Accordingly, 20 ml of 0.5 *M* solutions of tri-*n*-butylborane, tri-*sec*-butylborane, and triisobutylborane in THF, 0.2 *M* in iodine, contained individually in a 100-ml flask maintained at 0° was attached to a Brown$^{\square}$ apparatus[5] previously flushed with oxygen. The apparatus was further flushed by injecting 5 ml of 30% hydrogen peroxide into the generator. The flasks were stirred vigorously in the dark at 0° for several days. Samples were removed periodically and analyzed by glpc for butyl iodide. The results are shown graphically in Figure 1. It should be noted that the moles of butyl iodide produced are roughly equal to the number of moles of iodine which disappears in the course of the reaction. In the absence of oxygen, the formation of butyl iodides under the same conditions is negligible.

The results show that the rate of production of the iodide from tri-*n*-butylborane is considerably greater than those from triisobutylborane and tri-*sec*-butylborane. According to the arguments presented these must be equivalent to the rates of formation of free radicals from the reaction of oxygen with the organoboranes. The observed relative rates, $n\text{-Bu}_3\text{B} >> sec\text{-Bu}_3\text{B} > i\text{-Bu}_3\text{B}$, are very different from those observed for the oxidation process, in which the order for various alkyl derivatives is tertiary > secondary > primary.[8] Consequently, the chain-propagation step must be more favorable for tri-*sec*-alkylboranes than for the primary derivatives. The difference in the apparent rates of the initiation reaction is consistent with a steric interpretation. The attack of oxygen on the organoborane in the initiation state is apparently hindered by increasing crowding provided by the three alkyl groups attached to boron.

Oxygen is a diradical. The initiation stage may involve an attack on boron to displace an alkyl radical in an initial slow step[9] (eq 4). In order to account for

$$\cdot\text{OO}\cdot + \text{R}_3\text{B} \longrightarrow \text{R}_2\text{BO}_2\cdot + \text{R}\cdot \qquad (4)$$

the results, it is then necessary to postulate that iodine is effective in trapping the alkyl radical (eq 1) prior to its reaction with oxygen (eq 2), and also captures the dialkylborylperoxy radical with liberation of oxygen (eq 5) before this species can undergo other reactions incorporating oxygen into products.

$$\text{R}_2\text{BO}_2\cdot + \text{I}_2 \longrightarrow \text{R}_2\text{BI} + \text{O}_2 + \text{I}\cdot \qquad (5)$$

Iodine also effectively inhibits the rapid chain reaction involving tri-*n*-butylborane and acrolein.[10]

These results reveal that iodine is an exceptionally powerful inhibitor of the free-radical chain reactions of organoboranes. Utilization of this property of iodine has revealed that the fast reaction of oxygen with organoboranes is initiated by a slow attack of oxygen on the boron atom. Moreover, the rate of initiation is strongly dependent upon the structure of the organoborane, proceeding slower with increasing crowding about the boron atom. The free-radical reactions of the organoboranes are becoming of major theoretical and synthetic importance. The availability of an efficient inhibitor for these free-radical reactions of organoboranes provides a powerful tool for the exploration of these reactions.

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[8] O. Grummitt, *J. Amer. Chem. Soc.*, **64**, 1811 (1942). The rates are for the alkyl boronic acid anhydrides. We find the same order for trialkylboranes.[1]

[9] For example, a very rapid reaction of the *tert*-butoxy radical with organoboranes, $tert\text{-BuO}\cdot + \text{BR}_3 \rightarrow tert\text{-BuOBR}_2 + \text{R}\cdot$, has recently been demonstrated: A. G. Davies and B. P. Roberts, *Chem. Commun.*, 699 (1969); A. G. Davies, D. Griller, B. R. Roberts, and R. Tudor, *ibid.*, 640 (1970); J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3942 (1969).

[10] For a discussion of this interesting chain reaction with leading references see G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *ibid.*, **92**, 710 (1970).

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An Oxygen-Induced Reaction of Trialkylboranes with Alkyl Iodides. A Facile Coupling of Benzylic and Allylic Iodides *via* Triethylborane

Sir:

Trialkylboranes readily undergo an oxygen-induced reaction with organic iodides to produce the corresponding alkyl iodides. Moreover, benzylic and allylic iodides may readily be coupled in excellent yields under these mild conditions *via* the air-induced iodine abstraction using triethylborane as the reagent.

