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THE REACTION BETWEEN TRIALKYLBORANES AND COPPER(II) SALTS. AN UNUSUAL ELECTRON-TRANSFER OXIDATION–REDUCTION

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SUMMARY

Essentially no reaction is observed between trialkylboranes and cupric bromide when tetrahydrofuran is used as the solvent. However, the reaction is greatly enhanced in the presence of water and results in the conversion of a single alkyl group on boron into the corresponding alkyl bromide. The reaction stoichiometry indicates that two equivalents of copper(II) are required per alkyl group. Cupric chloride gave an analogous reaction, but no detectable amount of alkyl acetate was observed by GLC analysis for the reaction between trialkylboranes and cupric acetate.

A two-step reaction mechanism is proposed based on the stoichiometry and selectivity of the reaction and on the different mode of reaction for acetate *vs.* halide. The first step is a direct electron-transfer oxidation of a carbon–boron bond with generation of an alkyl free radical. This alkyl radical then undergoes a ligand-transfer reaction in the presence of cupric halides. Possible mechanisms are presented for this unusual electron-transfer oxidation of trialkylboranes.

INTRODUCTION

The reaction of a cupric salt with an organoborane was originally investigated by Ainley and Challenger[1]. They found that benzeneboronic acid in water under reflux reacts with cupric chloride or bromide to give chlorobenzene and bromobenzene, respectively [eqn. (1)].

$$PhB(OH)_2 + 2\,CuX_2 + H_2O \xrightarrow{\Delta} PhX + Cu_2X_2 + HX + B(OH)_3 \qquad (1)$$

The reaction of phenylboronic acid with hot copper sulphate solution gave benzene, diphenyl, and a minor amount of phenol[1]. Various other workers have reacted arylboranes with cupric salts. For example, 2-furanboronic acid was found to react very slowly with cupric chloride in water while the reaction with cupric bromide was rapid and exothermic, giving 2-bromofuran[2]; ferroceneboronic acid gave chloroferrocene, bromoferrocene, and biferrocene upon reaction with cupric chloride, bromide, and acetate, respectively[3]; and triphenylboroxime gave a small amount of chlorobenzene when heated at 275° in a sealed tube with anhydrous cupric chloride[4].

The reaction of copper salts with aliphatic boron compounds has received less attention, *i.e.*, primary aliphatic boronic acids were found to be inert toward cupric halides in aqueous solution[5] at 100° and recently it was reported that cupric chloride is quite unreactive towards trialkylboranes giving only a 42% yield of n-hexyl chloride when tri-n-hexylborane was allowed to react with cupric chloride in tetrahydrofuran (THF)/water[6] at 50°. When the reaction was run in the absence of water, only a trace of n-hexyl chloride was observed[6]. This reportedly sluggish reaction between tri-n-hexylborane and cupric chloride is in conflict with earlier results obtained in this laboratory for the reaction of trialkylboranes with various halogenating agents including cupric bromide (*vide infra*).

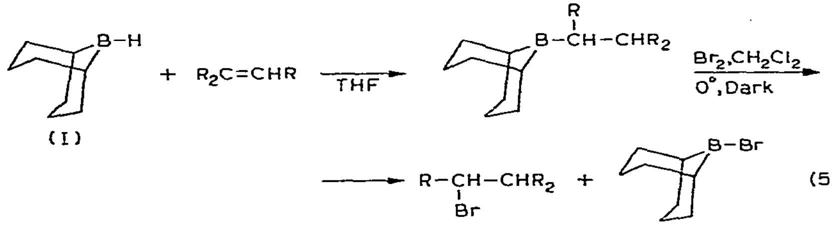
The reaction of trialkylboranes with halogens has been studied extensively in this laboratory and convenient procedures have been developed for the conversion of terminal olefins into primary halides via base-induced iodination[7] [eqn. (2)] and base-induced bromination[8] [eqn. (3)]. An alternate procedure involving the dark reaction[9] [eqn. (4)] of bromine with trialkylboranes has been developed for the

$$RCH{=}CH_2 \xrightarrow[THF]{BH_3} (RCH_2CH_2)_3B \xrightarrow[NaOH,\,CH_3OH]{I_2} RCH_2CH_2I \qquad (2)$$

$$(RCH_2CH_2)_3B + 3\,Br_2 + 4\,NaOCH_3 \rightarrow 3\,RCH_2CH_2Br + 3\,NaBr + NaB(OCH_3)_4 \qquad (3)$$

$$R_3B + Br_2 \xrightarrow[25°,\,Dark]{CH_2Cl_2} R_2BBr + RBr \qquad (4)$$

conversion of an internal olefin into the anti-Markovnikov bromide[10] [eqn. (5)]. This procedure requires the use of a selective hydroborating agent, 9-borabicyclo[3.3.1]nonane[11] (I).



