J. Org. Chem.*, **31**, 3989 (1966). We used a commercial model from Delmar Scientific Laboratories, Maywood, Ill. 60154.

(15) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

(16) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 3898 (1967).

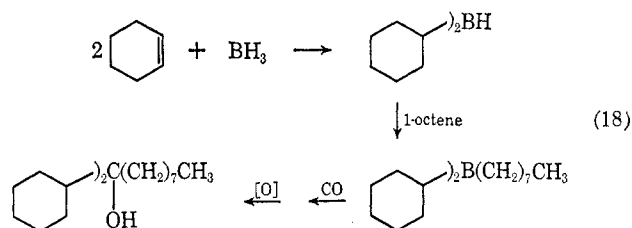
(17) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2737 (1967).

(18) P. D. Bartlett and A. Schneider, *ibid.*, **67**, 141 (1945).

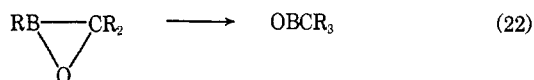
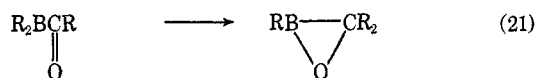
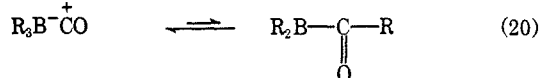
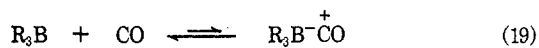


was no evidence for the presence of any mixed derivatives, such as diethyl-*n*-butylcarbinol or ethyl-di-*n*-butylcarbinol, which would have accompanied an intermolecular transfer of alkyl groups.<sup>19</sup>

Similarly, dicyclohexyl-*n*-octylborane, readily synthesized by the reaction of dicyclohexylborane and 1-octene, yielded dicyclohexyl-*n*-octylcarbinol in 82% yield, without evidence of any isomeric materials (18).



These results indicate that the groups are transferred intramolecularly from boron to carbon and are consistent with the mechanism (19–22) proposed by Hill-



man<sup>12a</sup> and slightly modified.<sup>20</sup>

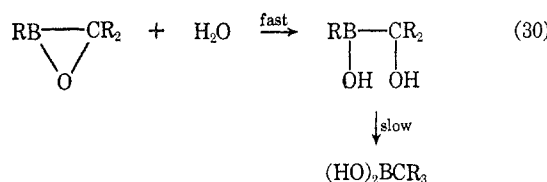
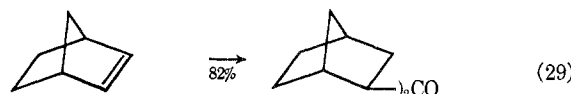
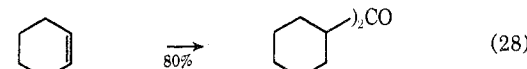
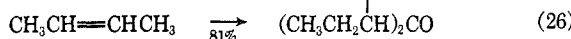
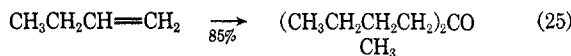
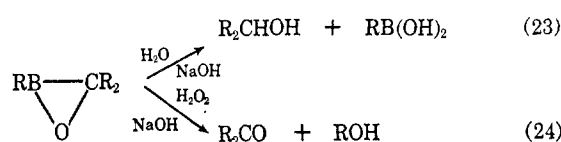
The boraepoxide (21) is presumably the precursor (by dimerization) of the 2,5-diboradioxane (II). Once the latter is formed, the transfer of the third alkyl group becomes very slow and requires heating at elevated temperatures in the presence of water or other materials to open up the stable diboradioxane system.<sup>12a</sup> The boronic anhydride (22) trimerizes to the corresponding boroxine (III). Presumably it is the sluggish oxidation of some of these polymeric derivatives which makes it advantageous to carry out the reaction in the presence of ethylene glycol.<sup>17</sup>

### Secondary Alcohols and Ketones<sup>20</sup>

It is evident from this mechanism that, were it possible to stop the reaction at the point where two alkyl groups had transferred from boron to carbon (21), hydrolysis would produce the secondary alcohol, R<sub>2</sub>CHOH (23), and oxidation would produce the corresponding ketone, R<sub>2</sub>CO (24).