In our study of the autoxidation of trialkylboranes we observed that the addition of small amounts of iodine greatly inhibits the reaction.[1] Alkyl iodides are formed. An examination of the effect of typical organic iodides on the rate of reaction of trialkylboranes with oxygen revealed that the rate is not significantly altered (unless substantial iodine is formed), but the products are very different. Thus when 2 mmol of typical organic iodides, such as benzyl, *p*-nitrobenzyl, or allyl iodide, iodoform, or 1,2-diiodoethane, was added to 10 mmol of tri-*n*-butylborane in 20 ml of tetrahydrofuran (THF) and the resulting solution was oxidized with oxygen, *n*-butyl iodide was formed equivalent to the amount of iodide added. A small amount of bibenzyl was detected in the experiments with benzyl iodide.

The products suggest that a chain transfer occurs during the free-radical oxidation[2] (eq 1–6). The

$$\text{R}_3\text{B} + \text{O}_2 \longrightarrow \text{R}_2\text{BO}_2\cdot + \text{R}\cdot \qquad (1)$$

$$\text{R}\cdot + \text{R}'\text{I} \longrightarrow \text{RI} + \text{R}'\cdot \qquad (2)$$

$$2\text{R}'\cdot \longrightarrow \text{R}'\text{–R}' \qquad (3)$$

$$\text{R}'\cdot + \text{O}_2 \longrightarrow \text{R}'\text{O}_2\cdot \qquad (4)$$

$$\text{R}'\text{O}_2\cdot + \text{R}_3\text{B} \longrightarrow \text{R}'\text{O}_2\text{BR}_2 + \text{R}\cdot \qquad (5)$$

$$\text{R}\cdot + \text{O}_2 \longrightarrow \text{RO}_2\cdot \qquad (6)$$

n-butyl free radicals abstract iodine from the alkyl halides even in the presence of oxygen. It appeared that by controlling the amount of oxygen introduced it would be possible to control the course of the reaction to produce alkyl iodide preferentially (eq 2). Indeed, we discovered that by introducing air at a moderate rate, 10 ml/min, through a syringe needle above the THF solution of the borane (R_3B), in the presence of an equimolar amount of allyl iodide, it was possible to produce a quantitative yield of the alkyl iodide (RI).

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[1] M. M. Midland and H. C. Brown, *J. Amer. Chem. Soc.*, **93**, 1506 (1971).

[2] (a) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311 (1969); (b) P. G. Allies and P. B. Brindley, *ibid.*, 1126 (1969); (c) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **92**, 1024 (1970).

Table I. The Air-Induced Reaction of Trialkylboranes with Alkyl Halides

Organoborane[a]	Alkyl halide[b]	Product	Yield,[c] %
Triethylborane	Allyl iodide	Ethyl iodide	100
Tri-*n*-butylborane	Allyl iodide	Butyl iodide	97 (10)
Tri-*n*-pentylborane	Allyl iodide	Pentyl iodide	98 (9)
Tri-*n*-hexylborane	Allyl iodide	Hexyl iodide	100 (11)
Tricyclohexylborane	Allyl iodide	Cyclohexyl iodide	75
Tri-*n*-hexylborane	Methyl iodide	Hexyl iodide	40 (20)
Tri-*n*-hexylborane	Ethyl iodide	Hexyl iodide	54 (13)
Tri-*n*-hexylborane	Isopropyl iodide	Hexyl iodide	64 (13)
Tri-*n*-hexylborane	*tert*-Butyl iodide	Hexyl iodide	85 (10)[d]
Tri-*n*-hexylborane	Allyl chloride	Hexyl chloride	Trace
Tri-*n*-hexylborane	Allyl bromide	Hexyl bromide	12
Tri-*n*-hexylborane	Benzyl bromide	Hexyl bromide	24

[a] All reactions used 10 mmol of borane in 20 ml of THF with air introduced at 10 ml/min. [b] 10 mmol. [c] Based on alkyl halide reactant by glpc. The per cent of secondary isomer of total iodide is in parentheses. The starting trialkylborane prepared from the olefin by hydroboration contained 6% secondary isomer. [d] A trace of hexamethylethane was detected.

