

# Preparation of Organoboranes: Reagents for Organic Synthesis

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## 1 Introduction

Recent years have seen tremendous advances in the application of organoboranes as synthetic reagents.<sup>1-3a</sup> They possess a number of features which give them unique potential in this context. Firstly, except for  $\beta\gamma$ -unsaturated examples, they are generally unreactive in the 'typical' organometallic sense, *e.g.* with carbonyl compounds, and this allows the existence of organoboranes containing a wide variety of functionalities. Secondly, boron-carbon bonds are strong [*cf.*  $D(\text{B}-\text{C}) = 365 \text{ kJ mol}^{-1}$  in  $\text{Me}_3\text{B}$ ;  $D(\text{C}-\text{C}) = 349 \text{ kJ mol}^{-1}$  in  $\text{Me}_4\text{C}^4$ ], so that stereochemically defined organoboranes retain their stereochemical integrity under even rather forcing conditions. Thirdly, boron may be bonded by up to three different organic groups or be part of ring systems, and in the absence of catalysts unsymmetrical organoboranes redistribute only slowly. Under appropriate conditions all of these features may be useful during synthetic operations.

In order to take full advantage of these applications it is essential to understand the advantages and limitations of all the various synthetic routes to organoboranes. This review outlines the general features of these methods and suggests the most likely approaches to particular classes of organoboron compounds. Literature to January 1974 is covered completely and some important results appearing since then are included. However, in the interests of brevity and simplicity, no comprehensive reference list can be provided. Instead, the references cited (wherever possible monographs, reviews, or extensively documented papers) should be considered only as a lead-in to the literature covering the aspect under discussion.

## 2 General Survey of Organoborane Preparations

The first preparation of an organoborane by Frankland over a century ago used triethoxyborane and diethylzinc,<sup>5</sup> but later the more readily prepared Grignard reagents largely superseded the organozincs. More recently the ether-catalysed

<sup>1</sup> H. C. Brown, 'Boranes in Organic Chemistry', Cornell Univ., Ithaca, New York, 1972.

<sup>2</sup> G. M. L. Cragg, 'Organoboranes in Organic Synthesis', Dekker, New York, 1973.

<sup>3</sup> H. C. Brown, 'Organic Synthesis *via* Boranes', in press.

<sup>3a</sup> M. A. Grassberger, 'Organische Borverbindungen' Verlag Chemie, Berlin, 1971.

<sup>4</sup> G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, 'Principles of Organometallic Chemistry', Methuen, London, 1968.

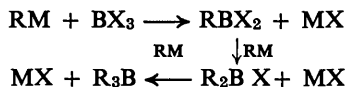
<sup>5</sup> E. Frankland, *J. Chem. Soc.*, 1862, 15, 363.

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addition of diborane to alkenes<sup>6</sup> has been most popular as a route to trialkylboranes.

The central objective of these reactions is the construction of boron-carbon bonds, but reactions which lead to no net increase, or even a decrease, in the number of these bonds may play an important role in the synthesis of partially substituted or unsymmetrically substituted organoboranes. This chapter will outline the characteristics of all major reactions which may be useful in organoborane synthesis.

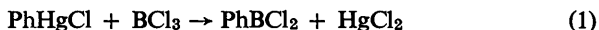
**Transmetallation.**—Scheme 1 shows the general scheme of the transmetallation reaction leading to organoboranes. A wide range of metals, M, and boron-bound



Scheme 1

groups, X, may be used, but correct choice is essential if good yields of pure compounds are to be obtained. This is the most general approach to organoboranes because potentially it can accommodate all kinds of organic groups, whether alkyl, aryl, alkenyl, or alkynyl.

When X is a halide and M is a metal which is significantly more electropositive than boron, the equilibrium in these reactions lies entirely with the organoborane and metal halide.<sup>4</sup> The same is probably true for X = alkoxide, but for other groups X (NR<sub>2</sub>, SR, *etc.*) the data are less conclusive. When the electronegativity of the metal is close to that of boron the thermodynamics may be finely balanced and directions of transmetallation may be reversed under appropriate conditions, as in reactions (1)<sup>7</sup> and (2).<sup>8a</sup>



Comparative kinetic data for reactions of given boron substrates with organic derivatives of different metals are scarce. The order of reactivity of phenyl derivatives towards B(OBu)<sub>3</sub> is Mg > Cd > Zn > Hg,<sup>9</sup> whilst towards B(NMe<sub>2</sub>)<sub>3</sub> methyl and ethyl derivatives decrease in reactivity in the order Al > Zn > Cd > Sn.<sup>10</sup> Already there is a conflicting order (between Zn and Cd) in these two systems, but these results taken together with qualitative comparisons of reaction conditions reported in a range of different studies suggest that, to a first approximation, the order of reactivity follows the order of electropositivity of the metal, *i.e.* K, Na > Li > Mg > Al > Zn, Cd > Pb, Hg, Sn.

<sup>6</sup> H. C. Brown, 'Hydroboration', Benjamin, New York, 1962.

<sup>7</sup> W. Gerrard, M. Howarth, E. F. Mooney, and D. E. Pratt, *J. Chem. Soc.*, 1963, 1582.

<sup>8</sup> See ref. 1; (a) p. 330; (b) p. 302; (c) p. 295; (d) p. 306; (e) p. 312; (f) Chapter 17; (g) p. 391; (h) p. 313.

<sup>9</sup> H. Gilman and L. O. Moore, *J. Amer. Chem. Soc.*, 1958, **80**, 3609.

<sup>10</sup> G. Abeler, H. Bayrhuber, and H. Nöth, *Chem. Ber.*, 1969, **102**, 2249.

The ease of displacement of various boron-bound groups X by Grignard reagents or organolithiums follows the order  $X = \text{Cl} > \text{OR} > \text{NR}_2$ ,<sup>11</sup> whilst towards triethylalane boron trihalides react in the order  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ .<sup>12</sup> Although reactivity orders may not be inviolate, these data and qualitative comparisons of a range of reaction conditions in other cases suggest the order halide  $> \text{OSiMe}_3, \text{OAc}, \text{OR} > \text{SR}, \text{H} > \text{R} > \text{NR}_2$ . It should be recognized that this is a very tenuous order based on comparisons of reactions which should not really be compared.

The stepwise order of reactivity towards a given organometallic is generally taken to be  $\text{BX}_3 > \text{RBX}_2 > \text{R}_2\text{BX}$ , but there is little genuine evidence to confirm this. In the reaction of triethylalane with halogenoboranes the differences are more marked for  $X = \text{Cl}$  than for the other halides, and the results for  $X = \text{F}$  may even suggest the reverse order.<sup>12</sup> Clearly the order must not be assumed, for it may be decisively influenced by the nature of X and R or even the metal.

Finally, alkenyl groups (and apparently phenyl even more so) are transferred more readily than alkyl groups from tin,<sup>13</sup> and possibly from other metals too.

Crude and uncertain though these generalizations are, they are necessary to assist in establishing the likely optimum combination(s) for a required synthetic operation. In addition other factors, such as the effect of the organometallic or the reaction conditions on redistribution processes (see below), must be considered. Several transmetallation reactions useful for specific types of organoborane syntheses have been described, and these are indicated in the appropriate sections below.

More comprehensive catalogues of transmetallation reactions which have been performed are available elsewhere.<sup>14,15a,16</sup> It is clear that much more investigation of these reactions is required before the factors discussed above can be properly understood.

**Hydroboration.**—The hydroboration reaction is a much more recent discovery than transmetallation, but its scope and limitations have been far better defined, due mainly to the mammoth efforts of H. C. Brown and his colleagues. The features of the reaction have been extensively reviewed,<sup>1,6,17</sup> and it is only necessary to give an outline here. The general reaction for ‘borane’ is shown in Scheme 2 (‘boranes’ written in inverted commas are really dimeric in the uncomplexed state).

Tetrasubstituted alkenes react readily only as far as the ‘monoalkylborane’. Trisubstituted alkenes and some disubstituted ones (*e.g.* cyclohexene) may

<sup>11</sup> M. F. Lappert and M. K. Majumdar, *J. Organometallic Chem.*, 1966, 6, 316.

<sup>12</sup> H. Nöth and W. Storch, *Synth. Inorg. Metal-Org. Chem.*, 1971, 1, 197.

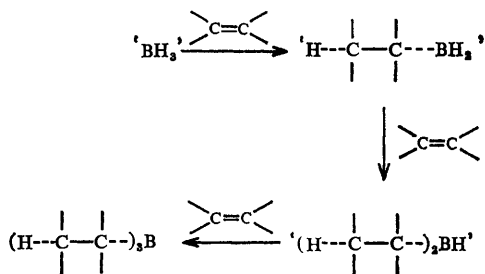
<sup>13</sup> F. E. Brinckman and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, 82, 6218.

<sup>14</sup> K. Smith, Ph.D. Thesis, Manchester, 1971.