Indeed, we discovered that the addition of equimolar quantities of water greatly inhibited the transfer of the third alkyl group, making possible a convenient synthesis of secondary alcohols and ketones (25–29).

The water apparently converts the boraepoxide into

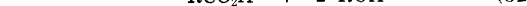
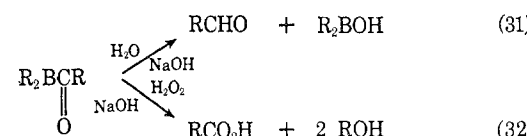


the corresponding hydrate (30) and the latter is evidently less susceptible to the transfer of the third alkyl group.

Hydrolysis of the reaction mixtures with aqueous sodium hydroxide readily produces the corresponding secondary alcohols. Unless the oxidation is carried out carefully, in accordance with the recommended procedure,<sup>20</sup> hydrolysis can accompany the oxidation, so that the product can consist of a mixture of ketone and alcohol.<sup>12a</sup>

### Primary Alcohols<sup>21</sup> and Aldehydes<sup>22</sup>

It is evident that if it were possible to stop the reaction at the point where a single alkyl group had been transferred from boron to carbon (20), hydrolysis should yield the corresponding aldehyde (31) and oxidation the corresponding acid (32).



Up to the present time we have been unable to stop the reaction at this stage without simultaneously changing the oxidation stage of the intermediate. Thus in the presence of lithium borohydride or lithium trimethoxyaluminumhydride an intermediate is obtained which hydrolyzes to the methylol derivative (33) and is oxidized to the corresponding aldehyde (34).

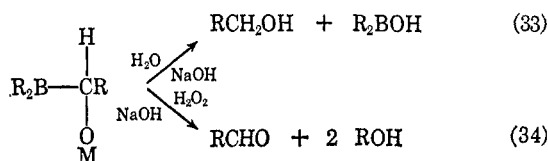
Not only do the complex hydrides reduce one of the intermediates (19 or 20), which permits the reaction to

(19) H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 4528 (1967).

(20) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2738 (1967).

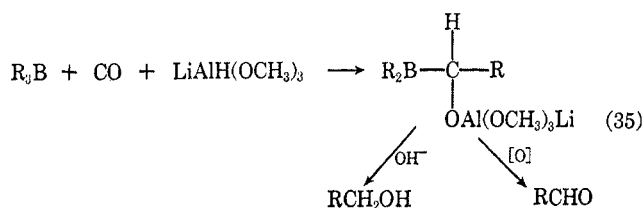
(21) M. W. Rathke and H. C. Brown, *ibid.*, **89**, 2740 (1967).

(22) H. C. Brown, R. A. Coleman, and M. W. Rathke, *ibid.*, **90**, 499 (1968).

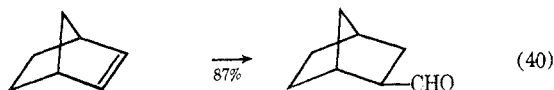
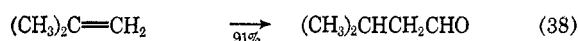
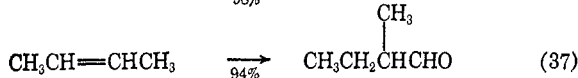
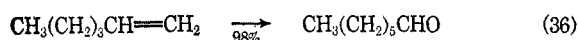


stop at the stage where only one of the three alkyl groups have been transferred from boron to carbon, but the reagents simultaneously strongly catalyze the absorption of carbon monoxide. Whereas the previous reactions are generally carried out at temperatures of 100–125°, the present reactions proceed relatively rapidly at temperatures of 25–45°.