(I)

(5)

A third method that is available for the anti-Markovnikov hydrobromination of terminal olefins via hydroboration is the mercuration–bromodemercuration of trialkylboranes[12] [eqn. (6), (7)].

$$R_3B + 3\,Hg(OAc)_2 \xrightarrow{THF} 3\,RHg(OAc) + B(OAc)_3 \qquad (6)$$

$$RHgX + Br_2 \xrightarrow{Pyridine} RX + HgX_2 \qquad (7)$$

These methods, taken together, provide valuable and useful synthetic procedures for the anti-Markovnikov hydroiodination and hydrobromination of olefins.

Although there was little motivation to study the reaction of trialkylboranes with cupric halides to see if an additional synthetic method could be developed for converting trialkylboranes into alkyl halides, the reaction itself is quite interesting. We have felt that any new reaction of organoboranes should be studied in view of their increasing importance as intermediates in organic synthesis. Consequently, the reaction between organoboranes and copper(II) salts was reinvestigated in detail.

RESULTS AND DISCUSSION

Effect of solvent

The reaction of tri-n-butylborane with cupric bromide was initially examined in THF. However, after a period of 25 h at 20–25°, only a trace amount of n-butyl bromide was present by GLC analysis.

The extremely low solubility of cupric bromide in THF coupled with the fact that most of the previous reactions of aryl boron compounds with cupric bromide were carried out in aqueous solutions, prompted an investigation of the effect of water upon the reaction. The presence of water was found to have a dramatic effect which is illustrated in Fig. 1.

This rate enhancement upon addition of water could be due to either the increased solubility of cupric bromide in THF/water or the possible incursion of water molecules in the reaction mechanism. It was quite easy to show that the effect of water is more than a simple solubility factor because when tri-n-butylborane was allowed to react with cupric bromide in THF/acetonitrile* or in THF with added lithium bromide**, the amount of bromobutane formed after 24 h at room temperature was substantially less than that formed when water was present. Consequently,

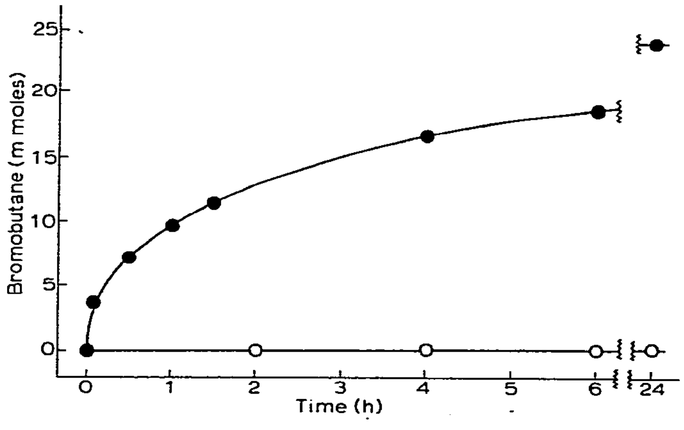


Fig. 1. Effect of water on the reaction of tri-n-butylborane (50 mmoles) with cupric bromide (50 mmoles) at 20–25°; ○, THF (50 ml); ●, THF (50 ml) plus H_2O (50 ml).

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* Acetonitrile forms coordination complexes with cupric salts[13] [eqn. (8)].

$$CuX_2+4\,CH_3CN \rightleftharpoons Cu(CH_3CN)_4X_2 \qquad (8)$$

** Cupric bromide (10 mmoles) dissolved completely in THF (20 ml) upon addition of lithium bromide (10 mmoles). An analogous effect has been observed for the chloride salts[14].

we feel that although water does increase the solubility of cupric bromide, it must have an additional function in this reaction. The exact nature of this function will be discussed later.