<sup>15</sup> A. N. Nesmeyanov and R. A. Sokolik, in ‘Methods of Elemento-Organic Chemistry, Volume 1, North Holland, Amsterdam, 1967. (a) Chapters 1 and 2; (b) Chapter 6; (c) Chapter 14; (d) Chapter 10.

<sup>16</sup> M. F. Lappert, in ‘Chemistry of Boron and its Compounds’, ed. E. L. Muetterties, Wiley, New York, 1967, p. 443.

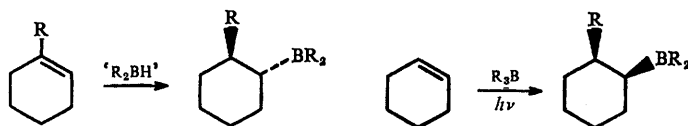
<sup>17</sup> G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, 13, 1.



Scheme 2

readily be stopped at the 'dialkylborane' stage, but simple unhindered alkenes proceed to the trialkylborane. The partially alkylated 'boranes' obtained from the more hindered alkenes may themselves be used to hydroborate alkenes of lower steric requirements. The products are then mixed trialkylboranes, and in some cases the steric requirements can be arranged so that stepwise hydroborations lead to totally unsymmetrical organoboranes. These invariably contain a 1,1,2-trimethylpropyl (thexyl) group, one group derived by hydroboration of a disubstituted alkene and the third from a mono- or di-substituted alkene.<sup>18</sup> Although in the wide context of unsymmetrical organoboranes these are of a very restricted type, they are very important in a number of organic syntheses.<sup>18</sup>

The addition of B—H occurs in a *cis* manner, giving stereochemically defined organoboranes in appropriate cases. The complementary stereochemistry may sometimes be achieved by the photochemically induced *cis*-addition of B—R to an alkene<sup>19</sup> (Scheme 3).



Scheme 3

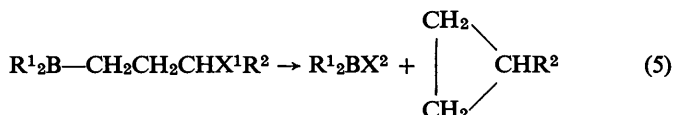
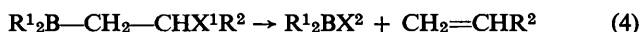
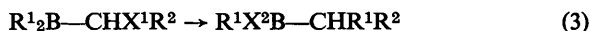
The direction of addition of B—H to an alkene is such as to place boron at the less-substituted position, and selectivity is enhanced for hydroborating agents

<sup>18</sup> E. Negishi and H. C. Brown, *Synthesis*, 1974, 77.

<sup>19</sup> N. Miyamoto, S. Isayama, K. Utimoto, and H. Nozaki, *Tetrahedron Letters*, 1971, 4597.

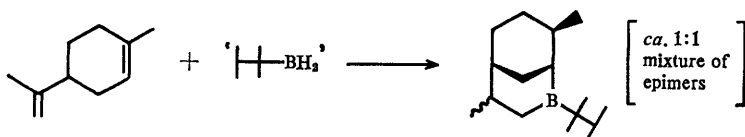
of greater steric requirements. [Hydroboration with  $\text{Et}_2\text{BH}$  followed by redistribution (see below) and removal of  $\text{Et}_3\text{B}$  enables this enhanced selectivity to be carried through to symmetrical trialkylboranes.<sup>19a</sup>] Substituents exerting a strong electronic influence may affect the orientation of addition, enhancing the proportion of boron attack at the more negatively charged end of the polarized  $\pi$ -cloud.

Hydroborations of functionalized alkenes are often possible because reductions of many functional groups by diborane are slower than hydroboration.<sup>1</sup> Extra caution is necessary when the product is  $\alpha$ ,  $\beta$ , or  $\gamma$ -functionalized because these compounds may be unstable and react, either spontaneously or under electrophilic or nucleophilic catalysis, as indicated in reactions (3)—(5). This is especially true when X is a good leaving group, and for reaction (4) if the



molecule can adopt a favourable stereochemistry (uncatalysed—*cis*; catalysed—*trans*). Details are given elsewhere.<sup>1,14,20</sup>

Alkynes may be mono- or di-hydroborated depending on the 'borane' used and the particular alkyne. 'Borane' itself dihydroborates terminal alkynes. The substitution pattern of allenes and the steric requirements of the 'borane' similarly influence whether attack occurs at the central carbon (giving vinylboranes), at a terminal position (giving allylboranes) or twice over.<sup>21–23a</sup> Non-cumulated dienes may be mono- or di-hydroborated,<sup>6</sup> and if the double bonds are suitably disposed with respect to each other, hydroboration may occur in a cyclic manner to give organoboron heterocycles.<sup>24</sup> An example of the use of 'thexylborane' for this purpose is given in Scheme 4.<sup>18</sup>



Scheme 4

<sup>19a</sup> R. Köster, G. Griasnow, W. Larbig, and P. Binger, *Annalen*, 1964, **672**, 1.

<sup>20</sup> D. J. Pasto and P. E. Timony, *J. Organometallic Chem.*, 1973, **60**, 19.

<sup>21</sup> D. S. Sethi, G. C. Joshi, and D. Devaprabhakara, *Canad. J. Chem.*, 1969, **47**, 1083.

<sup>22</sup> I. Mehrotra and D. Devaprabhakara, *Tetrahedron Letters*, 1972, 4871.

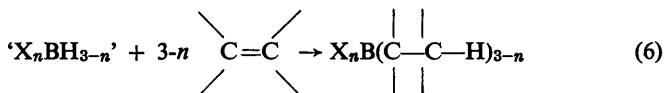
<sup>23</sup> B. M. Mikhailov, V. N. Smirnov, and O. D. Ryazanova, *Doklady Akad. Nauk S.S.S.R.*, 1972, **204**, 612.

<sup>23a</sup> L. Chevolut, J. Soulié, and P. Cadiot, *Tetrahedron Letters*, 1974, 3435.

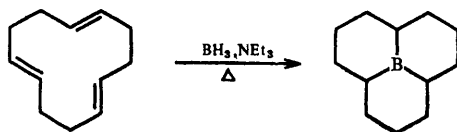
<sup>24</sup> H. C. Brown and E. Negishi, *Pure Appl. Chem.*, 1972, **29**, 527.

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In addition to 'borane' itself and the 'alkylboranes', several other hydroborating agents have been used. These are of the types 'X<sub>2</sub>BH', 'XBH<sub>2</sub>', and BH<sub>3</sub>L: Examples include X = Cl,<sup>25</sup> RO (especially 'catecholborane'<sup>26</sup>), R<sub>2</sub>N,<sup>27</sup> RS,<sup>28,29</sup> and L = R<sub>3</sub>N<sup>30</sup> or Me<sub>2</sub>S.<sup>31</sup> For a variety of reasons each of these hydroborating agents has a less-available vacant orbital in normal hydroboration solvents. This leads to a slower reaction and a necessity for extended reaction periods or more vigorous conditions. In the presence of catalytic  $\text{>B-H}$  bonds these conditions are often suitable for causing redistribution reactions (see below). Care should therefore be taken before utilizing a reaction of type (6) to ensure that the possibility of the occurrence of redistributions has been



eliminated. With 'chloroborane', for example, reaction in THF is slow and redistributions occur, whilst in the more weakly co-ordinating solvent diethyl ether, reaction is faster and redistribution is minimal.<sup>32</sup> On some occasions the presence of a low, steady concentration of 'borane' by thermal dissociation of borane-amine adducts may be an advantage, as in the synthesis of perhydro-9b-boraphthalenes (Scheme 5).<sup>33,33a,34</sup>



Scheme 5

A most significant development in the hydroboration reaction involves the *in situ* production of 'dialkylboranes' by reduction of derivatives R<sub>2</sub>BX (X = OR,<sup>35</sup> SR<sup>36</sup>) in the presence of an alkene. Rapid hydroboration results in the

<sup>25</sup> H. C. Brown and N. Ravindran, (a) *J. Org. Chem.*, 1973, **38**, 1617; (b) *J. Amer. Chem. Soc.*, 1973, **95**, 2396; (c) *J. Organometallic Chem.*, 1973, **61**, C5.

<sup>26</sup> H. C. Brown and S. K. Gupta, (a) *J. Amer. Chem. Soc.*, 1972, **94**, 4370; (b) *ibid.*, 1971, **93**, 1816.

<sup>27</sup> R. Köster, H. Bellut, S. Hattori, and L. Weber, *Annalen*, 1968, **720**, 32.

<sup>28</sup> T. A. Shchegoleva, E. M. Shashkova, V. G. Kiselev, and B. M. Mikhailov, *Zhur. obshchei Khim.*, 1965, **35**, 1078.

<sup>29</sup> D. J. Pasto, C. C. Cumbo, and P. Balasubramanian, *J. Amer. Chem. Soc.*, 1966, **88**, 2187.

<sup>30</sup> C. S. L. Baker, *J. Organometallic Chem.*, 1969, **19**, 287.

