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ORGANOBORANES FOR SYNTHESIS. 6. A CONVENIENT, GENERAL SYNTHESIS OF ALKYLHYDROPEROXIDES *via* AUTOXIDATION OF ORGANOBORANES[1,2]

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Abstract - The low temperature autoxidation of organoboranes in tetrahydrofuran leads to the formation of diperoxyboranes, which provide the corresponding alkylhydroperoxides in excellent yields, upon treatment with hydrogen peroxide. However, only two of the three alkyl groups on boron are used for the formation of hydroperoxides. This difficulty was solved by employing alkyldichloroborane etherates instead of trialkylboranes. The alkyldichloroborane etherates react cleanly with one molar equivalent of oxygen in ether solvent. The product is readily hydrolyzed to form the corresponding hydroperoxides in excellent yields. The autoxidation of organoboranes is inhibited by iodine or such free-radical scavengers. A study of the inhibition by iodine of the oxidation of representative trialkylboranes indicates that the rate of initiation decreases with an increase in the steric crowding about the boron atom. The rate of inhibition of the autoxidation of trialkylboranes by iodine reveals that the reaction involves a relatively slow rate of radical initiation, followed by a very fast rate of chain propagation.

Organoboranes undergo a facile autoxidation, which may be stoichiometrically controlled to give essentially quantitative conversion to alcohols.[1,4] The oxidation proceeds through a radical chain reaction,[5] the mechanism of which has been studied by ESR[6] and NMR[7] spectroscopic methods. This initial oxidation produces a peroxide (eqs 1-3), which may either react with a second mole of oxygen (eq 4), or undergo an intermolecular redox reaction (eq 5).[8] In concentrated solutions (∿ 0.5 *M*), the intermolecular reaction predominates at 0°C and results in a substantial decrease in peroxide content.

$$R_3B + O_2 \longrightarrow R_2BO_2\cdot + R\cdot \quad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \quad (2)$$

$$RO_2\cdot + R_3B \longrightarrow RO_2BR_2 + R\cdot \quad (3)$$

$$RO_2BR_2 + O_2 \longrightarrow (RO_2)_2BR \quad (4)$$

$$RO_2BR_2 + R_3B \longrightarrow 2\ ROBR_2 \quad (5)$$

The intermolecular reaction may be minimized by using highly dilute solutions (0.01-0.05 *M*) when two moles of oxygen are absorbed to form a diperoxide. The remaining boron-carbon bond can be oxidized by the addition of an oxidizing agent, such as perbenzoic acid.[9] This method has been used as a possible synthetic route for alkyl hydroperoxides.[10] However, the procedure suffers from several difficulties. For example, the synthesis requires large volumes of solvent. The reaction in dilute solutions is rather sluggish so that long reaction times, up to 48 h, are required. Furthermore, the use of water-immiscible solvents requires the utilization of less convenient oxidizing systems, such as peracids or hydrogen peroxide, in *t*-butanol. Therefore, it is desirable to achieve the synthesis of hydroperoxides using relatively concentrated solutions of the organoborane in tetrahydrofuran (THF).

The autoxidation of organoboranes was long thought to proceed *via* a polar pathway (eq 6) because the usual free-radical inhibitors, such as hydroquinone, had no effect on this reaction.[9]

It was later found that the oxidation of optically active 1-phenylethylboronic acid gave racemic product, suggestive of a process involving radicals.[11] Indeed, it was observed that the autoxidation of this boronic acid exhibits a remarkable induction period in the presence of added inhibitors, such as copper (II)-*N,N*-dibutyldithiocarbamate (1) and galvinoxyl (2). It was then discovered that galvinoxyl also effectively inhibits the autoxidation of many other boranes.[5c,12] However, tri-*n*-butylborane was a notable exception. In this case, the autoxidation was slightly retarded, rather than being inhibited.[5a]

$$R_3B + O_2 \longrightarrow R\text{-}B(R)\text{-}O\text{-}O^{+} \longrightarrow R\text{-}B(R)\text{-}OR \qquad (6)$$

$[n\text{-}Bu_2NCS_2]Cu$

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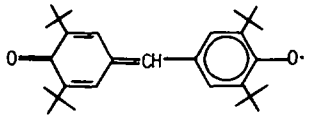

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Iodine was previously tested in an attempt to inhibit the autoxidation of triethylborane, but was reported to be ineffective.[13] However, recent results reveal that it is an effective inhibitor of such autoxidations.[2c,14] The availability of an efficient inhibitor for free-radical reactions of organoboranes provides a powerful tool for the exploration of these reactions.

RESULTS AND DISCUSSION

Previously, dilute solutions were required to obtain peroxyorganoboranes[9] in order to prevent the intermolecular redox reaction (eq 5).[13] We undertook to establish the conditions for a clean oxidation of organoboranes to peroxyboranes. Consequently, we examined the nature of the product, effect of temperature on oxidation, and the scope of this reaction. It was found that the reaction was extremely rapid, even at -78°C, in tetrahydrofuran. In fact, tri-*n*-butylborane was oxidized in hexane with a half-life of about 30 sec, with the absorption of one mol of oxygen per mol of borane.

Nature of the Oxidation Product. We utilized the automatic gas generator for the controlled oxidation of organoboranes.[1] When 10 mmol of tricyclopentylborane in THF was oxidized at -78°C, 20 mmol of oxygen was absorbed in 45 min. The product was reduced with excess lithium aluminum hydride, followed by hydrolysis. Analysis by GC revealed the presence of 19.0 mmol of cyclopentanol. Treatment with sodium hydroxide produced 19.4 mmol of alcohol, while the reaction with hydrogen peroxide provided 10.1 mmol of the alcohol. Titration for peroxide, after the removal of excess hydrogen peroxide, revealed the presence of 19.0 mmol of peroxide. These results can be rationalized as follows: organoborane (per mol) absorbs 2 mol of oxygen, producing the diperoxide (eq 7). Oxidation with hydrogen peroxide provides two mol of alkylhydroperoxide and one mol of alcohol (eq 8). Reduction of the diperoxide with lithium aluminum hydride affords two mol of alcohol, indicating that two B–C bonds were oxidized (eq 9). Addition of base causes the reduction of one peroxide linkage with the concurrent oxidation of the remaining B–C bond (eq 10).