Stoichiometry study

As can be seen in Fig. 1, after 24 h at room temperature, the yield of butyl bromide was only 50% of one alkyl group. However, the dark green color of a copper(II) solution had been completely replaced by a clear colorless reaction mixture containing a white precipitate (Cu_2Br_2). Since equimolar amounts of organoborane and cupric bromide were used for this initial study, the reaction is presumably obeying a stoichiometry [eqn. (9)] analogous to that reported previously[1] [eqn. (1)].

$$R_3B + 2\,CuBr_2 + H_2O \xrightarrow{THF} RBr + R_2BOH + Cu_2Br_2 + HBr \qquad (9)$$

The use of two equivalents of cupric bromide (plus 10% excess) for each equivalent of tri-n-butylborane resulted in a quantitative conversion of a single alkyl group into bromobutane. The use of additional cupric bromide gave a partial reaction with a second alkyl group. However, the yield was quite low and the results summarized in Table 1 seem to indicate that only a single alkyl group of a trialkylborane can be converted into the corresponding alkyl bromide in any reasonable length of time.

The reaction of cupric chloride with tri-n-hexylborane was also examined and found to follow a similar stoichiometry. However, the cupric chloride reaction was somewhat slower and the conversion of an alkyl group on boron into the corresponding alkyl chloride was always somewhat less than quantitative. The results of the cupric chloride stoichiometry study are summarized in Table 2.

Scope of the reaction

The hydroboration reaction is extremely versatile and all but a limited number of olefins can be readily converted into trialkylboranes[15] [eqn. (10)]. These trialkylboranes can be divided into two classes based on the structure of the alkyl groups;

TABLE 1

THE REACTION OF TRI-n-BUTYLBORANE WITH CUPRIC BROMIDE. STOICHIOMETRY STUDY[a]

$CuBr_2$ (mmol)	Products (mmol)[b]		Yield (%)[c]
	1-Bromobutane	2-Bromobutane	
10	4.25	0.60	48.5
20	7.89	1.08	89.7
22	8.98	1.08	100.6
30	9.17	1.15	103.0
40	9.89	1.20	110.9
40[d]	10.8	1.14	119.4
40[e]	12.0	0.64	126.4

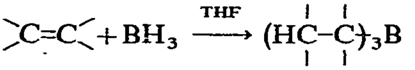
[a] Reactions were run for 24 h at 20–25° in THF/H_2O using 10 mmoles of R_3B. [b] By GLC analysis. [c] Based on the production of 10 mmoles of RBr from 10 mmoles of R_3B. [d] Analysis after 4 days at 20–25°. [e] Analysis after heating for 24 h at reflux.

TABLE 2

THE REACTION OF TRI-n-HEXYLBORANE WITH CUPRIC CHLORIDE. STOICHIOMETRY STUDY[a]

$CuCl_2$ (mmol)	Products (mmol)[b]		Yield (%)[c]
	1-Chlorohexane	2-Chlorohexane	
10	4.25	Trace	42.5
20	6.94	0.21	71.5
22	6.95	0.28	72.3
30	7.64	0.51	81.5
40	7.84	0.75	85.9
40[d]	8.11	0.60	87.1

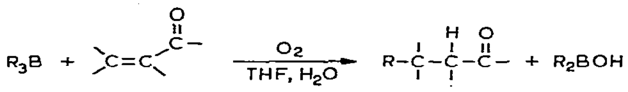
[a] Reactions were run for 24 h at 20–25° in THF/H_2O using 10 mmoles of R_3B. [b] By GLC analysis. [c] Based on the production of 10 mmoles of RCl from 10 mmoles of R_3B. [d] Analysis after heating for 24 h at reflux.



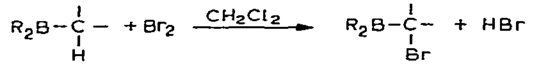
$$>C{=}C< + BH_3 \xrightarrow{THF} (HC{-}C)_3B \qquad (10)$$

tri-prim-alkylboranes or "primary" boranes obtained by hydroboration of terminal olefins and tri-sec-alkylboranes or "secondary" boranes obtained by hydroboration of internal olefins.