Table II. Air-Induced Coupling of Benzylic and Allylic Iodides *via* Triethylborane

Alkyl iodide	Product	Yield,[a] %
Benzyl[b]	Bibenzyl	90 (87)
p-Nitrobenzyl[b]	4,4′-Dinitrobibenzyl	(43)
Allyl[b,c]	Biallyl	97
2-Methylallyl[b]	2,5-Dimethyl-1,5-hexadiene	90
Benzyl and allyl, 1:1[d]	4-Phenyl-1-butene	41
Benzyl and allyl, 1:2[d]	4-Phenyl-1-butene	60
Benzyl and allyl, 1:3[d]	4-Phenyl-1-butene	64
Benzyl and allyl, 1:4[d]	4-Phenyl-1-butene	72

[a] By glpc (isolated yields in parentheses). [b] The reactions used 10 mmol of alkyl iodide and 20 mmol of triethylborane in 20 ml of THF. Air was introduced at a rate of 50 ml/min, the complete reaction requiring approximately 45 min. [c] The solvent was diethyl ether. [d] Benzyl iodide, 5 mmol, was used in 20 ml of THF. Triethylborane was used in a 2:1 molar ratio to total alkyl iodide.

The reaction was applied to a series of trialkylboranes with allyl iodide and to tri-*n*-hexylborane with a series of organic halides. The results are listed in Table I.

Even methyl iodide undergoes the chain-transfer reaction and produces 40% of hexyl iodide. Allyl iodide gave quantitative results. Consequently, this reaction may be used for the preparation of alkyl iodides as an alternative to the base-induced iodination of trialkylboranes.[3] It should be especially valuable for alkyl groups which are sensitive to the alkaline conditions of the latter synthesis.

Oxygen has been used to initiate 1,4 addition of trialkylboranes to α,β-unsaturated compounds.[4] In those reactions only a catalytic amount of oxygen is required. In the present reaction approximately 1 mol of oxygen is required per mole of alkyl iodide formed. The reaction is not a chain reaction but is terminated with coupling (eq 3). The rate of reaction depends upon the rate of addition of air. However, the introduction of too much oxygen can divert the reaction to a chain oxidation (eq 4). Consequently, it is necessary to introduce the oxygen at such a rate that it can be utilized completely by the triethylborane present. It was observed that a rate of introduction of air at 50 ml/min gave satisfactory results.

With allyl iodide as the iodine donor, biallyl is produced. Initially the molar quantity of biallyl formed is one-half that of the alkyl iodide produced in the reaction. However, in the later stages of the reaction the amount of biallyl formed failed to increase significantly, even though additional alkyl iodide was being produced. A possible explanation for this phenomenon appeared to be that in the latter stages of the reaction the autoxidation of the residual organoborane (proceeding *via* ethyl radicals) fails to compete effectively against the allyl radicals for the oxygen dissolving in the solution. It is clear that to obtain high yields of the coupled product, the reaction of the allyl radical (and related radicals) with oxygen must be minimized. This objective was readily achieved by increasing the amount of the organoborane over that required by the stoichiometry of the reaction. We finally adopted the readily available triethylborane as the reagent and utilized it in 100% excess to explore the efficacy of this new approach to biallyl and related coupled products.

The reaction was applied to a series of alkyl iodides. The results are summarized in Table II.

Oxidation with sodium hydroxide and hydrogen peroxide removes unoxidized borane. The reaction was very clean. No detectable amount of coupling with ethyl radicals was observed. Evidently the ethyl radicals abstract iodide or react with oxygen rapidly and do not couple.

Mixed coupling products could be obtained from mixed allylic and benzylic iodides. The coupling gave a nearly statistical distribution of products. If one wanted to couple an expensive iodide with a less expensive iodide, an excess of the less expensive iodide could be used to increase the conversion of the more valuable material. Thus a 72% yield of 4-phenyl-1-butene was obtained when allyl iodide was used in fourfold excess.

The free-radical coupling of olefins may be readily achieved by hydroboration followed by treatment of the organoborane with alkaline silver nitrate.[5] The air-induced coupling of allylic and benzylic iodides now provides a mild method of coupling alkyl groups not available *via* hydroboration. Both methods may accommodate a wide variety of functional groups.[6] It is evident that the organoboranes constitute a versatile new source of free radicals and that these reactions can be readily controlled to give very clean synthetically useful synthetic procedures.

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