$$R_3B + 2\ O_2 \longrightarrow (RO_2)_2BR \qquad (7)$$

$$(RO_2)_2BR + H_2O_2 \longrightarrow 2\ RO_2H + ROH \qquad (8)$$

$$(RO_2)_2BR + LiAlH_4 \longrightarrow \longrightarrow 2\ ROH \qquad (9)$$

$$(RO_2)_2BR + NaOH \longrightarrow \left[R\text{-}O\text{-}O\text{-}B(R)\text{-}OH\ \ OOR\right]^{-} Na^{+} \qquad (10)$$

$$\longrightarrow (RO)_2BOOR \longrightarrow 2\ ROH + RO_2H$$

Effect of Temperature. Tri-*s*-alkylboranes absorb two mol of oxygen (per mol of R_3B) in 1 h at -78°C. Warming the reaction mixture to -45°C considerably increased the rate of oxidation, requiring only 8-10 min. However, reduction with lithium aluminum hydride produced more than 2 mol of alcohol, indicating that intermolecular redox reaction was competing. This side reaction became even more prevalent at 0°C. The results are summarized in Table 1.

Little is known about the effect of temperature on the autoxidation of organoboranes. One study reported that *n*-Bu_3B, *s*-Bu_3B and *i*-Bu_3B all rapidly absorb one mol of oxygen at -78°C in dilute solutions.[12] The reaction is then reported to stop. We observed that the reaction stops after the absorption of one mol of oxygen for terminal organoboranes. However, internal organoboranes continue to absorb oxygen, although at a much slower rate. The initiation step for the oxidation of the second alkyl group is apparently less efficient and therefore requires more concentrated solutions. Since the secondary radicals are more stable than the primary, organoboranes con-

taining secondary alkyl groups react much more readily. The secondary alkylboranes absorb a second mol of oxygen in 8-10 min at -45°C, while the primary alkylboranes require warming to 0°C for the complete uptake of the second mol.

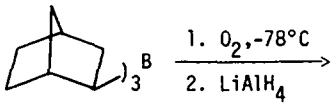
At -78°C, the intermolecular reaction is minimized. At higher temperatures, this reaction becomes more important, depending upon the structure of the borane. Hindered boranes, such as tris-(2-methyl-1-pentyl)borane, do not undergo extensive intermolecular redox reactions, even at 0°C. Presumably, the steric hindrance of this borane prevents the intermolecular reaction.

Table 1. Effect of temperature on the oxidation of trialkylboranes with oxygen

Olefin in R_3B[a]	Temp °C	O_2 mmol	T_1,[b] min	T_F,[c] min	Mmol ROH[d] LiAlH$_4$	NaOH	H_2O_2
cyclopentene	-78	19.4	3	45	19.0	19.4	10.1
	-47	19.6	1.3	8	20.6	20.4	11.1
cyclohexene	-78	19.0	5.5	60	20.0	19.5	—
	-45	19.0	4	11	22.7	23.1	—
	0	18.6	1	10	26.2	23.4	—
1-methylcyclopentene	-78	19.6	4	60	19.4	19.9	9.95
norbornene	-78	19.0	4.5	75	19.4	20.5	8.7
2-methyl-1-pentene	-78	9.6	6	6	10.1	19.2	—
	-47	9.6	7	7	9.9	16.8	—
	0	14.7	3	60	16.2	30.2	—
	0	19.3	3	360	20.6	19.8	—

[a]All reactions were run with 10 mmol of R_3B in 20 ml of tetrahydrofuran. [b]Time for absorption of 10 mmol of oxygen. [c]Time of final reading of oxygen absorption. [d]By GC as trimethylsilyl derivatives.

Stereochemistry of Oxidation. It is known that the free-radical oxidation of organoboranes results in the loss of stereochemistry of alkyl groups.[11,12,15] The diperoxide intermediate was reduced with lithium aluminum hydride and the resulting alcohol was analyzed for isomers. Tri-*exo*-norbornylborane gave 20.4% *endo*- and 79.6% *exo*-alcohols. The borane from 1-methylcyclopentene provided 28% *cis*- and 72% *trans*-2-methylcyclopentanol (eqs 11 and 12). The stereoselectivity is slightly better at -78°C than at 0°C. Thus, at 0°C, tri-*exo*-norbornylborane affords 76:24 mixture of exo:endo alcohols and the borane from 1-methylcyclopentene provides 63:27 mixture of trans:cis alcohols.



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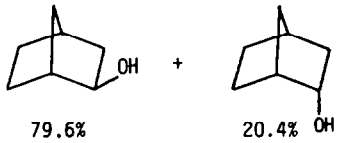

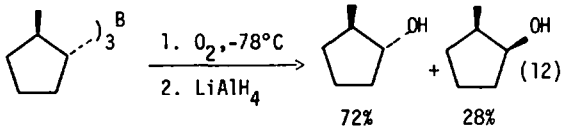

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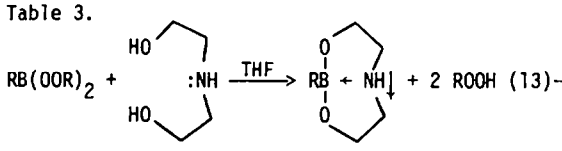
Oxidation of Representative Organoboranes to Hydroperoxides. The temperature study revealed that the best results were obtained at -78°C. Hydrogen peroxide was used for oxidizing the remaining boron-carbon bond and the hydroperoxide was estimated by iodometric titration. Representative alkenes were hydroborated in THF and subjected to low temperature oxidation using the automatic gasimeter.[16] The reaction in all cases was initially very fast, the first mole of oxygen being absorbed in 2-5 min. Organoboranes derived from internal disubstituted alkenes, such as cyclohexene, continue to absorb the second mol of oxygen over a period of 1 h. On the other hand, those derived from terminal alkenes, such as 1-butene, fail to absorb the second mol at -78°C. However, this can be achieved at 0°C. Organoboranes derived from terminal disubstituted alkenes, such as 2-methyl-1-pentene, require a much longer period, 6 h, for absorption of the second mol of oxygen, even at 0°C. Addition of 30% hydrogen peroxide then liberates the alkyl hydroperoxide with concurrent oxidation of the remaining boron-carbon bond. The results are summarized in Table 2.