<sup>31</sup> R. A. Braun, D. C. Brown, and R. M. Adams, *J. Amer. Chem. Soc.*, 1971, **93**, 2823.

<sup>32</sup> H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, 1972, **94**, 2112.

<sup>33</sup> G. W. Rotermond and R. Köster, *Annalen*, 1965, **686**, 153.

<sup>33a</sup> N. N. Greenwood and J. H. Morris, *J. Chem. Soc.*, 1960, 2922.

<sup>34</sup> H. C. Brown and W. C. Dickason, *J. Amer. Chem. Soc.*, 1969, **91**, 1226.

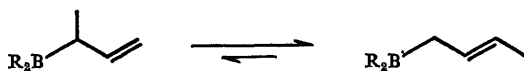
<sup>35</sup> H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, 1971, **93**, 1818; *J. Organometallic Chem.*, 1971, **32**, C1.

<sup>36</sup> A. Pelter and D. N. Sharrocks, *J.C.S. Chem. Comm.*, 1972, 566.

formation of mixed trialkylboranes,  $R^1_2BR^2$ . The major limitation of this approach is the great power of the reducing agents used ( $LiAlH_4$ ,  $AlH_3$ ), which will not tolerate many functional groups. This has been partially overcome for aluminium hydride, but there is clearly much scope for improvements based on milder reducing agents.

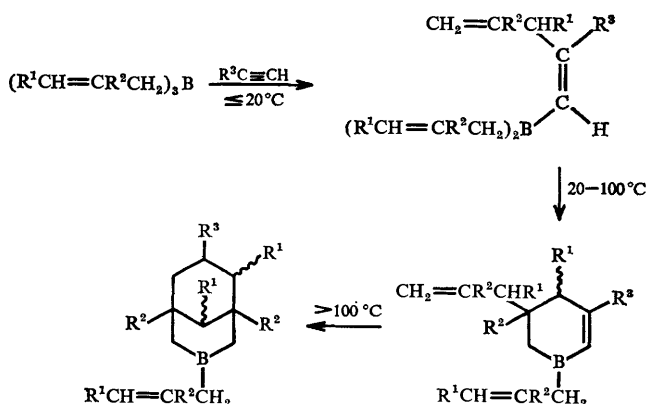
Where it is applicable hydroboration is the most convenient route to organoboranes. It is not applicable to the production of boron compounds bearing aryl, alkynyl, or methyl groups, or groups lacking a  $\beta$ -hydrogen atom (*e.g.* neopentyl), or indeed to many tertiary alkyl groups (hexyl is the important exception). It is limited in its application for secondary groups which would be derived from alkenes which are 1,2-disubstituted by different groups of comparable steric and electronic requirements.

**Allylboronation.**—Allyl groups bonded to boron undergo a permanent allyl rearrangement at ambient temperatures when there is an essentially vacant orbital on boron.<sup>37</sup> The equilibrium favours the isomer which involves lower steric interactions at boron (Scheme 6).



Scheme 6

Allylboranes are much more reactive than other classes of organoboranes and react more like 'typical' organometallics with carbonyl compounds, nitriles, and water. The reactions proceed with allyl rearrangement. In addition they react with certain carbon-carbon multiple bonds to form new B—C bonds. The most widely studied reactions are with alkynes where the 1:1 reaction proceeds in three well-defined stages (Scheme 7). The reaction has been performed with



Scheme 7

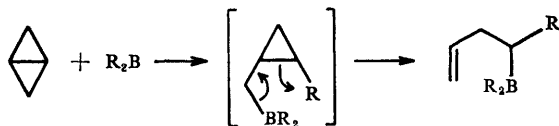
<sup>37</sup> B. M. Mikhailov, *Organometallic Chem. Rev. (A)*, 1972, 8, 1.

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$R^3 = H$ , alkyl, alkenyl, phenyl, alkoxy, trimethylsilyl, trimethylsilylmethyl, chloromethyl and for  $R^1R^2 = HH, HMe$ , or  $MeH$ .<sup>37</sup> In most cases the products are formed in good yields and substantially pure, but isomeric mixtures are formed in the case of  $R^3 = \text{chloromethyl}$ .<sup>38</sup> The initial diallyl(alkadienyl)boranes are clearly not very stable at ambient temperatures, but hydrolysis of the allyl groups produces alkadienylboron compounds which are stable.

Allenes undergo related allylboronation reactions which lead ultimately to derivatives of 3-borabicyclo[3,3,1]nonane.<sup>37,39</sup> Anomalous, 1-chloro-3,3-dimethylallene gives a boracyclopentane system rather than a boracyclohexane.

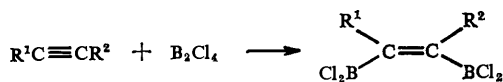
Cyclopropenes are also allylboronated with allyl rearrangement, but there is a side-product derived by unrearranged allylboronation of one of the saturated bonds. It emerges that this latter reaction is general for *trialkylboranes* reacting with small, highly strained ring systems such as cyclopropenes and bicyclobutane (Scheme 8).<sup>40</sup>



Scheme 8

The range of products available by allylboronation or the other reactions referred to in this section is clearly restricted. However, where these products are required they present a direct and convenient approach.

**Diboration, Haloboration and Friedel-Crafts-type Reactions.**—*Diboration.* Highly electrophilic diboron compounds add to unsaturated carbon-carbon links such as alkenes, alkynes, or cyclopropanes to give 1,2- or 1,3-diboryl compounds.<sup>41</sup> The reaction of  $B_2Cl_4$  with an alkyne is shown in Scheme 9.  $B_2F_4$  reacts similarly, but  $B_2(OR)_4$ ,  $B_2(NMe_2)_4$ , or amine complexes of  $B_2Cl_4$  are unreactive.



Scheme 9

<sup>38</sup> B. M. Mikhailov, B. I. Bryantsev, and T. K. Kozminkskaya, *Zhur. obshchei Khim.*, 1973, 43, 1108.

<sup>39</sup> B. M. Mikhailov, V. N. Smirnov, and E. P. Prokof'ev, *Dokl. Akad. Nauk S.S.S.R.*, 1972, 206, 125.

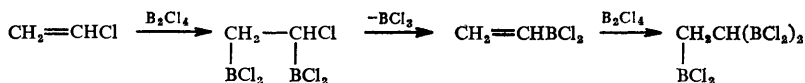
<sup>40</sup> B. A. Kazansky, Yu. N. Bubnov, S. V. Zotova, N. M. Abramova, V. G. Kiselev, and B. M. Mikhailov, *Tetrahedron Letters*, 1974, 567.

<sup>41</sup> T. D. Coyle and J. J. Ritter, *Adv. Organometallic Chem.*, 1972, 10, 237.



The effect of the structure of the unsaturated compound on the rate of reaction appears to follow a trend which correlates with steric factors. Thus, the rate of reaction decreases in the order ethylene > propene > but-2-ene, whilst vinyl chloride is also slower than ethylene.

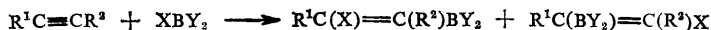
The stereochemistry of the addition is *cis*-. Alkynes generally give *vic*-diboryl-alkenes (Scheme 9), but a tetraboryl derivative can be obtained from acetylene itself. Alkenes give *vic*-diborylalkanes whilst cyclopropanes give 1,3-disubstituted compounds. Halogenoalkenes lead ultimately to triboryl compounds, as shown in Scheme 10.



Scheme 10

The major drawback of the diboronation reaction, in any case one of limited scope, is the lack of availability of  $\text{B}_2\text{X}_4$ .  $\text{B}_2\text{Cl}_4$  is fairly unstable at ambient temperatures and is prepared only with great difficulty.  $\text{B}_2\text{F}_4$ , though less reactive, is more stable, so that if a convenient preparation or commercial source should emerge the diboronation reaction would become more attractive.

**Haloboronation.** Haloboronation of an alkyne is shown in Scheme 11. Mixtures of geometrical isomers (*E/Z* mixtures) of each of the two positional isomers are obtained, and some of the factors which affect the proportions have been investigated.<sup>42</sup> The reaction with simple alkenes is complicated by a very ready reverse reaction, especially for  $\text{X} = \text{Cl}$ :<sup>43</sup> there is some evidence that  $\text{X} = \text{I}$  gives a more stable product.<sup>44</sup> More reactive alkenes such as dienes are also more satisfactory.



Scheme 11

Competition from addition of  $\text{B}-\text{Y}$  (Scheme 11) across the unsaturated linkage is yet another problem. All in all the reaction is preparatively extremely limited at the present state of knowledge.

**Friedel-Crafts Type.** Friedel-Crafts type reactions (equation 7) are rather more useful for the preparation of arylboron compounds.<sup>45</sup> All of the trihalogeno-

<sup>42</sup> J. R. Blackborow, *J.C.S. Perkin II*, 1973, 1989.