These two types of trialkylboranes exhibit quite different reactivities in a number of reactions. Primary boranes undergo rapid mercuration[12] [eqn. (6)] while the secondary boranes react only sluggishly with mercuric acetate[16]. A similar, although less dramatic, structural effect was also observed in the base-induced iodination[7] and bromination[8] reactions. In contrast to the above reactions, the oxygen catalyzed 1,4-addition reaction[17] [eqn. (11)] and the α-bromination reaction[9,10,18] [eqn. (12)] show an opposite structural effect, *i.e.*, the secondary boranes are more reactive than the primary boranes*. This effect of structure upon the reaction has given important clues as to the mechanisms for the above reactions. Consequently, we next examined the reaction of cupric bromide and chloride with trialkylboranes of varying structural types including various unsymmetrical trialkylboranes obtained by using either 9-borabicyclo[3.3.1]nonane (9-BBN) (I), dicyclohexylborane[19], or bis-3-methyl-2-butylborane[20] as hydroborating agents.



$$R_3B + >C{=}C<^{C(=O)-} \xrightarrow[THF,\,H_2O]{O_2} R{-}C{-}\overset{H}{C}{-}\overset{O}{\overset{\|}{C}}{-} + R_2BOH \qquad (11)$$



$$R_2B{-}\underset{H}{C}{-} + Br_2 \xrightarrow{CH_2Cl_2} R_2B{-}\underset{Br}{C}{-} + HBr \qquad (12)$$

As standard procedures the reactions were run for 24 h at 20–25° (procedure A) or for one hour at 64–66° (procedure B) using a 10% excess of cupric bromide and a 50% excess of cupric chloride. The results of this study (Tables 3–5) show that the reactions are quite general in scope.

Although the reaction rates were not quantitatively determined, it was observed that the relative reactivity of the trialkylborane appeared to increase upon

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* A similar structural effect has been reported for the reaction of organoboranes with lead tetraacetate/lithium chloride.

TABLE 3

THE REACTION OF VARIOUS REPRESENTATIVE TRIALKYLBORANES WITH CUPRIC BROMIDE[a]

R_3B from olefin	Procedure[b]	Product	Yield (%)[c]
1-Butene	A	1-Bromobutane[d]	89.8
	B		89.2
2-Butene	A	2-Bromobutane	83.1
Isobutene	A	Isobutyl bromide	38.9
	B		45.0
	C		89.5
Cyclopentene	A	Bromocyclopentane	75.2
Cyclohexene	A	Bromocyclohexane	92.1
	B		91.6
Norbornene	A	2-Bromonorbornane[e]	77

[a] Reactions run in THF/H_2O with 10 mmoles of R_3B and 22 mmoles of $CuBr_2$. [b] Procedure A, 24 h at 20–25°; B, 1 h at 65°; C, 24 h at 65°. [c] By GLC analysis. [d] The 2-bromoalkane was also formed in an 11–13% yield. [e] *exo/endo* ratio of ~4 by GLC analysis.

TABLE 4

THE REACTION OF VARIOUS REPRESENTATIVE TRIALKYLBORANES WITH CUPRIC CHLORIDE[a]

R_3B from olefin	Procedure[b]	Product	Yield (%)[c]
1-Hexene	A	1-Chlorohexane[d]	76.4
	B		76.9
1-Octene	A	1-Chlorooctane[d]	68.4
3,3-Dimethyl-1-butene	A	1-Chloro-3,3-dimethylbutane	71.2
Cyclhexene	A	Chlorocyclohexane	61.6
	B		63.1
Norbornene	A	2-Chloronorbornane[e]	43.4

[a] Reactions run in THF/H_2O with 10 mmoles of R_3B and 30 mmoles of $CuCl_2 \cdot 2\ H_2O$. [b] Procedure A, 24 h at 20–25°; B, 1 h at 65°. [c] By GLC analysis. [d] The 2-chloroalkane was also formed in a 5–7% yield. [e] Stereochemistry was not established.

α-substitution and decrease upon β-substitution.