Purification of Hydroperoxides. The procedure described above provides hydroperoxide containing the corresponding alcohol in 2:1 ratio (eq 8). The pure hydroperoxide may be obtained by treating the solution with an excess of potassium hydroxide, which dissolves hydroperoxide, leaving the

alcohol in the organic phase. The hydroperoxide can be obtained by acidifying the aqueous phase. Cyclohexylhydroperoxide was isolated in 82% yield, following this procedure.

However, this method presents some problems. Long chain alkyl hydroperoxides, such as *n*-octyl hydroperoxide, form sparingly soluble potassium salts and can be extracted in the aqueous layer only with difficulty. Consequently, other methods were examined to purify hydroperoxides. Diethanolamine is known to form insoluble complexes with boronic acids and esters.[17] When diethanolamine was added to an oxidized THF solution of tricyclopentyl-, tricyclohexyl- or trinorbornylborane, a heavy precipitate was formed (eq 13). The precipitate was removed by filtration and the filtrate was titrated for hydroperoxide and boronic acid. The results are summarized in Table 3.



Diethanolamine works very well for the removal of *s*-alkylboronic acids, but fails for straight-chain alkylboronic acids. The diethanolamine complex is formed, as indicated by NMR analysis, but it is not precipitated out of the solution. Variations in solvent and reaction conditions failed to remove the complex. A large number of other complexing agents were also tried, but none gave satisfactory results.[1b]

Table 2. The formation of alkyl hydroperoxide *via* autoxidation of organoboranes

Olefin[a] in R_3B	Time[b] min	Product % Yield[c]	Product Hydroperoxide
1-butene[d]	20	92	1-butyl
1-octene[d]	20	81	1-octyl
2-methyl-1-pentene[d]	360	90	2-methyl-1-pentyl
2-butene	60	91	2-butyl
cyclopentene	45	95	cyclopentyl
1-methylcyclopentene	60	91	2-methylcyclopentyl
cyclohexene	60	95	cyclohexyl
norbornene	75	84	norbornyl

[a]10 Mmol of R_3B in 20 ml of tetrahydrofuran. [b]Time for absorption of 2 mol of O_2/R_3B. [c]By iodometric titration based on a maximum of 2 mol of $ROOH/R_3B$. [d]The solution was warmed to 0°C after completion of absorption of 1 mol O_2 at -78°C.

Table 3. Removal of boronic acids from oxidized trialkylboranes

Olefin to Form R_3B	Yield Hydroperoxide[a]	Yield Diethanolamine Complex[b]	$RB(OH)_2$[c] Removed
cyclopentene	93	88	94
cyclohexene	93	92	96
norbornene	86	91	94
1-butene	70	0	0

[a]By iodometric titration. [b]By isolation. [c]By NaOH/mannitol titration.

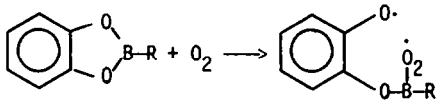
Oxidation of Mixed Trialkylboranes. The procedure described above for the synthesis of alkylhydroperoxides utilizes only two of the three alkyl groups on boron. While the yields are good and the procedure is more convenient and general than other methods of preparing hydroperoxides, it is desirable that all groups on boron be utilized.

Tricyclohexylborane absorbed two mol of oxygen at -78°C. A third mol was absorbed over 3 h when the solution was warmed to 50°C. However, the yield of peroxide was only 63%. A number of free radical reactions of organoboranes proceed with only one alkyl group undergoing the desired reaction. In most cases, *B*-alkyl-3,5-dimethylborinane can be used to transfer the *B*-alkyl group selectively.[18] Autoxidation of *B*-cyclohexyl-3,5-dimethylborinane at -78°C proceeded with the absorption of two moles of oxygen in 20 min. However, the reaction could not be controlled to oxidize the cyclohexyl group selectively.

Oxidation of Heterosubstituted Alkylboranes. Trialkylboranes are reported to oxidize faster than heterosubstituted mono- or dialkylborane derivatives.[19] The relative reactivities are in the order: $R_3B > R_2BOH > RB(OH)_2$ for boron acids, $R_3B > R_2BOR > RB(OR)_2$ for esters and $R_3B > R_2BCl > RBCl_2$ for the alkylchloroboranes. Boronic acids and esters are inert toward autoxidation under normal conditions, while the dihalides ignite spontaneously in air.[20] Consequently, the oxidation of representative partially alkylated boron derivatives was examined.

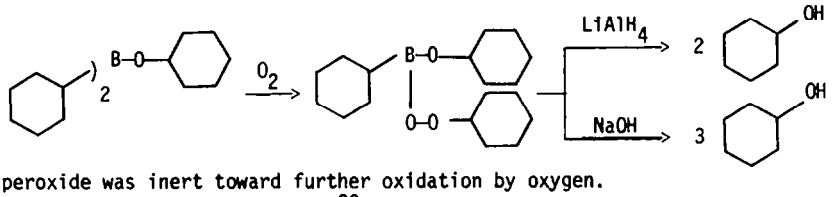
Alkylcatecholboranes are readily available *via* hydroboration.[21] Oxidation of cyclohexylcatecholborane proceeded smoothly at 0°C in hexane or THF. The solution turned black and titration

revealed the presence of only 20% and 5% peroxide in hexane and THF respectively. Possibly a phenoxy radical is displaced in preference to the alkyl radical, leading to the oxidation or polymerization of catechol (eq 14).



(14)

Cyclohexyl dicyclohexylborinate (10 mmol) in THF at 0°C showed a short induction period, followed by a rapid absorption of 9.4 mmol of oxygen in 5 min. But there was no further absorption of oxygen. Reduction with lithium aluminum hydride provided 20.2 mmol of cyclohexanol, while treatment with 3 *N* sodium hydroxide afforded 28.8 mmol of cyclohexanol (eq 15).



(15)

The intermediate peroxide was inert toward further oxidation by oxygen.

The oxidation of dicyclopentylchloroborane[22] in ether proceeded rapidly at 0°C, with the uptake of one mole of oxygen in 4 min. Further uptake was slow. Titration revealed the presence of only 0.34 moles of peroxide per mole of borane. At -78°C, one mole of oxygen was absorbed in 3 min and 1.7 moles in 1 h, with the formation of 1.36 moles of peroxide per mole of borane. The reaction was faster in toluene at -78°C, absorbing 1.72 moles of oxygen in 20 min, with the formation of 1.44 moles (72%) of peroxide.