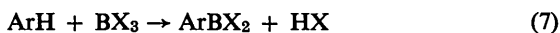
<sup>43</sup> F. Joy, M. F. Lappert, and B. Prokai, *J. Organometallic Chem.*, 1966, 5, 506.

<sup>44</sup> H. Mongeot, *Bull. Soc. chim. France*, 1970, 2505.

<sup>45</sup> E. L. Muetterties and F. N. Tebbe, *Inorg. Chem.*, 1968, 7, 2663.

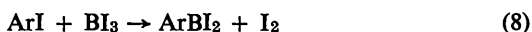
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boranes except  $\text{BF}_3$  are useful in this reaction, and  $\text{B}_2\text{Cl}_4$  gives a similar reaction



with benzene (though not with polynuclear aromatics).<sup>41</sup> The  $\text{BX}_3$  reaction is catalysed by a number of reagents, particularly aluminium,<sup>45</sup> or may be photochemically induced.<sup>46</sup> Benzene gives high yields of phenyldihalogenoboranes, but substituted compounds may give mixtures of products, some of which may involve rearrangement of substituents about the ring. The reaction has found recent application in the synthesis of ferrocenylboron compounds.<sup>47</sup>

The redox reaction between  $\text{BI}_3$  and aryl iodides (equation 8) is more specific in that the boron generally attaches to the point where iodine was originally attached. However, traces of moisture ( $\text{BI}_3 \rightarrow \text{HI}$ ) and long reaction times at



*ca.* 100 °C can cause isomerizations by a deborylation–Friedel–Crafts borylation mechanism.<sup>48</sup> The problem appears to be more acute for *o*-iodotoluene than for other isomers, possibly because of a steric effect. This reaction has considerable potential if these difficulties can be properly overcome.

**Action of Heat on Organoboranes.**—The effect of heat on organoboranes can be discussed in terms of three processes—redistribution, isomerization, and cyclo-elimination. Redistributions of organoboranes are discussed separately in the next section, but the other two processes are considered here. Redistribution and isomerization processes pose a serious threat to the success of particular organoborane syntheses, especially those of mixed organoboranes.

**Isomerization.** Alkylboron compounds isomerize above *ca.* 130 °C, but the

process is catalysed by  $\text{B—H}$  bonds so heating should be avoided as far as

possible during hydroboration reactions. Although the actual mechanism is probably somewhat different, most of the factors of interest for synthetic chemists can be understood in terms of a retrohydroboration-rehydroboration mechanism (Scheme 12). The boron migrates past a single, but not a double branch, and the equilibrium mixture has boron attached primarily to the least hindered carbon atom.<sup>6,8b</sup> Tertiary alkylboron compounds isomerize especially readily. Organoboranes possessing functional groups may give unusual equilibrium structures owing to the formation of boron–heteroatom bonds in cyclic structures.<sup>49</sup>

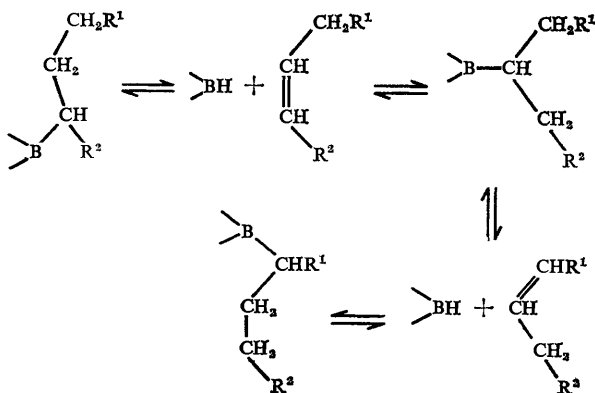
Although isomerization is a danger which should normally be avoided, in some cases it may be that the equilibrium product mixture is cleaner than the

<sup>46</sup> R. A. Bowie and O. C. Musgrave, *J. Chem. Soc. (C)*, 1970, 485.

<sup>47</sup> W. Ruf, M. Fueller, and W. Siebert, *J. Organometallic Chem.*, 1974, **64**, C45.

<sup>48</sup> W. Siebert, F. R. Rittig, and M. Schmidt, *J. Organometallic Chem.*, 1970, **25**, 305.

<sup>49</sup> K. Sisido, M. Naruse, A. Saito, and K. Utimoto, *J. Org. Chem.*, 1972, **37**, 733.



Scheme 12

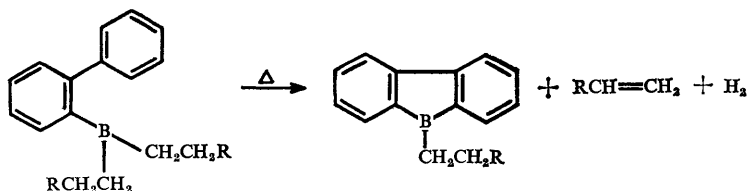
kinetic product mixture. Isomerization is then an advantage, *e.g.* in the formation of '9-borabicyclo[3,3,1]nonane' (9-BBN) from cyclo-1,5-octadiene and diborane.<sup>8c</sup>

**Cycloelimination.** Under still harsher conditions ( $\geq 200^\circ\text{C}$ ) trialkylboranes eliminate olefin and hydrogen to give organoboron heterocycles.<sup>50</sup> Five- and six-membered rings predominate in the products, which depend on the chain lengths in the original trialkylborane. Thus, whilst tripropyl- and trihexyl-boranes give monocyclic compounds, trioctylborane can give (1) and trinonylborane (2). For more complex trialkylboranes the processes are complicated by isomerizations,



and mixtures result.<sup>8d</sup> In any case, when the appropriate di- or tri-enes are available, their hydroboration is a more direct route to these products.<sup>8e</sup>

However, aryl- or aralkyl-boron compounds cyclize both more specifically and under milder conditions than the aliphatic analogues, providing a very elegant route to the corresponding heterocycles (*e.g.* Scheme 13).<sup>50</sup> Recently it

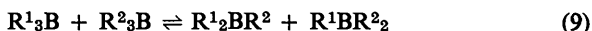


Scheme 13

<sup>50</sup> R. Köster, G. Benedikt, W. Fenzl, and K. Reinert, *Annalen*, 1967, **702**, 197.

has been suggested that pyridine-arylboranes have advantages for this procedure.<sup>51</sup> Cycloelimination is not likely to be competitive under the conditions of most organoborane syntheses. Used synthetically it is limited in scope but may provide the most direct route to many organoboron heterocycles.

**Redistribution Reactions.**—Redistribution reactions present one of the greatest threats to the successful synthesis of unsymmetrical organoboranes, but they may also be of great utility in preparation of partially alkylated compounds. Equations (9) and (10) represent the general reactions.



Pure unsymmetrical trialkylboranes are generally stable below 100 °C and can be distilled unchanged below this temperature. However, B—H compounds

and especially aluminium alkyls strongly promote equilibrium (9) so that redistributed products may be obtained even at low temperatures.<sup>52</sup> The ready formation of mixed bridging species is presumably responsible. Furthermore, although the possibility has not been investigated it appears likely that Group I and other organometallics may also catalyse redistribution through processes such as (11) (compare ref. 52*a*). This could account for several failures to obtain high yields of unsymmetrical organoboranes by organometallic routes.



Since both of the major approaches to organoboranes may involve reagents which catalyse redistribution processes, very great care must be taken to ensure that reactions are rapid, and occur under mild conditions with a slight deficiency of reagent, if any success in preparing mixed trialkylboranes is to be achieved.

The final equilibrium composition of a redistributed mixture is known in very few cases. Although triethylaluminium-catalysed redistribution of triethylborane-triisopropylborane mixtures leads to an almost statistical product distribution,<sup>53</sup> it is unlikely that this is general when the alkyl groups have significantly different steric requirements.

Redistributions of type (10) are also catalysed by B—H compounds. The nature of X and the organic group determine the rate of reaction and the equilibrium position. To a first approximation the rate appears to increase with

<sup>51</sup> R. van Veen and F. Bickelhaupt, *J. Organometallic Chem.*, 1973, **47**, 33.

<sup>52</sup> R. Köster, G. Benedikt, W. Larbig, K. Reinert, and G. Rotermund, *Angew. Chem. Internat. Edn.*, 1964, **3**, 174.

<sup>52*a*</sup> M. A. Grassberger and R. Köster, *Angew. Chem. Internat. Edn.*, 1969, **8**, 275.