The study with the unsymmetrical boranes also contains a number of interesting observations. For example, the *B*-alkyl-9-BBN compounds are extremely reactive relative to normal trialkylboranes*, n-hexylbis(3-methyl-2-butyl)borane is very unreactive**, and the reaction is highly selective.

The selectivity of this reaction is most apparent in the reaction of n-hexyldicyclohexylborane with cupric bromide which gave almost exclusively bromocyclohexane. Also, the reactions with *B*-R-9-BBN must have resulted in selective attack at the *B*–cyclooctyl bond. It is unfortunate that the selectivity was always exactly opposite to that desired from a synthetic viewpoint. However, the results of this study are important when one considers the mechanistic implications.

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* When cupric bromide was added to *B*-R-9-BBN in THF/H_2O at 20°, the reaction became very exothermic and the green copper(II) solution decolorized in less than 5 min.

** Under normal conditions this borane gave essentially no reaction with cupric chloride, and an incomplete reaction with cupric bromide.

TABLE 5

THE REACTION OF UNSYMMETRICAL TRIALKYLBORANES WITH CUPRIC HALIDES[a]

Organoborane	CuX_2[b]	Procedure[c]	Product	Yield (%)[d]
B-n-Hexyl-9-BBN	$CuBr_2$	D	1-Bromohexane	6.9
		E		3.7
	$CuCl_2$	A	1-Chlorohexane	0
B-Cyclohexyl-9-BBN	$CuBr_2$	D	Bromocyclohexane	Trace
		E		Trace
	$CuCl_2$	A	Chlorocyclohexane	Trace
n-Hexyldicyclohexylborane	$CuBr_2$	A	Bromocyclohexane	86.9
			1-Bromohexane	2.2
		B	Bromocyclohexane	82.2
			1-Bromohexane	3.3
	$CuCl_2$	A	Chlorocyclohexane	56.2
			1-Chlorohexane	11.3
n-Hexylbis(3-methyl-2-butyl)-borane	$CuBr_2$	A	2-Bromo-3-methylbutane	34.7
			1-Bromohexane	Trace

[a] Reactions run in THF/H_2O with 10 mmoles of R_3B. [b] $CuBr_2$, 22 mmoles; $CuCl_2 \cdot 2\,H_2O$, 30 mmoles.
[c] Procedure A, 24 h at 20–25°; B, 1 h at 65°; D, 0.5 h at 20–25°; E, 0.5 h at 0° followed by 0.5 h at 20–25°.
[d] By GLC analysis.

Mechanism

Although a detailed investigation of the reaction mechanism has not been undertaken at the present time, a number of interesting conclusions can be arrived at based solely on a product study. The reaction undoubtedly involves two separate steps each of which is responsible for the reduction of one equivalent of copper(II). The first step* [eqn. (13)] is believed to involve the formation of alkyl radical with an electron transfer** reduction of the cupric salt.

$$R_3B+Cu^{II}X+H_2O \rightarrow R^{\cdot}+R_2BOH+Cu^{I}+HBr \tag{13}$$

This alkyl radical then reacts with the second equivalent of cupric halide to give the corresponding alkyl halide by a ligand-transfer process*** [eqn. (14)].

$$R^{\cdot}+Cu^{II}X \xrightarrow[\text{(X=Br or Cl)}]{\qquad\qquad} RX+Cu^{I} \tag{14}$$

Excellent evidence to support the idea that this reaction involves a ligand-transfer oxidation [eqn. (14)] of an alkyl radical came about through an investigation of other copper(II) salts. It has previously been established that while cupric bromide and chloride are very effective ligand-transfer oxidizing agents, the acetate and sulfate salts oxidize alkyl radicals by an electron-transfer mechanism[25] [eqn. (15)]. Consequently, when tri-n-butylborane was treated with cupric acetate in THF/H_2O

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* The cupric ion would exist in solution as an octahedral coordination complex. However, the ligands shown will only be those pertinent to the discussion of the reaction mechanism.

** Various reviews are available which discuss the electron-transfer oxidation–reduction reactions of octahedral complexes of transition metal ions[21–24].