Unlike cyclohexyl borinate, dicyclopentylchloroborane can be made to absorb two moles of oxygen. At -78°C, oxygen absorption in ether or toluene approaches that required for the formation of diperoxide (eq 16). At 0°C in ether, only one mole of oxygen is absorbed by dicyclopentylchloroborane. The peroxide content is low, perhaps due to intermolecular or intramolecular redox reactions (eqs 17-19). Such side reactions are minimized at -78°C.

$$R_2BCl + 2\ O_2 \xrightarrow{-78°C} (RO_2)_2BCl \quad (16)$$

$$R_2BCl + O_2 \longrightarrow RBCl(O_2R) \quad (17)$$

$$RBCl(O_2R) + R_2BCl \longrightarrow 2\ RBCl(OR) \quad (18)$$

or

$$RBCl(O_2R) \longrightarrow (RO)_2BCl \quad (19)$$

The autoxidation of organoboranes is initially a rapid process, probably limited by the rate of absorption of oxygen by the solution. Thus, tricyclohexylborane absorbs one mole of oxygen in less than one min. On the other hand, borinic ester (cyclohexyl dicyclohexylborinate) requires five min, and boronic ester is relatively inert toward oxygen at 0°C. Such decrease in reactivity with increased substitution is attributed to the overlap of lone pairs of oxygen with the empty orbitals of boron.

The oxidation of both cyclohexyl borinate and dialkylchloroborane has a short, but reproducible induction period. Such an induction period is also observed with *s*-butylboronic anhydride.[23] The initiation stage for these systems apparently is much less efficient than for trialkylboranes.

Oxidation of Alkyldichloroboranes. The autoxidation of *n*-butyldichloroborane in toluene was very fast at 0°C, with the absorption of 0.5 mol of oxygen per mol of borane in 1.5 min. Titration revealed the presence of only a trace of peroxide. At -78°C, after an induction period of 1 min, 0.5 mol of oxygen was absorbed in 3 min, providing only 13% of the peroxide.

Since the alkyldichloroboranes are strong Lewis acids, an intermolecular redox reaction takes place as soon as the peroxydichloroborane is formed (eqs 20,21). This can be developed into a convenient synthesis of alkoxydichloroboranes, although it has not been explored.

$$RBCl_2 + O_2 \longrightarrow RO_2BCl_2 \quad (20)$$

$$RO_2BCl_2 + RBCl_2 \longrightarrow 2\ ROBCl_2 \quad (21)$$

It appeared desirable to control this extremely rapid oxidation. It has been reported that complexation of organoboranes with Lewis bases hinders the attack by oxygen.[24] Accordingly, the ether complex of alkyldichloroborane was examined. *n*-Hexyldichloroborane in ether failed to absorb oxygen at -78°C and the absorption was slow at -30°C. At 0°C, however, 0.9 mol of oxygen per mol of borane was absorbed in 5 min with the formation of 94% peroxide. Reduction with lithium aluminum hydride provided 1-hexanol in 100% yield. Cyclohexyldichloroborane in ether was oxidized readily at -18°C, providing a 93% yield of

peroxide. Reduction of an aliquot of this solution with lithium aluminum hydride revealed a 100% yield of cyclohexanol. Representative alkyldichloroboranes were oxidized in ether at -15 to -18°C and the results are summarized in Table 4.

The formation of a strong complex, alkyldichloroborane etherate, moderates the rate of oxygen uptake and prevents the intermolecular redox reaction shown in eq 21. However, at higher temperature, -18°C, the oxidation proceeds rapidly and cleanly to the corresponding peroxide (eq 20). The reaction is applicable to both primary and secondary boranes.

Table 4. The oxidation of alkyldichloroboranes for the formation of hydroperoxide

Alkyldichloroborane[a]	Time[b] min	% Yield[c] ROOH
1-hexyl	20	94
3-hexyl	5	93
2-methyl-1-pentyl	5	84
cyclopentyl	30	91
cyclohexyl	4	93
norbornyl	5	91

[a] 5 Mmol of 10 ml of ether at -15°C to -18°C. [b] Time for absorption of 5 mmol of oxygen. [c] By iodometric titration.

Inhibition of Autoxidation. Contrary to an earlier report,[13] we have found that iodine is a powerful inhibitor of autoxidation. The long induction periods produced by iodine suggest that the oxidation of organoboranes must involve a relatively slow initiation stage, followed by a highly efficient chain-propagation stage. Oxygen reacts with the organoborane to produce alkyl radicals. These radicals may either react with oxygen to carry on the chain, or with iodine in a chain-terminating step (eqs 22-24).

The reaction was carried out using the automatic gasimeter.[16] When tri-*n*-butylborane was oxidized in tetrahydrofuran or hexane at 0°C in the presence of 5 mol % iodine, no reaction occurred. After about 12-13 min, the iodine color vanished and the oxidation proceeded as normal. See Figure 1. Clearly, the iodine was inhibiting the initiation stage of the free-radical autoxidation.

$$R_3B + O_2 \longrightarrow R\cdot \quad (22)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \longrightarrow \text{chain} \quad (23)$$

$$R\cdot + I_2 \longrightarrow RI + I\cdot \longrightarrow \text{no chain} \quad (24)$$

Effect of Iodine Concentration on Inhibition. The inhibition period, as measured by the disappearance of the iodine color, was not a direct function of iodine concentration. More iodine greatly increased the length of induction period. Both tri-*n*- and -*s*-butylborane were studied at various iodine concentrations. The results are listed in Table 5. At low iodine concentrations, there must be a competition between the reaction of alkyl radicals with oxygen, favoring the chain pathway, and the reaction of the radicals with iodine, leading to chain-termination. At the higher iodine concentrations, oxygen fails to compete effectively and the reaction is terminated. This accounts for the increasing molar effectiveness of iodine at higher concentrations.