The reaction with lithium trimethoxyaluminumhydride<sup>23</sup> is especially interesting. Neither the reagent nor the trialkylborane individually reacts with carbon monoxide at atmospheric pressure at any appreciable rate at 25°. However, their presence together in the same reaction vessel (Figure 1) results in a rapid uptake of carbon monoxide which is complete in a matter of minutes. The reaction exhibits a simple 1:1:1 stoichiometry for the three components (35).

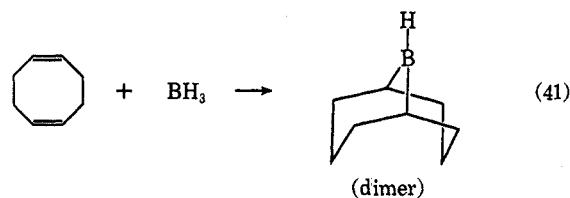


Based on this stoichiometry, the yields of aldehyde are almost quantitative (36–40).

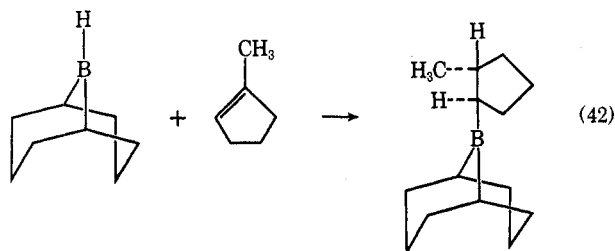


Hydrolysis of the reaction mixture with alkali, without oxidation, produces essentially quantitative yields of the corresponding methylol derivatives. An obvious disadvantage of this procedure is the fact that only one of the original three alkyl groups on boron is utilized. Fortunately, it has proven possible to circumvent this difficulty.<sup>24</sup>

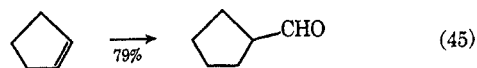
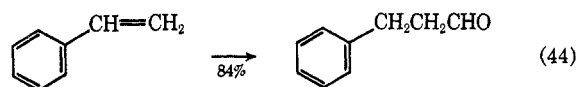
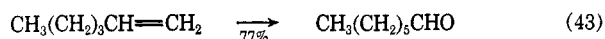
Treatment of 1,5-cyclooctadiene with borane in a 1:1 mole ratio under controlled conditions yields 9-borabicyclo[3.3.1]nonane (41), a material which is



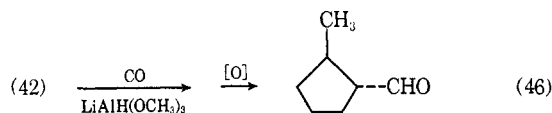
remarkably stable thermally and so insensitive to atmospheric oxygen that it can be handled in the open air.<sup>25</sup> In spite of its chemical stability toward oxygen, it readily hydroborates even hindered olefins<sup>26</sup> (42).



Reaction of these B-R-9-borabicyclo[3.3.1]nonane derivatives with carbon monoxide and lithium trimethoxyaluminumhydride results in the preferential reaction of the B-alkyl group (43–45).



The introduction of the aldehyde group takes place with retention of configuration<sup>27</sup> (46).



Moreover, preliminary results indicate that there is no difficulty in carrying out this synthesis in the presence of many functional groups.<sup>28</sup> Consequently, it now appears that we are in a position to introduce the CH<sub>2</sub>OH or CHO group in excellent yield into a wide variety of complex molecules at the position of a carbon-carbon double bond.