*** The ligand-transfer and electron-transfer oxidation of alkyl radicals by copper(II) salts has been studied extensively by Kochi and coworkers[25], and a recent review article is available which summarizes most of Kochi's work along with the contributions of others[26].

$$R^{\cdot}+Cu^{II}Y \xrightarrow[(Y=OAc \text{ or } SO_4)]{} \text{olefin}+ROH+HY+Cu^{I} \qquad (15)$$

there was a rather rapid[*] decolorization of the dark blue-green solution with combinative precipitation of a finely divided copper-colored solid. Analysis of the clear colorless supernate by GLC showed that no detectable amount of n-butyl acetate was formed. An analogous reaction of tri-n-hexylborane with cupric acetate occurred at a somewhat slower rate, but again GLC analysis showed no detectable amount of n-hexyl acetate.

While it is evident that the second step of these reactions involves either an electron-transfer or ligand-transfer oxidation of an alkyl radical, the question still remains as to how the radical is produced. There would appear to be two possible pathways for the production of alkyl radicals from trialkylboranes by metal ions. The reaction could involve a transmetallation process [eqn. (16)] which gives a new organometallic[**]. Now if this organometallic was unstable under the reaction con-

$$R_3B+MY \rightarrow R_2BY+RM \qquad (16)$$

ditions, it might be expected to undergo homolytic decomposition to an alkyl radical with a corresponding reduction of the metal[***] [eqn. (17)]. The other pathway that one might envision is a process whereby the alkyl radical is formed via a direct

$$RM^{n} \rightarrow R^{\cdot}+M^{n-1} \qquad (17)$$

electron-transfer oxidation of a carbon–boron bond by a metal ion. Although such a process has not previously been proposed, it is not completely unreasonable[†].

At this time we do not have any evidence which unequivocally rules out the intermediacy of an organocopper compound, but the study with the unsymmetrical boranes provides strong evidence against such a process. The migratory aptitude of the alkyl groups of trialkylboranes in the reaction with mercuric acetate[12] is primary > secondary, while the reverse is observed with the cupric salts[††]. Consequently, the direct electron-transfer oxidation of the organoborane gives a picture which is more consistent with the experimental facts.

A detailed discussion of the mechanism of this electron-transfer oxidation would be beyond the scope and purpose of this article. However, there are two possible mechanisms which deserve some consideration, one involves an "inner-sphere" activated complex (II) and the other involves an "outer-sphere" activated complex (III)[‡]. In the inner-sphere mechanism [eqn. (18)] a bromo or chloro ligand is shared between the copper and boron in the transition state (II) and provides a bridge

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[*] The reaction appeared to proceed at an enhanced velocity relative to the cupric halide reactions, *i.e.*, 20–30 min at 20–25°.

[**] The mercuration of organoboranes[12] [eqn. (6)] is an example of such a process.

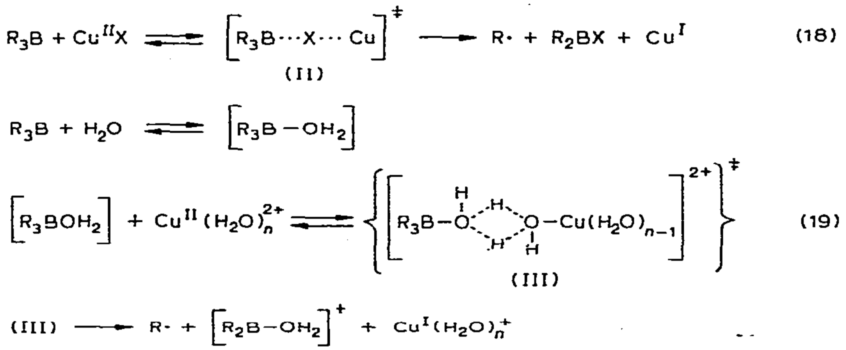
[***] The coupling reaction[27] of trialkylboranes is thought to involve such a process, *i.e.* an alkylsilver intermediate is formed which decomposes to alkyl radicals plus silver metal[28]. These alkyl radicals then dimerize.

[†] A reaction which also produces alkyl radicals as intermediates is the oxygen oxidation of trialkylboranes[29]. This process may not be completely analogous with the metal-ion oxidation, but the oxygen oxidation is thought to involve an attack on boron by oxygen with loss of an alkyl radical[30].