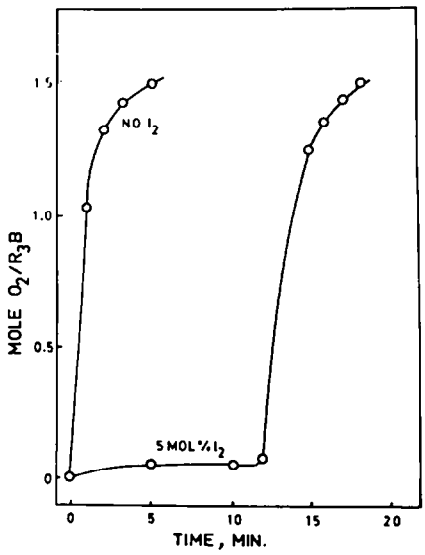


Figure 1. Iodine-inhibited oxidation of tri-*n*-butylborane

No oxygen absorption was observed during the reaction. In order to account for the results, it is then necessary to postulate that iodine is effective in trapping the alkyl radical prior to its reaction with oxygen. The iodine must also capture the dialkylborylperoxy radical with liberation of oxygen before this species can undergo other reactions incorporating oxygen into products (eq 25). Such a reaction would also account for the observation that only one-half of the iodine is converted to alkyl iodide (eq 26).

The inhibition produces alkyl iodide. The rate of oxidation of organoboranes is not affected by organic halides, but the reaction follows another course.[1b]

Effect of Temperature on Inhibition. Lowering the temperature greatly increased the induction period. For example, the autoxidation of tri-*n*-butylborane was inhibited by 5 mol % of iodine for 12.5 min at 0°C, 9.6 min at 25°C, and for greater than 4800 min at -78°C. As a convenient standard, 0°C was chosen for all inhibition studies.

Products in the Iodine-Inhibited Autoxidation. Tri-*n*-butylborane (10 mmol) was oxidized in the presence of 10 and 20 mol % iodine. Analysis following the disappearance of iodine revealed 1.7 and 3.5 mmol of *n*-butyl iodide respectively. Analysis for alcohol after hydrogen peroxide/sodium hydroxide oxidation gave 29.2 and 27.2 mmol of *n*-butanol respectively (eq 27).

Table 5. The effect of iodine concentration on the inhibition of autoxidation of trialkylboranes

Borane[a]	Iodine mol %	Induction Period min
n-Bu_3B	20	915
	10	96
	5	12.5
	2.5	∿ 2
s-Bu_3B	2	50
	1	43
	0.5	12

[a]Ten mmol of borane in 20 ml of tetrahydrofuran at 0°C.

$$R_2BO_2\cdot + I_2 \longrightarrow R_2BI + O_2 + I\cdot \quad (25)$$

$$R_3B + I_2 \xrightarrow{O_2} R_2BI + RI \quad (26)$$

$$n\text{-}Bu_3B + O_2 \begin{cases} \xrightarrow{I_2} \text{1 mmol} \rightarrow \text{BuI} \ 1.7 \text{ mmol} \xrightarrow[H_2O_2]{NaOH} \text{BuOH} \ 29.2 \text{ mmol} \\ \xrightarrow{I_2} \text{2 mmol} \rightarrow 3.5 \text{ mmol} \xrightarrow[H_2O_2]{NaOH} 27.2 \text{ mmol} \end{cases} \quad (27)$$

At higher iodine concentrations, 40 mol %, only 4.9-4.6 mmol of butyl iodide were formed. Oxidation gave 25.4 mmol of butyl alcohol. No other products were detected by GC.

Effect of Structure. A variety of organoboranes were oxidized in the presence of small amounts of iodine to determine the effect of structure on the initiation stage. The results are listed in Table 6.

The initiation stage may either involve direct attack by oxygen on boron, or abstraction of α-hydrogen by oxygen (eq 28). Such α-radicals would be trapped to produce α-iodoorganoboranes, which, upon treatment with base,[25] followed by oxidation, would provide the corresponding secondary alcohols (eq 29). Absence of such alcohol in the product indicates that the initial reaction consists of direct attack of oxygen on boron. Moreover, thexyldivinylborane (3), which has no α-hydrogens, and thexyl-9-BBN (4), which is not expected to give a stable α-radical because the radical will be orthogonal to the empty orbital on boron, are both readily oxidized. Therefore, the initiation step must be a direct attack of oxygen on boron.

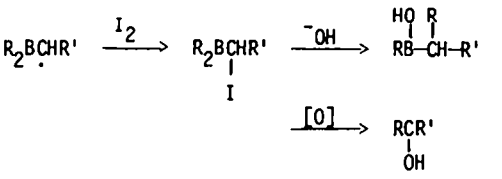
Table 6. Inhibition of the autoxidation of representative organoboranes by iodine

Organoborane[a]	Iodine mol %	Induction Period min
tri-*n*-butyl	5	12.5
n-butyl-9-BBN	5	0.4
tris(2-methyl-1-pentyl)	1	32
tri-*s*-butyl	1	43
tris(2-butyl-3-methyl)	0.5	164
tricyclohexyl	1	34
tri-*exo*-norbornyl	1	17

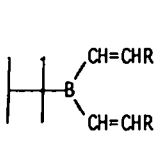
[a]Ten mmol in 20 ml of tetrahydrofuran at 0°C.

$$R_2BCH_2R' + O_2 \longrightarrow R_2B\dot{C}HR' + HO_2\cdot \quad (28)$$

Both the rate of initiation and the length of induction period depend greatly on the structure of the borane. With *n*-Bu_3B, 5 mol % of iodine in solution effectively halts the uptake of oxygen for 12.5 min. The presence of a β-methyl substituent results in a much longer inhibition period, 32 min for 1 mol % of iodine. Likewise, a *s*-butyl group causes an inhibition period of 43 min with 1 mol % of iodine. The observed relative rates of initiation at 0°C are: *n*-Bu_3B >> *s*-Bu_3B > *i*-Bu_3B. These are opposite to the order of autoxidation: tertiary > secondary > primary. The differences in rates of initiation can be explained on steric grounds. The attack of oxygen on borane in the initiation stage is hindered by increased crowding provided by the three alkyl groups attached to boron.



(29)



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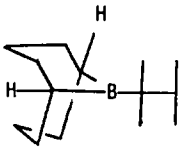
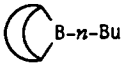


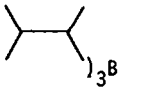
4

To test this hypothesis, two organoboranes, one with relatively low steric crowding, *B*-*n*-butyl-9-BBN (5), and one with a relatively high degree of steric crowding, tris(3-methyl-2-butyl)-borane (6), were subjected to autoxidation with added iodine and compared to tri-*n*- and -*s*-butylborane (Table 6). The sterically open borane has a very short induction period and the sterically crowded borane a very long one. The induction period is directly related to the relative rate of initiation. Thus, increased crowding around the boron atom has a marked effect on the rate of initiation of autoxidation.