A word may be in order concerning the mechanism. The tremendous accelerating effect on the rate of uptake of carbon monoxide brought about by the reagent suggests that it must react rapidly with a small equilibrium concentration of an intermediate. If both stages (19) and (20) are reversible equilibria, as represented, then the reagent might operate by converting the carbonyl derivative, R<sub>2</sub>BCOR, into the reduced product. On the other hand, if only the first stage (19) is reversible, then the reagent must react with the small

(23) This reagent is readily synthesized by adding 3 mol of methanol to 1 mol of lithium aluminum hydride in tetrahydrofuran solution. The solution is used, without isolation of the reagent: H. C. Brown and C. J. Shoaf, *J. Am. Chem. Soc.*, **86**, 1079 (1964). For a survey of its reducing characteristics, see H. C. Brown and P. M. Weissman, *ibid.*, **87**, 5614 (1965).

(24) Research in progress with R. A. Coleman and E. F. Knights.

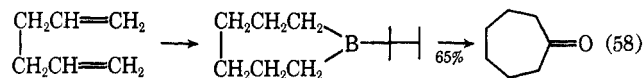
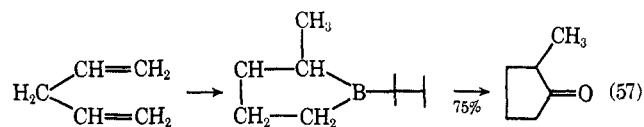
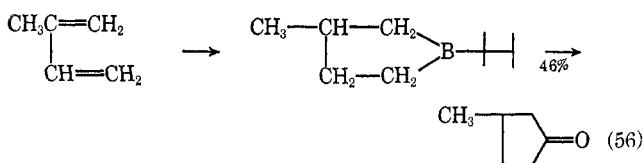
(25) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280 (1968).

(26) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281 (1968).

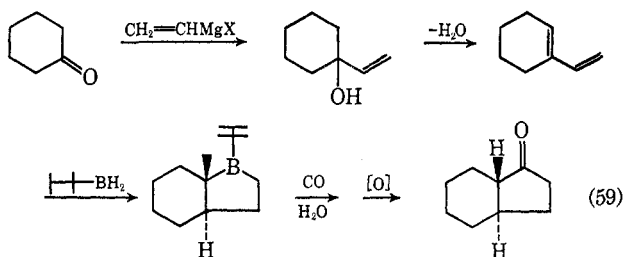
(27) Research in progress with M. M. Rogić, G. W. Kabalka, and M. W. Rathke.

(28) Research in progress with R. A. Coleman.

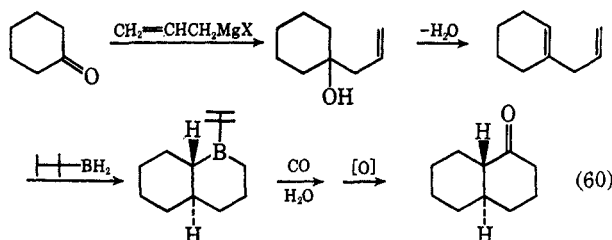




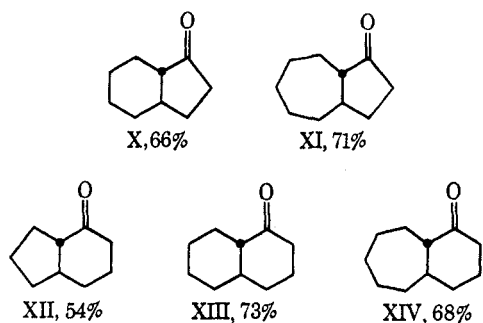
trated for the stereospecific conversion of cyclohexanone to the thermodynamically disfavored *trans*-perhydro-1-indanone (59). Similarly, by use of the allyl Grignard,



one can convert cyclohexanone stereospecifically to the corresponding *trans*-1-decalone (60). The reaction