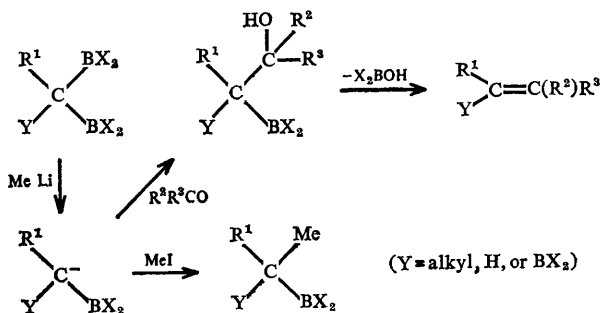
<sup>53</sup> R. Köster and G. Bruno, *Annalen*, 1960, **629**, 89.

increased ease of bridge formation. Thus, secondary alkyl groups redistribute more slowly than primary and this can lead to problems associated with isomerization (see above).<sup>54</sup> Lewis bases inhibit redistribution.<sup>55</sup>

Equilibrium constants are known in only a few cases. Redistribution of the system  $\text{Ph}_3\text{B}-\text{B}(\text{NMe}_2)_3$  gives predominantly  $\text{Ph}_2\text{BNMe}_2$  [disproportionation constant *ca.* 70 times lower than for  $\text{PhB}(\text{NMe}_2)_2$ ], whilst in the system  $\text{Ph}_3\text{B}-\text{B}(\text{OMe})_3$  the product mixture is almost statistical.<sup>56</sup> Systems which give substantially a single product are  $2\text{R}_3\text{B}-\text{B}(\text{OAr})_3$  (product  $\text{R}_2\text{BOAr}$ )<sup>57</sup> and trimethyleneborate- $\text{R}_3\text{B}$  (boron ratio 2:1; product 2-alkyl-1,3,2-dioxaborinane, an alkaneboronic acid cyclic ester).<sup>58</sup> Although others are not so clear-cut, use of an excess of  $\text{BX}_3$  ensures maximum utilization of organic groups as  $\text{RBX}_2$ . This has been employed for alkyldihalogenoboranes<sup>54,55</sup> and for 'arylboranes'.<sup>59</sup>

Sometimes redistributions affect exocyclic alkyl groups more readily than ring systems, but the borolane ring is particularly readily cleaved by 'borane'. More details of redistribution reactions are given elsewhere.<sup>14,15b,16</sup>

**Other Relevant Reactions.—Modification of Boron-bound Groups.** Introduction of  $\alpha$ -branches into alkyl groups attached to boron can be achieved by alkylation of boron-stabilized carbanions. These anions may be obtained by direct deprotonation with a hindered base,<sup>60</sup> but a more reliable route involves nucleophilic displacement of boron from polyborylmethanes, themselves obtained from tetrakis(dialkoxyboryl)methanes<sup>61</sup> or by dihydroboration of terminal alkynes.<sup>62</sup> Diborylmethyl carbanions react with carbonyl compounds to give alkenylboron compounds. These reactions are generalized in Scheme 14.



Scheme 14

<sup>54</sup> H. C. Brown and A. B. Levy, *J. Organometallic Chem.*, 1972, **44**, 233.

<sup>55</sup> R. Köster and M. A. Grassberger, *Annalen*, 1968, **719**, 169.

<sup>56</sup> H. K. Hofmeister and J. R. van Wazer, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1209.

<sup>57</sup> H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, 1971, **93**, 2802.

<sup>58</sup> H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, 1970, **92**, 6983.

<sup>59</sup> B. M. Mikhailov and V. A. Dorokhov, *Zhur. obshchei Khim.*, 1969, **31**, 4020.

<sup>60</sup> R. Kow and M. W. Rathke, *J. Amer. Chem. Soc.*, 1973, **95**, 2715.

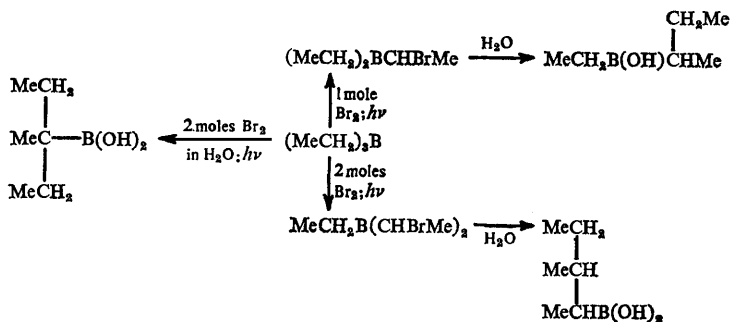
<sup>61</sup> D. S. Matteson and P. B. Tripathy, *J. Organometallic Chem.*, 1974, **69**, 53.

<sup>62</sup> G. Zweifel, R. P. Fisher, and A. Horng, *Synthesis*, 1973, 37.

## Preparation of Organoboranes: Reagents for Organic Synthesis

Many standard organic reactions may be performed on organoboranes without rupture of the B–C bonds. These have been used most frequently for establishing the structure of allylboronation products<sup>37</sup> or in modifying the substitution patterns of areneboronic acids,<sup>15c</sup> but other examples are also in the literature. Although areneboronic acids are amongst the most stable of organoboranes, it is perhaps surprising to realize that they may be ring-nitrated in 80% yield with fuming nitric acid.<sup>15c</sup> This gives hope for many other transformations not yet investigated.

**Rearrangement Reactions.** All reactions of organoboranes<sup>1–3a</sup> are potentially of significance in organoborane synthesis, but a full discussion is not warranted here. However, certain rearrangement reactions<sup>63</sup> are particularly useful. These include ‘riveting’ reactions (where boron is directly replaced by a functionalized carbon atom) using carbon monoxide,<sup>8f</sup> sodium cyanide–trifluoroacetic anhydride,<sup>64</sup> or dichloromethyl ether–strong base<sup>65</sup> (reaction 12); rearrangement of  $\alpha$ -bromo-organoboranes (Scheme 15);<sup>6a,66</sup> and reaction of trialkylalkynylborates with electrophiles (reaction 13).<sup>67,68</sup> Points of interest to note are relative



**Scheme 15**



migratory aptitudes ( $1^\circ > 2^\circ > 3^\circ$  for ‘riveting’ and bromination reactions, but little selectivity for alkynylborates), site of attack of bromine ( $2^\circ > 1^\circ$ ) and the possibility of *E/Z* mixtures (reaction 13). In many cases the boron compounds formed have not been isolated, but their existence is established by oxidation and/or hydrolysis.

<sup>63</sup> P. I. Paetzold and H. Grundke, *Synthesis*, 1973, 635.

<sup>64</sup> A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, *J.C.S. Perkin I*, in press; see *Chem. Comm.*, 1971, 1048.

<sup>65</sup> H. C. Brown, J.-J. Katz, and B. A. Carlson, *J. Org. Chem.*, 1973, **38**, 3968.

<sup>66</sup> Y. Yamamoto and H. C. Brown, *J. Org. Chem.*, 1974, **39**, 861.

<sup>67</sup> P. Binger and R. Köster, *Synthesis*, 1974, 350.

<sup>68</sup> A. Pelter and K. J. Gould, *J.C.S. Chem. Comm.*, 1974, 347.

**Dealkylation.** Dealkylation reactions of type (14) may be the simplest route to compounds  $R_2BX$ . However, water, alcohols, amines, and even mineral acids do



not react with trialkylboranes under mild conditions. Alkanethiols (with radical initiators)<sup>86</sup> or carboxylic acids<sup>8h</sup> do. The carboxylic acid reaction has been more widely studied. Here it is known that the ease of cleavage decreases in the order  $1^\circ > 2^\circ > 3^\circ$  and that two groups are readily removed. Pivalic acid may be used as a catalyst for monodealkylation with water or alcohols.<sup>69</sup>

### 3 Preparation of Compounds with One B—C Bond

There are three major approaches to compounds of the type  $RBX_2$ : (i) double dealkylation of readily available  $R_3B$ ; (ii) redistribution between  $R_3B$  and  $BX_3$ ; (iii) direct synthesis of only one B—C bond. Process (i) involves wastage of two organic groups and will only be useful when these are simple and inexpensive. Process (iii) is conceptually ideal, but in practice it is frequently difficult, so that process (ii) is sometimes more convenient. Subsequent modification of a boron-bound group should always be considered.

**Alkylboron Compounds.**—Hydroboration is the most attractive route to alkylboron compounds in general, but except for tetrasubstituted alkenes<sup>6,18</sup> or alkenes with co-ordinating groups in the alkyl residue<sup>31</sup> it is usually impossible to stop at the 'monoalkylborane' stage with diborane. Mixed hydroborating agents of the type ' $X_2BH$ ' may directly give  $RBX_2$  when redistribution is not competitive, and conditions where this holds have been worked out in the cases  $X = Cl$ <sup>25b</sup> and  $X_2 =$  benzenedioxy.<sup>26b</sup> Alkyldichloroboranes are particularly useful compounds for conversions into other species,  $RBX_2$ .<sup>15d</sup> Some compounds of the type ' $RBH_2$ ' may be prepared by displacement of 2,3-dimethylbut-2-ene from 'hexylmonoalkylboranes' with triethylamine,<sup>70</sup> but in this case R is always derived from a disubstituted alkene; decomplexation of the amine adduct releases the free 'alkylborane', which rapidly redistributes if not utilized.