B-*n*-butyl-9-BBN

5



tris(3-methyl-2-butyl)-borane

6

The rates calculated for initiation using iodine compare favorably to those calculated using galvinoxyl as an inhibitor. However, galvinoxyl could not be used to determine the initiation rate for tri-*n*-butylborane.

The differences in the relative order of reactivity for the initiation stage and the oxidation stage are not contradictory. The initiation stage involves a direct attack on boron, the rate of which is controlled by the steric crowding around the boron. The relative rate of oxidation involves attack by an oxygen radical on a single species, R_2BR', in which the most stable alkyl radical is displaced.

Rates of Initiation. At high iodine concentrations, alkyl radicals should be effectively trapped by iodine. By following the rate of alkyl iodide production, one can follow the rate of initiation of autoxidation. Accordingly, tri-*n*-, -*s*- and -*i*-butylborane were each oxidized in the presence of 40 mol % iodine. The flasks were stirred vigorously at 0°C in the dark under oxygen. Samples were removed periodically and analyzed for alkyl halide. In the absence of oxygen, the formation of butyl iodide was negligible. The products also were not destroyed appreciably under the reaction conditions. The results are shown graphically in Figure 2. From this data, the rates of initiation were calculated. These are summarized in Table 7.

CONCLUSIONS

This study provides a method for the rapid, convenient synthesis of alkyl hydroperoxides. The reaction is applicable to a wide variety of structures. Unlike the reaction of alkylmethanesulfonates with hydrogen peroxide, which produces hydroperoxides in 10-50% yield,[26] the present procedure readily accommodates substrates which do not readily undergo nucleophilic substitution, such as cyclohexyl and norbornyl. The organoborane route also accommodates a wide variety of functional groups, unlike the Grignard reaction,[27] so that a wide variety of functionally substituted hydroperoxides should now be readily available.

Alkyldichloroboranes offer the method of choice for the synthesis of hydroperoxides when maximum use of an alkyl group is desired. Furthermore, this suggests that the chloroboranes may be used in other free-radical reactions.

The availability of an efficient free-radical inhibitor provides a powerful tool to investigate such reactions. Thus, the free-radical addition of organoboranes to acrolein or methylvinyl ketone is inhibited by both galvinoxyl[28] and iodine.[2c]

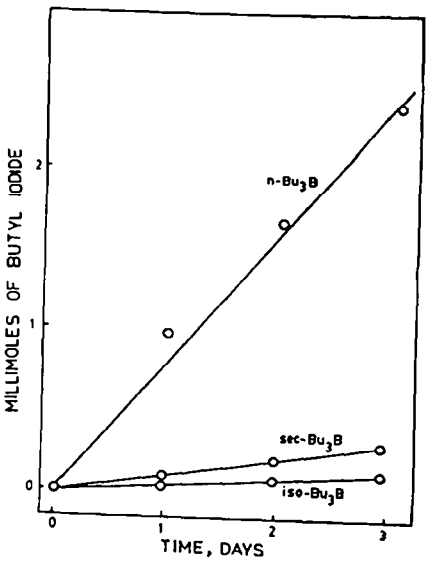


Figure 2. Rate of iodine-inhibited oxidation of the tributylboranes in tetrahydrofuran at 0°C

Table 7. Rates of initiation of autoxidation of tributylboranes

Organoborane	Rate (mol^{-1} min^{-1}) From Iodine	From Galvinoxyl[12]
tri-*n*-butyl	26×10^{-6}	—
tri-*s*-butyl	3.5×10^{-6}	3×10^{-6}
tri-*i*-butyl	1.6×10^{-6}	7×10^{-6}

EXPERIMENTAL SECTION

Methods. The techniques employed in handling air-sensitive materials are described elsewhere.[25] The alcohols and iodides were analyzed on a Varian 1200 gas chromatograph using a suitable internal standard. The peroxides were analyzed by titration.

Material. Diethanolamine (Aldrich) was stored under nitrogen and used directly. Tri-Sil (Pierce Chemical Co.) was used for the silylation of alcohols. Lithium borohydride (Alfa Inorganics), boron trichloride (Matheson, Coleman & Bell) and iodine (Mallinckrodt) were used directly. Trialkylboranes from Callery Chemicals were also used without further purification. Cyclohexylcatecholborane and alkyldichloroboranes were prepared as described elsewhere.[25]

Low Temperature Autoxidation of Organoboranes. A dry, 100-ml flask equipped with a septum inlet and a magnetic stirrer with a Teflon collar was flushed with nitrogen. The flask was charged with 10 mmol of organoborane in 20 ml of tetrahydrofuran. The flask was maintained under a positive nitrogen pressure and cooled to -78°C with a Dry Ice-acetone bath. A calcium chloride/ice bath was used for -47°C. One ml of methanol was added as an antifreeze agent. The flask was placed on an automatic oxidizer, which was previously filled with oxygen (the system was evacuated by a water aspirator, then refilled by injecting 5 ml of 30% hydrogen peroxide into the generator) and the remaining oxygen was removed by injecting 1.5 ml of 30% hydrogen peroxide into the generator. The stirrer was started to initiate the reaction. Organoboranes containing primary alkyl groups absorbed one mol of oxygen per mol of borane. Warming to 0°C caused absorption of the second mol of oxygen. Organoboranes containing secondary alkyl groups absorbed 2 mol of oxygen at -78°C. Undecane (10 mmol) was added as internal standard. One ml of the solution was removed and added to 1 ml of 1.65 *M* of lithium aluminum hydride in tetrahydrofuran. A vigorous reaction ensued. To the remainder was added 10 ml of 3 *N* sodium hydroxide. The lithium aluminum hydride solution was acidified with 1 *M* HCl and both portions saturated with potassium carbonate. The alcohol was estimated by adding 2-3 drops of the solution to 0.8 ml of Tri-Sil, shaking for 1 min and analyzing by GC (1/4" x 6' SE-30 column).