[††] This relative reactivity of secondary > primary is also observed in oxygen oxidation[29], which is known to involve direct displacement of an alkyl radical[30].

[‡] These two mechanisms have been proposed for redox-reactions of transition metals and are discussed in various review articles[21–23].

through which the electron transfer to copper can occur. In the outer-sphere mechanism [eqn. (19)] there is no sharing of a ligand on copper and the electron transfer could be envisioned as occurring through a hydrogen-bonded outer-sphere activated complex (III)*.



Either of these mechanisms could be operating depending upon the reaction conditions, *e.g.*, in the absence of water and when lithium bromide is added to dissolve cupric bromide, then the electron transfer might be occurring through the inner-sphere pathway [eqn. (18)] in the presence of water the outer-sphere pathway [eqn. (19)] would provide an alternative mechanism. If the rate of outer-sphere electron transfer is faster than the inner-sphere transfer, then one would have an explanation for the enhanced rate in the presence of water.

These mechanisms are also capable of explaining the observation that when the steric crowding around boron is increased, the rate of reaction decreases**. This could be due due to steric hindrance to formation of the activated complexes (II), (III). More importantly, these mechanisms can account for the high degree of selectivity found in the reactions (*vide supra*). One might expect that the ease of formation of an alkyl radical from activated complex (II) or (III) would be a function of the stability of the alkyl radical, *i.e.*, secondary > primary as is observed.

EXPERIMENTAL

General comments

All reactions were carried out under a positive pressure of dry nitrogen in flame-dried glassware.

Gas-liquid partition chromatography (GLC) was used exclusively for yield determinations via the internal standard method. The identification of the alkyl halides was by comparison with authentic samples. The instrument used was a Hewlett–Packard Model 5750 temperature-programmed gas chromatograph equipped with a thermal conductivity detector and a 6′ × $\frac{1}{4}$″, 10% SE-30 on chromosorb W

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* Similar hydrogen-bonded outer-sphere activated complexes have previously been proposed in certain redox reactions of transition metals[22].

** The relatively open[11] *B*-R-9-BBN compounds react at a rate much faster than normal trialkylboranes while the relatively crowded alkylbis(3-methyl-2-butyl)boranes react only extremely sluggishly.

column. The stereochemistry of the bromonorbornane was determined on a 20′ × ¼″, 5% Zonyl E-7 on chromosorb W column.

Materials

THF, 1-hexene, cyclopentene, cyclohexene, 1-octene, 1-decene, 3,3-dimethyl-1-butene, 1,5-cyclooctadiene, and 2-methyl-2-butene were obtained from various commercial sources, dried over lithium aluminum hydride, distilled, and stored under nitrogen. Norbornene was used directly as obtained from Aldrich Chemical Company. Cupric bromide, chloride, and acetate were used directly as obtained from J. T. Baker Chemical Company.

The borane/THF solution was prepared and standardized by the procedure of Brown and Sharp[31], and the 9-BBN/THF solution was prepared and standardized by the procedure of Knights and Brown[11]. n-Hexylbis(3-methyl-2-butyl)borane and n-hexyldicyclohexylborane were prepared according to the procedure of Larock and Brown[12a]. The *B*-alkyl-9-BBN compounds were prepared as previously described[10]. The tri-n-butylborane was obtained from Callery Chemical Company, distilled, and stored under nitrogen. All other trialkylboranes were obtained in the usual manner by hydroboration of olefins with borane/THF.

Reaction between trialkylboranes and cupric halides

The cupric halide was added under a blanket of nitrogen to a 100 ml flask containing the trialkylborane (10 mmoles), THF (20 ml), water (10 ml), and internal standard (n-alkane, 1 ml). The reaction was then allowed to stir for 24 h at 20–25° or heated at reflux for 1 h, whereupon, a 1 ml aliquot was removed under nitrogen and injected into a vial containing n-hexane (0.5 ml), water (0.5 ml), and ammonium hydroxide (1.0 ml). After several min of vigorous shaking, the clear colorless organic layer was removed, dried over anhydrous potassium carbonate, and analyzed via GLC. The results of these reactions with cupric bromide (22 mmoles) and cupric chloride (30 mmoles) are summarized in Tables 3–5.

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