The advantages of hydroboration may alternatively be retained by redistribution processes. The reaction of polymeric trimethylene borate with trialkylboranes (boron ratio 2:1) cleanly gives alkaneboronic acid cyclic esters,<sup>58</sup> but the simple expedient of employing an excess of  $BX_3$  allows quantitative formation of  $RBX_2$  (based on  $R_3B$ ) in other cases. This may be more convenient, especially for  $X = Cl$ <sup>54,55</sup> because of the synthetic utility of alkyldichloroboranes.

Tertiary alkylboron compounds other than the xethyl derivatives are not normally available by hydroboration. They may be synthesized by an organometallic route but a simpler approach when the appropriate starting organoborane is available may be a rearrangement process, particularly 'riveting' reactions (equation 12)<sup>8f,64,65</sup> or bromination-rearrangement reactions (Scheme 15).<sup>8g,66</sup>

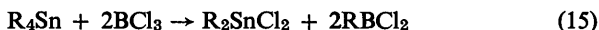
Other alkyl groups which cannot be attached cleanly or conveniently by

<sup>69</sup> R. Köster, H. Bellut, and W. Fenzl, *Annalen*, 1974, 54.

<sup>70</sup> H. C. Brown, E. Negishi, and J.-J. Katz, *J. Amer. Chem. Soc.*, 1972, 94, 5893.

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hydroboration must be attached *via* transmetallation. Reactions of Grignard reagents with trialkoxyboranes have often been used to attach a single, even functionalized group,<sup>71</sup> but the yields are seldom better than 60%. Although better results are claimed for reactions of BCl<sub>3</sub> with tetra-alkylstannanes,<sup>72</sup> only two alkyl groups are transferred (reaction 15), so that yields based on this



component cannot be better than 50% unless some marked selectivity of transfer should be discovered. The route has the advantage that clean boron products are obtained, and possibly difficult separations are thereby avoided.

Ethylidihalogenoboranes have been obtained fairly cleanly and with quantitative utilization of ethyl groups by the reaction of triethylaluminium with trihalogenoboranes (except BF<sub>3</sub>).<sup>12</sup> If this should prove to be general it is a significant development, particularly in view of the availability of many organoaluminium compounds. Another promising approach involves using a boron substrate from which only one group X is readily displaced, *e.g.* *N*-trimethyl-*B*-trichloroborazine. Grignard reagents may then be employed.<sup>15a</sup>

**Arylboron Compounds.**—Redistribution processes have received less attention for production of ArBX<sub>2</sub>, but they are presumably subject to considerations similar to those for aliphatic analogues. 'Arylboranes', 'ArBH<sub>2</sub>', have been prepared in this way.<sup>59</sup>

The most general route to ArBX<sub>2</sub> involves transmetallation,<sup>15a</sup> followed when necessary by modification of the aryl residue.<sup>15c</sup> Reactions of Grignard reagents or organolithiums with trialkoxyboranes have often been used,<sup>15a</sup> but the reaction of tetra-arylstannanes with BCl<sub>3</sub><sup>73</sup> is superior. Unlike the alkytin reaction all four aryl groups are transferred, so yields based on aryl groups are high. In view of the ease of synthesis of many arylmercury compounds, their convenience may sometimes compensate for poorer yields (on reaction with BCl<sub>3</sub><sup>7</sup>) than in the tetra-arylstannane route.

Less general routes to monoarylboron compounds are Friedel-Crafts and related reactions. The most useful of these is the redox reaction, equation (8).<sup>48</sup>

**Alkenyl and Other Organic Groups.**—Many monoalkenylboron compounds can be prepared by hydroboration of alkynes with 'dichloroborane' in pentane<sup>25c</sup> or 'catecholborane' in ether solvents.<sup>26a</sup> Examples lacking a β-hydrogen atom may be obtained from reaction of diborylmethyl carbanions with ketones (Scheme 14).<sup>61</sup> Vinyldichloroborane itself has been prepared from vinyltin derivatives.<sup>74</sup> Only two vinyl groups are transferred from tetravinylstannane, but vinyl groups are transferred selectively from divinylidibutylstannane.<sup>13</sup> It is not clear how far competing reactions such as halogenoboration limit the generality of this

<sup>71</sup> L. Miginiac and J. Blais, *J. Organometallic Chem.*, 1971, 29, 349.

<sup>72</sup> K. Niedenzu, J. W. Dawson, and P. Fritz, *Inorg. Synth.*, 1967, 10, 126.

<sup>73</sup> J. Hooz and J. G. Calzada, *Org. Prep. Proced. Internat.*, 1972, 4, 219.

<sup>74</sup> G. C. Brown, B. E. Deuters, W. Gerrard, and D. B. Green, *Chem. and Ind.*, 1965, 1634.



procedure.<sup>75</sup> Reactions using alkenyl-lithiums and trialkoxyboranes give low yields, but alkenyl Grignard reagents give yields in the region 50—90%.<sup>15a</sup>

$\beta$ -Chloroalkenylboron compounds are available from  $\beta$ -chloroalkenyl-mercury derivatives,<sup>15a</sup> or by chloroboration of alkynes.<sup>42</sup> Monoalkenylboron compounds can only be prepared by transmetallation, but few systems have been studied.

A simple route to alka-1,4-dienylboron compounds involves the low temperature 1:1 reaction of triallylboranes with alkynes (Scheme 7), followed by hydrolytic removal of the residual allyl groups.<sup>37</sup> The best route yet discovered for preparation of monocyclopentadienylboron compounds involves reaction of potassium cyclopentadienide with *B*-trichloro-*N*-trimethylborazine, but the yield is still only 40%.<sup>76</sup>

**Compounds with Two Boryl Groups.**—The most general route to 1,2-diborylalkanes or 1,2-diborylalkenes involves diboration of alkenes or alkynes,<sup>41</sup> but the reagents are inconvenient. In the trivial case of 1,2-diborylethanes, the products may be obtained by redistribution between  $BX_3$  and the polymeric hydroboration product of acetylene,<sup>77</sup> but this is not general for other alkynes.

1,1-Diborylalkenes are available by the reactions of triborylmethylcarbanions with carbonyl compounds, whilst alkylation of diborylmethylcarbanions gives 1,1-diborylalkanes.<sup>61</sup> A potentially useful approach to 1,1-diborylalkanes, as yet unexplored, involves dihydroboration of alkynes, followed when necessary by redistribution.

1,3-Diborylalkanes are available by diboration of cyclopropanes,<sup>41</sup> and probably by hydroboration of allylboron compounds with dichloroborane, though the experiment has not been performed. Other 1,*n*-diborylalkanes ( $n \geq 4$ ) are only specific examples of monoalkylboron compounds, but an additional preparation involves redistribution between  $BX_3$  and the indeterminate products from hydroboration of dienes.

#### 4 Preparation of Compounds with Two B—C Bonds

The three basic approaches (dealkylation of  $R_3B$ , redistribution of  $R_3B/BX_3$ , and direct attachment) which were applied to synthesis of compounds  $RBX_2$  may also be applied for  $R_2BX$ . Dealkylation is less wasteful in this case and may represent an attractive approach when the organic moiety is not too valuable, but its applicability to mixed compounds,  $R^1R^2BX$ , is limited by the degree of selectivity of cleavage from compounds  $R^1_2BR^2$ , and by their availability. Redistribution reactions are less general because the simple expedient of employing an excess of  $BX_3$  cannot now be used. Instead, the equilibrium must strongly favour formation of  $R_2BX$ , a condition which appears to hold for  $BX_3 = B(NMe_2)_3$  ( $R = Me, Et^{10}$  or  $Ph^{56}$ ) or  $B(OAr)_3$  ( $R = alkyl^{57}$ ) and in some cases  $BCl_3$ .<sup>55</sup> Redistribution is essentially useless as a general route to mixed species,

<sup>75</sup> Y. Tanigawa, I. Moritani, and S. Nishida, *J. Organometallic Chem.*, 1971, **28**, 73.

<sup>76</sup> B. L. Therrell and E. K. Mellon, *Inorg. Chem.*, 1972, **11**, 1137.

<sup>77</sup> G. F. Clark and A. K. Holliday, *J. Organometallic Chem.*, 1964, **2**, 100.

$R^1R^2BX$ . Cyclic compounds are a special category which, from the point of view of dealkylation or redistribution, are often like symmetrical compounds.

**Two Identical Groups.**—Dealkylation and redistribution reactions as routes to  $R_2BX$  have been discussed above. Their success depends on the availability of  $R_3B$  (see below).