Preparation of Hydroperoxides. The preparation of cyclohexyl hydroperoxide is representative. A dry 200-ml flask equipped with a septum inlet and a magnetic stirring bar with a Teflon collar was flushed with nitrogen. The flask was charged with 75 ml of dry THF and 12.3 g of cyclohexene (150 mmol) and then cooled to 0°C. Hydroboration was achieved by the dropwise addition of 16.3 ml of a 3.07 *M* solution of borane (150 mmol of hydride), followed by heating at 50°C for 3 h to complete the hydroboration. The solution was cooled to -78°C and 1.0 ml methanol was added to facilitate the solution of borane. The flask was then attached to the automatic oxygenator which had been previously flushed with oxygen by injecting 15 ml of 30% hydrogen peroxide into the generator with an empty 100-ml flask in place of the reaction flask. The system was further flushed by injecting 5 ml of 30% hydrogen peroxide into the generator. The stirrer was started and the oxygen absorption was followed by reading the buret filled with standardized 3% aqueous hydrogen peroxide. After the absorption of 2 mol of oxygen was complete, the solution was warmed to 0°C and 16.5 ml of 30% aqueous hydrogen peroxide was added dropwise. The solution was stirred an additional 0.5 h at 0°C. Hexane (50 ml) was added and the solution washed with 25 ml of water. Iodometric titration on a 10-mmol scale reaction gave a 95% yield of hydroperoxide. The hydroperoxide was separated from the alcohol by extraction with four 25-ml portions of 40% potassium hydroxide. The combined aqueous extracts were washed with 50 ml of hexane and then neutralized at 0°C with HCl. The hydroperoxide was then recovered with 50 ml of hexane. The hexane layer was separated, dried ($MgSO_4$) and distilled. There was recovered 9.5 g (82%) of cyclohexylhydroperoxide, bp 39-40° (0.08 mm), $n^{20}D$ 1.4645 [lit.[27] bp 42-43° (0.1 mm), $n^{20}D$ 1.4645].

Titration of Hydroperoxide.[29] The above reaction was run using 10 mmol of organoborane. After hydrogen peroxide oxidation and hexane extraction, the solution was diluted to 100 ml with ethanol. A 10-ml aliquot was removed and added to 3 ml of saturated potassium iodide and 3 ml of acetic acid under nitrogen. The solution was refluxed for 10 min and then titrated under nitrogen with 0.1 *M* sodium thiosulfate.

Titration of Boronic Acids. The remaining solution above was diluted with about 100 ml of water and 2 g of mannitol added. The solution was titrated to the phenophthalein endpoint with 2.0 *M* potassium hydroxide.

Precipitation of Diethanolamine Boronic Esters From Hydroperoxides. The reaction with tricyclohexylborane is representative. The autoxidized solution (10 mmol of R_3B in 20 ml of tetrahydrofuran) was treated with 10 mmol of diethanolamine at 0°C. An immediate heavy precipitate formed. Hexane (20 ml) was added and the solution filtered. There was recovered 1.80 g (92%) of the diethanolamine ester, mp 222-223°C. Titration of the solution for peroxide gave a 93% yield and titration for boronic acid revealed that 96% was removed. Likewise, tricyclopentylborane gave a precipitate, 88%, mp 207-207.5°C, and tri-*exo*-norbornylborane gave a precipitate, 91%, mp 217-218°C. Each compound gave a satisfactory mass spectrum.

Preparation and Oxidation of Cyclohexyl Dicyclohexylborinate. A dry 100-ml reaction flask was flushed with nitrogen and charged with 10 mmol of borane in 20 ml of tetrahydrofuran. The solution was cooled in an ice bath and 1.64 g (20 mmol) of cyclohexene added dropwise. The solution was stirred for 1 h at 0°C to form dicyclohexylborane. Then 1.06 g (10.5 mmol) of cyclohexanol was added. The solution was stirred at room temperature for 12 h, then cooled to 0°C and placed on an automatic oxidizer previously filled with oxygen. The system was flushed with oxygen by injecting 1.5 ml of 30% hydrogen peroxide into the generator. Rapid stirring was then started. After a slight induction period, about 1 min, oxygen absorption was rapid. After 5 min, 9.4 mmol of oxygen had been absorbed. Undecane (10 mmol) was added as an internal standard. One ml of solution was removed and added slowly to 1 ml of 1.65 *M* lithium aluminum hydride in tetrahydrofuran at 0°C. This solution was acidified (HCl) and dried over K_2SO_3. The remaining solution was treated with 3.3 ml of 3 *N* sodium hydroxide at 0°C. The aqueous phase was saturated (K_2CO_3) and the organic phase separated. Two drops of each solution were added to 0.8 ml of Tri-Sil, the solution mixed for 1 min, and then analyzed on an SE-30 column. The lithium aluminum hydride treated solution gave 20.2 mmol of cyclohexanol and the sodium hydroxide treated solution gave 28.8 mmol of cyclohexanol.

Preparation of Chloroborane Etherate. The method of Brown and Ravindran was used.[22,30]

Preparation and Oxidation of Chlorodicyclopentylborane. The usual 100-ml reaction flask under nitrogen was charged with 5.5 ml of a 0.91 *M* solution of chloroborane etherate. Cyclopentene, 10 mmol, was added dropwise to the stirred solution at 0°C. The solution was stirred an additional hour at 0°C, then attached to the oxidizer. The nitrogen was flushed by injecting 2 ml of 30% hydrogen peroxide into the generator. The stirrer was started and oxygen absorption followed by reading the buret filled with 3% hydrogen peroxide. After completion of oxygen absorption, 5 mmol in 4 min, the solution was diluted to 100 ml with ethanol and 10.0 ml of this solution was titrated for hydroperoxide, as previously described. Analysis showed 1.7 mmol of peroxide (34% based on oxygen or on one alkyl group). The reaction at -78°C was run in a Dry Ice-acetone bath. Analysis revealed 6.8 mmol (68% of 2 alkyl groups) of peroxide. The dicyclopentylchloroborane (5 mmol) was prepared as above in ether. The ether was then removed with a water aspirator and replaced by 5 ml of toluene under nitrogen. The solution was cooled to -78°C and oxidized on the automatic oxidizer. After 20 min, 8.6 mmol of oxygen was absorbed. There was no further absorption of oxygen after 30 min. The solution was diluted to 100 ml with ethanol and 10.0 ml titrated for peroxide. Analysis revealed 7.2 mmol (72%) of peroxide.