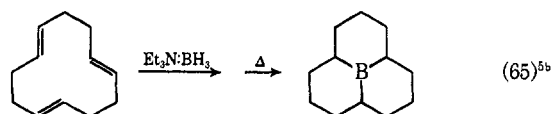
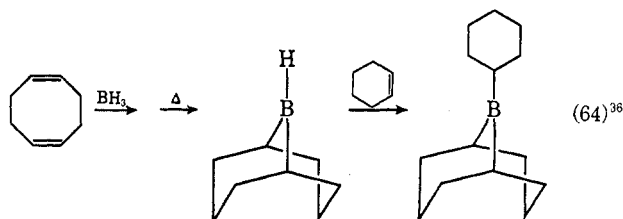
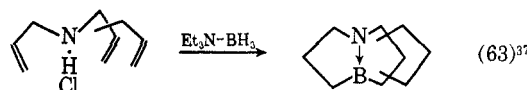
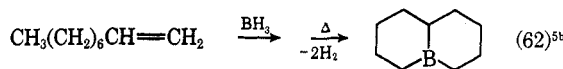
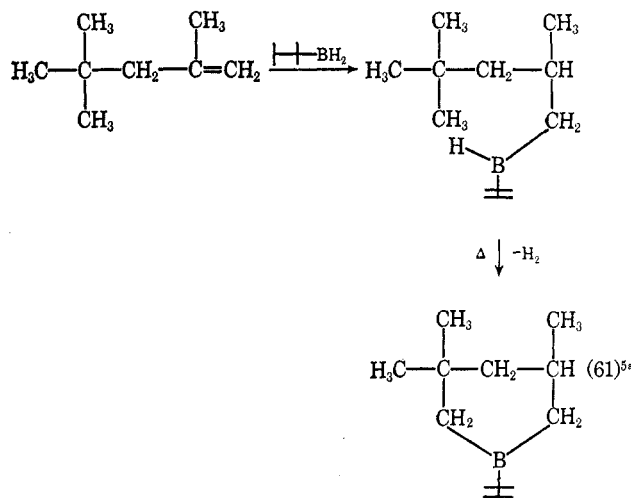
appears to be of considerable generality, as indicated by the following syntheses (the yields shown are based on diene (X-XIV)).



### Polycyclics<sup>35, 36</sup>

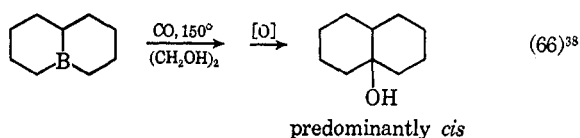
The remarkably easy addition of the boron-hydrogen bond to carbon-carbon double and triple bonds,<sup>2</sup> the less easy but still facile substitution of carbon-hydrogen

bonds by boron-hydrogen bonds,<sup>5a, b</sup> and the ready isomerization of organoboranes<sup>2</sup> all combine to give the organic chemist an unparalleled opportunity to utilize the unique characteristics of boron to bring together widely separated portions of a carbon structure into a more compact cyclic or polycyclic entity. Some representative examples follow (61-65).



It is evident that if the boron atom in these "stitched together" structures could be replaced by carbon, we could have a major new approach to the synthesis of complex carbon structures. We have tested this possibility on several representative systems and discovered that transformations proceed with remarkable ease (66-68).

Thus it is now possible to "stitch" with boron and

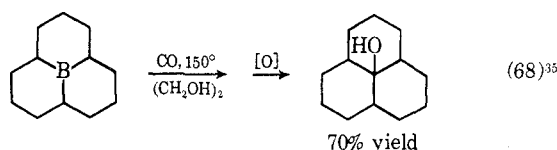
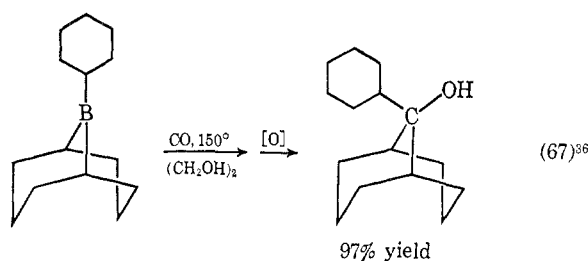


(35) H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5478 (1967).