Trisubstituted alkenes and some disubstituted alkenes may be hydroborated directly to the 'dialkylborane' stage with 'borane'. Dithexylborane may also be prepared in low yield.<sup>78</sup> For other alkenes, 'chloroborane' in ether may be used for hydroboration without incurring redistribution, and this same reagent may be applied in the synthesis of dialkenylchloroboranes from alkynes.<sup>25a</sup>

For organic groups which cannot easily be attached to boron by hydroboration, transmetallation may be used. It is significant that, with proper control of conditions, good yields of diethylhalogenoboranes can be obtained on reaction of triethylaluminium with trihalogenoboranes (not  $BF_3$ ).<sup>12</sup> Reactions of aryl Grignard reagents with trialkoxyboranes have often been employed for preparation of  $Ar_2BOH$ . Although yields are only *ca.* 60%, the products are readily purified as their ethanalamine esters.<sup>15a</sup> Claims made for the preparation of diphenylchloroborane from phenylmercuric chloride and  $BCl_3$  appear to be unjustified, since the yield does not appear to be better than 50%.<sup>74</sup>

Bis-(2-iodoethyl)iodoborane,  $(ICH_2CH_2)_2BI$ , has been prepared by iodoboration of ethylene,<sup>44</sup> but the generality of this method is questionable.

**Two Dissimilar Groups.**—Redistribution and dealkylation are of lesser importance for preparation of  $R^1R^2BX$ , although exceptional cases may always be found; *e.g.* the synthesis of  $RB(X)(CH_2)_4Br$  by brominolysis of *B*-alkylborolanes in pyridine.<sup>79</sup>

Except for some hexylmonoalkylboranes<sup>18</sup> and some hexyl(halogenoalkenyl)boranes,<sup>80</sup>  $R^1R^2BX$  are not generally available by stepwise hydroborations starting from 'borane'.<sup>6</sup> Perhaps more success is possible starting from 'chloroborane', but the necessary experiments have not been reported.

Transmetallation studies (reaction 16) have centred mainly on reactions of Grignard reagents or organolithiums with alkoxyboron compounds,<sup>15a</sup> but



unfortunately these are probably poor systems from the point of view of redistributions unless considerable care is taken (see above). Yields are rarely better than 60%, but once the reactions have been quenched the products may

be purified as ethanalamine esters.<sup>15a</sup> Use of  $RB(Cl)OCH_2CH_2NH_2$  as reagent

<sup>78</sup> E. Negishi, J.-J. Katz, and H. C. Brown, *J. Amer. Chem. Soc.*, 1972, **94**, 4025.

<sup>79</sup> L. S. Vasil'ev, V. P. Dmitrikov, and B. M. Mikhailov, *Zhur. obshchei Khim.*, 1972, **42**, 1015.

<sup>80</sup> E. Negishi and T. Yoshida, *J. C. S. Chem. Comm.*, 1973, 606.

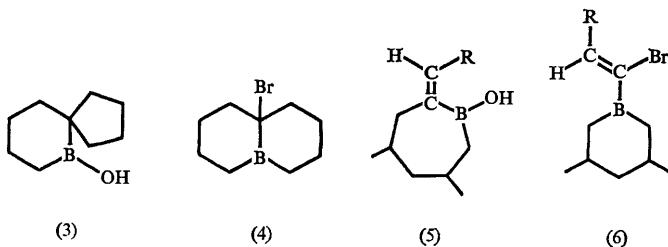
seems somewhat better,<sup>81</sup> and claims have also been made for specific types of  
 B—OSiMe<sub>3</sub> compound in this context.<sup>82</sup>

Two types of rearrangement reaction are useful for certain compounds R<sup>1</sup>R<sup>2</sup>BX; (i)  $\alpha$ -halogeno-organoboranes rearrange to compounds of type R<sup>1</sup>B(X)CH(R<sup>1</sup>)R<sup>2</sup> (Scheme 15)<sup>83,66</sup> or hexylB(X)C(R<sup>1</sup>)=CHR<sup>2</sup><sup>80</sup> and (ii) stopping the carbonylation<sup>8f</sup> or cyanidation<sup>64</sup> reactions (equation 12) after two migrations instead of three gives compounds of general type RB(X)CR<sub>2</sub>Y. Clearly the scope is limited.

**Boron in an Otherwise Carbocyclic Ring System.**—Cyclic disubstituted boron compounds may be obtained by redistribution<sup>55</sup> of the dumb-bell shaped or polymeric molecules formed in the 3:2 reactions of some dienes with 'borane'.<sup>24</sup> Sometimes the 1:1 reactions give cyclic 'dialkylboranes' directly.<sup>24</sup> Five-, six-, and seven-membered rings are readily formed during cyclic hydroborations, but borolane rings are readily cleaved by excess 'borane' so that the 1:1 reaction is most suitable for six- and seven-membered rings.<sup>24,83</sup> Other hydroborating agents, 'XBH<sub>2</sub>', may give all three types of ring system.<sup>28</sup> Mixtures may be formed in all cases; sometimes isomerization may lead to a cleaner product.<sup>24</sup>

Some cyclic dialkylboron compounds have been prepared from dilithium reagents<sup>15a</sup> or cyclic organomercury compounds,<sup>84</sup> but the reactions have not been investigated in any systematic way. A similar comment applies to intramolecular Friedel-Crafts type reactions, or pyrolysis reactions, which have been used, for example, in preparation of dihydro-9b-bora-anthracene derivatives.<sup>51</sup>

Boracyclohexenes and 3-borabicyclo[3,3,1]nonenes may be obtained by hydrolytic removal of an allyl group from the products of allylboration (Scheme 7).<sup>37</sup> Other rather specific types of ring compound are available from rearrangements of various kinds of  $\alpha$ -halogeno-organoboron compounds, e.g. (3) from (4)<sup>66</sup> and (5) from (6).<sup>85</sup>



<sup>81</sup> B. M. Mikhailov, T. V. Kostroma, and N. S. Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1957, 589.

<sup>82</sup> B. Roques and D. Florentin, *J. Organometallic Chem.*, 1972, 46, C38.

<sup>83</sup> H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, 1973, 95, 6757.

<sup>84</sup> R. Clement, *Compt. rend.*, 1965, 261, 4436.

<sup>85</sup> G. Zweifel and R. P. Fisher, *Synthesis*, 1972, 557.

## 5 Preparation of Compounds with Three or Four B—C Bonds

**Three Identical Groups.**—Unless the group R is bulky or leads to an unstable organoborane, compounds of the type  $R_3B$  are probably the most readily synthesized organoboron compounds.

Where it is possible, hydroboration is the most convenient approach to trialkylboranes, but other compounds are readily prepared by transmetallation. Transmetallation requires a reactive boron substrate, usually a trihalide but possibly  $B(OR)_3$  or  $'BH_3'$ , and a fairly reactive organometallic reagent, usually a Grignard reagent, but possibly a derivative of Li, Na, Al or even Zn or Pb. The most popular system is a Grignard reagent with  $BF_3$ ,<sup>15a</sup> and a recent modification using diborane as substrate<sup>86</sup> appears to offer no advantage. The reaction is applicable to trialkylboranes, triallylboranes, or triarylboranes.<sup>15a</sup> Recently, optimum conditions for preparation of  $Ph_3B$  by this method have been described.<sup>87</sup>

Occasional use of the system  $RLi-BF_3$  for preparation of  $R_3B$  is exemplified by the preparation of tri-indenylborane.<sup>88</sup> More widespread application is deterred by a report that  $Li^+Bu_4B^-$  is the simplest product from the system  $BuLi-BF_3$  even with a deficiency of  $BF_3$ .<sup>89</sup>

The availability of organoaluminium compounds encourages their use for preparation of  $R_3B$ <sup>15a</sup> ( $R = Me, Et$ ,<sup>90</sup> or allyl<sup>91</sup>) and the method holds considerable promise.

The best route to trivinylborane uses tetravinyl-lead,<sup>92</sup> but involves net transfer of less than two vinyl groups per lead, so that it is limited as a general method for trialkenylboranes. Some of these may be obtained by hydroboration;<sup>1,6</sup> otherwise a less wasteful transmetallation reaction must be employed. Tris(alka-1,4-dienyl)boranes are available by the 1:3 reaction of triallylboranes with alkynes.<sup>37</sup>

**Two Identical and One Different Groups.**—Some compounds  $R_1_2BR^2$  are available by stepwise hydroborations with diborane.<sup>9,18</sup> This method is limited by the availability of the appropriate partially alkylated 'boranes'. However, a wide range of compounds  $R^1BX_2$  and  $R^2_2BX$  is available (see above) and reduction of these to  $'R_nBH_{3-n}'$  in the presence of olefin can lead to rapid hydroboration before redistribution can occur. This approach has been used,<sup>35,36</sup> and there is considerable scope for more development. As well as mixed trialkylboranes, dialkylalkenylboranes or alkylalkenylboranes are available by final hydroboration of alkynes<sup>6,18</sup> or some allenes<sup>21,23a</sup> (other allenes give allylboron compounds). In a few cases it may be useful to prepare  $R^1_2BR^2$  by redistribution of

<sup>86</sup> S. W. Breuer and F. A. Broster, *J. Organometallic Chem.*, 1972, **35**, C5.

<sup>87</sup> R. Köster, P. Binger, and W. Fenzl, *Inorg. Synth.*, 1974, **15**, 134.

<sup>88</sup> B. M. Mikhailov, T. K. Baryshnikova, and V. S. Bogdanov, *Zhur. obshchei Khim.*, 1973, **43**, 1949.