Oxidation of Alkyldichloroboranes. The following general procedure was utilized. The usual 100-ml reaction flask was charged with 5 mmol of alkyldichloroborane, followed by 10 ml of solvent. (Ether was added slowly at 0°C to moderate the very exothermic reaction.) The solution was cooled to the desired temperature, then placed on the automatic oxidizer previously filled with oxygen. The system was flushed by injecting 1.5 ml of 30% hydrogen peroxide into the generator and the stirrer started. Oxygen absorption was followed by reading the buret filled with 3% hydrogen peroxide. After oxygen absorption ceased, the solution was titrated for peroxide. In toluene at 0°C, 2.5 mmol of oxygen was absorbed in 1.5 min by *n*-butyldichloroborane and only a trace of peroxide was formed. At -78°C, 2.5 mmol of oxygen was absorbed in 3.5 min and 4.5 mmol in 60 min.

Titration gave 0.65 mol of peroxide (13%). In ether, dichloro-*n*-hexylborane (10 mmol) absorbed 9.0 mmol of oxygen in 5 min at 0°C. Titration gave 8.5 mmol of peroxide. At -78°C or -45°C, no oxygen was absorbed. At -30°C, there was a slow absorption of oxygen, 5 mmol after 1 h. At -18°C, 10 mmol was absorbed in 20 min. Titration gave 9.4 mmol (94%) of peroxide. Cyclohexyldichloroborane (5 mmol) in ether absorbed 5.0 mmol of oxygen in 3 min at -15°C and gave 4.65 mmol (93%) of peroxide. These two oxidations were then repeated with 5 mmol of undecane, added as an internal standard. A 1-ml aliquot was removed and added dropwise to 3 ml of ether containing 0.08 g, 2 mmol, of lithium aluminum hydride. The solution was stirred for 3 min, then cautiously hydrolyzed with 6 *N* hydrochloric acid. The solution was saturated with potassium carbonate and analyzed by GC for alcohol. *n*-Hexyldichloroborane (4.5 mmol) gave 4.5 mmol (100%) of 1-hexanol, cyclohexyldichloroborane (5 mmol) gave 5 mmol (100%) of cyclohexanol.

Iodine Inhibition Study. A dry 100-ml flask equipped with a septum inlet and magnetic stirring bar with Teflon collar was flushed with nitrogen and charged with 20 ml of tetrahydrofuran. The organoborane (10 mmol) was prepared by hydroboration, as previously described, and the solution cooled to 0°C (or -78°C). Iodine was introduced from a standard solution in benzene (0.2 *M*). For a 5 mol % solution, 2.5 ml of the standard solution was used. The flask was then placed on an automatic oxidizer filled with oxygen and the nitrogen removed by injecting 5 ml of 30% hydrogen peroxide into the generator. The stirrer and timer were started. After an interval of time, the iodine color suddenly vanished and the oxygen uptake proceeded at a rate similar to that observed for a normal oxidation. At the point of iodine disappearance, the time was noted and recorded as the inducting period. In the case of tri-*n*-butylborane using 10 and 20 mol % of iodine, the solution was analyzed by GC for *n*-butyl iodide using undecane as an internal standard. There was found 1.7 and 3.5 mmol of butyl iodide respectively. The solution was then oxidized by the addition of 3.3 ml of 3 *N* sodium hydroxide, followed by 3.3 ml of 30% hydrogen peroxide. The solution was stirred for 1 h at room temperature and the aqueous phase saturated (K_2CO_3). The organic phase was analyzed for alcohol by GC. The 10 mol % of iodine reaction gave 29.2 mmol of butanol and the 20 mol % of iodine reaction gave 27.2 mmol of butanol.

Preparation of *B*-*n*-Butyl-9-BBN. 9-BBN was prepared by the method of Knights and Brown[31] as an 0.61 *N* solution in tetrahydrofuran. To 16.5 ml (10 mmol) of this solution at 0°C in a dry 100-ml reaction flask was added 1.1 g (20 mmol) of 1-butene. After stirring for 1 h at room temperature, the solution was cooled to 0°C and 0.5 mol of iodine added. The solution was oxidized as above. After 0.4 min, the iodine color vanished and oxygen absorption became rapid.

Preparation and Reaction of Trisiamylborane. A dry 100-ml reaction flask was flushed with nitrogen and charged with 14 ml of tetrahydrofuran and 3.26 ml of borane in tetrahydrofuran, 3.07 *M* (30 mmol of hydride). Hydroboration was achieved by the dropwise addition of 2.31 g (33 mmol, 10% excess) of 2-methyl-2-butene. The mixture was stirred for 24 h at room temperature to complete the hydroboration of this exceedingly sluggish olefin. The solution of organoborane was then cooled to 0°C and 0.05 mol of iodine added. The solution was subjected to oxidation as above. On two runs the iodine vanished after 150 and 174 min for an average of 162 min.

Rate Determination. The usual reaction flask was charged with 20 ml of a 0.5 *M* solution of a tributylborane in tetrahydrofuran, 0.2 *M* in iodine. Decane (10 mmol) was added as an internal standard. The flask was placed on an oxidizer filled with oxygen and the nitrogen removed by injecting 5 ml of 30% hydrogen peroxide into the generator. The solution was stirred at 0°C in the dark (the flask was covered with aluminum foil). Periodically, samples (0.25 ml) were removed and injected under nitrogen into a vial containing 0.1 ml saturated sodium thiosulfate. Hexane (1.0 ml) was immediately added and the solution analyzed by GC for alkyl iodide. Under these conditions, the reaction of trialkylboranes with iodine, as followed by loss of borane and appearance of alkyl iodide, in the absence of air, was negligible. Likewise, under these conditions, the reaction of the alkyl iodides with oxygen was negligible. In the case of tri-*n*-butylborane, the iodine disappeared in about five days. Analysis for alkyl iodide gave 4.0 and 4.6 mmol on two separate runs. The solution was oxidized by the addition of 3.3 ml of 3 *N* sodium hydroxide, followed by the dropwise addition of 3.3 ml of 30% hydrogen peroxide. After stirring for 1 h at room temperature, the aqueous phase was saturated with K_2CO_3. Analysis by GC revealed 25.4 mmol of *n*-butyl alcohol and no other alcoholic product. The rates of initiation were determined by determining the slopes of the lines in Figure 2. These were found to be: tri-*n*-butyl, 26×10^{-6} ml^{-1} min^{-1}; tri-*s*-butyl, 3.5×10^{-6}; tri-*i*-butyl, 1.6×10^{-6}.

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