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

(37) N. N. Greenwood, J. H. Morris, and J. C. Wright, *J. Chem. Soc.*, 4753 (1964).

(38) Research with E. Negishi.



then "rivet" with carbon, providing a remarkably simple new route to complex carbon structures.

### Conclusion

It is difficult to realize that less than 2 years has passed (at the time of this writing) since the initial experiments with carbon monoxide. However, progress can be very rapid with the assistance of competent, interested coworkers. It is important to have the right men at the right place at the right time. The development of hydroboration was greatly facilitated by the major contributions of Dr. B. C. Subba Rao and Dr. George Zweifel. The development of carbonylation was especially facilitated by the major contributions of Michael W. Rathke (now Dr.) and Dr. Eiichi Negishi. Developments in newer areas are being facilitated by the major contributions of George W. Kabalka, Dr. Milorad M. Rogić, and Dr. Akira Suzuki.

*It is a pleasure to acknowledge the assistance of Grant GM 10937 from the National Institutes of Health.*

## Coordination Compounds with Delocalized Ground States. The Transition Metal Derivatives of Dithiodiketones and Ethylene(1,2)dithiolates (Metal Dithienes)

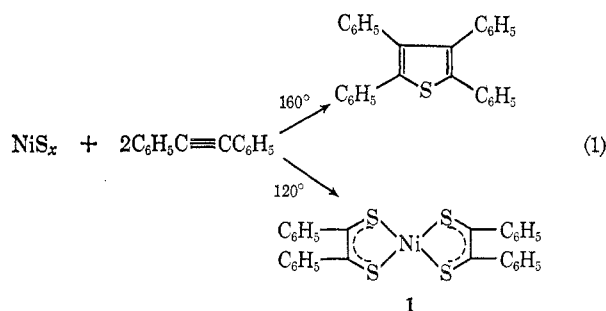
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*Received August 9, 1968*

### Early Developments

In 1961 the reaction of nickel sulfides with diphenylacetylene was studied<sup>1</sup> as a modification of Steinkopf's historical thiophene synthesis<sup>2</sup> from acetylene and pyrite. With technical grade nickel sulfide containing excess sulfur the formation of tetraphenylthiophene was observed to occur at higher reaction temperatures. Under milder conditions a complex was isolated for which structure **1** was proposed<sup>1</sup> on the basis of degradation experiments (eq 1). The structure of **1** was con-



firmed by X-ray analysis.<sup>3</sup> Complex **1** was also obtained from the combined reaction of sulfur with diphenylacetylene and metallic nickel (or Ni(CO)<sub>4</sub>).<sup>1</sup>

In substantiation of the initial working hypothesis, **1** was found to react with alkynes to yield thiophene derivatives. The reaction involves a 1,4 addition of the alkyne to a C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>S<sub>2</sub> ligand in the complex, producing a dithiadene intermediate which cleaves off sulfur to yield the thiophene. Due to the low yield of **1** obtained, the new thiophene synthesis at this stage was of course devoid of practical utility. Therefore, a more convenient synthesis of **1** was sought.

In the reaction of benzoin with P<sub>2</sub>S<sub>10</sub>,<sup>4</sup> thiophosphates of stilbenedithiol are formed which on treatment with metal salts afford the desired complexes. The reaction could be extended to acyloins and has become the most widely applicable method of synthesis.

Shortly after the appearance of the first report on "dithiobenzilnickel," several complex salts derived from maleonitriledithiol (MNT) were described.<sup>5</sup>

(1) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **84**, 3221 (1962).

(2) W. Steinkopf and G. Kirchoff, *Ann.* **403**, 1 (1914); **403**, 11 (1914).

(3) D. Sartain and M. R. Truter, *J. Chem. Soc.*, **A**, 1264 (1967).

(4) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Inorg. Chem.*, **4**, 1615 (1965).

(5) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, **84**, 4756 (1962).