<sup>89</sup> D. K. Jenkins and C. Dixon, *Chem. and Ind.*, 1966, 1887.

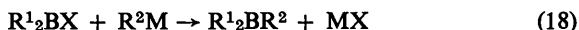
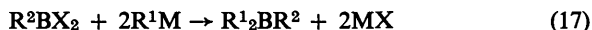
<sup>90</sup> R. Köster, P. Binger, and W. V. Dahlhoff, *Synth. Inorg. Metal-Org. Chem.*, 1973, **3**, 359.

<sup>91</sup> B. M. Mikhailov and V. F. Pozdnev, *Izvesti. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 1477.

<sup>92</sup> A. K. Holliday and R. E. Pendlebury, *J. Organometallic Chem.*, 1967, **10**, 295.

$R^2_3B$  with a large excess of  $R^1_3B$  when the latter is relatively inexpensive and easily removed from the product.

Reactions (17) and (18) represent general approaches to the synthesis of  $R^1_2BR^2$ , but disproportionations are a constant threat to their success. A



deficiency of organometallic reagent and a rapid work-up are advisable, and it would be prudent to test (*e.g.* by *g.c.*) for redistribution under the reaction conditions before relying on reports which do not include such checks. Boron substrates for reaction (17) include trialkylboroxines<sup>93</sup> and *B*-alkylbenzo-1,3,2-dioxaboroles,<sup>94</sup> whilst for (18)  $X = OR^{15a}$  and  $X = \text{halide}$  are most popular.  $X = \text{halide}$  is probably better because the intermediate ate-complex is (presumably) short-lived, so that redistribution does not occur by mechanisms analogous to (11). In addition to alkyl- and aryl-boron compounds, this approach has been applied to dialkylalkynylboranes<sup>95</sup> and dialkylcyclopentadienylboranes,<sup>96</sup> where amine complexes of the boron substrates appear to offer advantages. Although 'reactive' organometallics are usually employed, there are examples of the use of arylmercury compounds.<sup>97</sup>

Specific examples of compounds  $R^1_2BR^2$  available by less general methods include diallyl(alka-1,4-dienyl)boranes (Scheme 7)<sup>97</sup>, dialkylalkenylboranes (reaction 13,<sup>87,88</sup> or *via* boron-stabilized carbanions<sup>80</sup>) and mixed trialkylboranes by photochemical addition of  $R_3B$  to alkenes (Scheme 3)<sup>19</sup>.

**Three Dissimilar Groups.**—There is no well-developed and general route to totally mixed triorganoboranes. A limited range of hexyldialkylboranes is available by stepwise hydroborations,<sup>18,80</sup> but the generality is restricted by the availability of ' $R^1R^2BH$ '. A possible approach involves reduction of  $R^1R^2BX$  in the presence of an alkene, but the method has not yet been developed.

Alternatively, reaction (19) may be used. In practice it has been applied mainly



for triarylboranes although yields have not been particularly good.<sup>81</sup> Grignard reagents and  $Ar^1Ar^2BCl$  were used. The method is limited by availability of  $R^1R^2BX$  and the extent of redistribution, but careful control of conditions may give success. Certainly there is scope for more development.

**Boron as Part of One or More Ring Systems.**—Monocyclic triorganoboranes (7) may be obtained from derivatives (8), in which case the synthesis is only a special case of that for  $R^2_2BR^1$  from cyclic  $R^2_2BX$ . Hydroboration ( $X = H^{8c,24,83}$ ) or

<sup>93</sup> J. C. Perrine and R. N. Keller, *J. Amer. Chem. Soc.*, 1958, **80**, 1823.

<sup>94</sup> S. Cabiddu, A. Maccioni, and M. Secci, *Gazzetta*, 1972, **102**, 555.

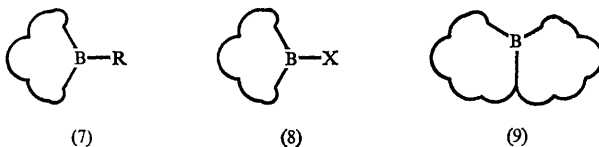
<sup>95</sup> R. Köster, H.-J. Horstschäfer, and P. Binger, *Annalen*, 1968, **717**, 1.

<sup>96</sup> H. Grundke and P. I. Paetzold, *Chem. Ber.*, 1971, **104**, 1136.

<sup>97</sup> J. Deberitz, K. Dirscherl, and H. Nöth, *Chem. Ber.*, 1973, **106**, 2783.

## Preparation of Organoboranes: Reagents for Organic Synthesis

transmetallation (variety of X)<sup>98,99</sup> may be employed. The complementary route

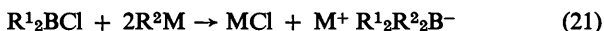


from  $\text{RBX}_2$  involves cyclic hydroboration of dienes ( $\text{X} = \text{H}$ , method limited by availability of ' $\text{RBH}_2$ '; normally  $\text{R} = \text{hexyl}$ )<sup>18,24</sup> or transmetallation with a dimetallic<sup>100</sup> or cyclic organometallic compound.<sup>100,101</sup> There is scope for considerable development. Some *B*-allylboracyclanes are available directly by allylboronation (Scheme 7).<sup>37</sup>

Hydroboration of trienes can lead directly to borapolycyclanes, (9),<sup>8e,33</sup> and similar products are available by pyrolysis of alkyl- or aralkyl-boron compounds<sup>50,51</sup> (see above). The reported synthesis of 1-bora-adamantane<sup>102</sup> involves a redistribution reaction, albeit of a rather specific type.

**Borate Salts: Four B—C Bonds.**—Symmetrical tetraorganoborate salts are fairly readily obtained by interaction of a 'reactive' organometallic (organolithium or Grignard reagent) with a boron substrate such as  $\text{BF}_3$  or  $\text{KBF}_4$  (ratio  $\geq 4:1$ ). Tetra-alkyl-,<sup>89</sup> tetra-aryl-, and tetra-alkynylborates<sup>15a</sup> may be prepared in this way.

The increasing importance of organoborates in organic synthesis means an increased need for unsymmetrical compounds. These may be prepared from reactions such as (20) or (21). Totally unsymmetrical tetra-arylborates have been prepared by reaction (20),<sup>81</sup> for example. However, a cautionary note should be sounded. Redistributions according to reaction (11) are a danger, so rapid and quantitative formation of the borate is essential. Reaction conditions should



therefore be as mild as possible and a small excess of  $\text{RM}$  is advisable. Unfortunately, some experimenters have used high temperatures, although it is clear that even insoluble reagents such as  $\text{NaCN}$ <sup>64</sup> and alkynyl-lithiums<sup>68</sup> will react rapidly with ether solutions of trialkylboranes. Whilst the procedure may have been successful in the particular examples it should be avoided whenever possible. Isomerizations (see above) are a further danger on heating.

<sup>98</sup> B. M. Mikhailov, M. E. Kuimova, and E. A. Shagova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 548.

<sup>99</sup> H. C. Brown and M. M. Rogić, *J. Amer. Chem. Soc.*, 1969, **91**, 4304.

<sup>100</sup> J. J. Eisch, N. K. Hota, and S. Kozima, *J. Amer. Chem. Soc.*, 1969, **91**, 4575.

<sup>101</sup> P. Jutzi, *J. Organometallic Chem.*, 1969, **19**, P1.

<sup>102</sup> B. M. Mikhailov and V. N. Smirnov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1973, 2165.

## 6 Conclusion

**Practical Aspects.**—In common with Grignard reagents and many other organometallics, organoboranes are sensitive to oxygen in the air. Although many are not sensitive to moisture, the reagents used in their preparation frequently are, so it is advisable to carry out all reactions in an atmosphere of dry nitrogen. Normal laboratory glassware may be used. Standard analytical techniques such as gas chromatography may also be applied. An excellent treatise on practical techniques will appear shortly.<sup>3</sup>

For preparation of mixed organoboron compounds the methods of work-up are critical. A first priority is to remove the product from any components which might catalyse redistribution (excess organometallic reagent, diborane; some metal salts?). It is perhaps unfortunate in this context that early reports emphasized the advantages of *in situ* hydroborations with, for example, borohydride-BF<sub>3</sub> etherate. In the author's experience it is better to use standard solutions of 'borane' in THF if anything more intricate than immediate oxidation of the initial organoborane is intended. Dimethylsulphide-borane complex may be similar.

Interconversions of X groups in R<sub>n</sub>BX<sub>3-n</sub> are discussed elsewhere.<sup>15d</sup>

**The Way Ahead.**—Since the discovery of hydroboration stimulated a search for useful reactions of organoboranes the clock has turned full circle. The reactions are so numerous, varied, and useful<sup>1-3a</sup> that there is now a need for new preparations. This review has outlined the characteristics of available methods and indicated likely approaches to various classes of organoboranes. A number of problems have been highlighted and suggestions made. It is hoped that these will provide a basis on which to found future research.

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