ments, Miss Katie Reimer and Miss Patricia Fogle for our NMR spectra, and Mr. Victor Bartosewitz and Mr. Dale Reed for special glassware and Teflon machining constructions. S.A.S. thanks Drs. R. R. McGuire and J. K. Erbacher (FJSRL) for their constructive comments.

Registry No.—*trans*-1,2-Cyclohexanediol, 1460-57-7; cyclohexene, 110-83-8; xenon trioxide, 13776-58-4; *exo*-2,3-norbornene oxide, 3146-39-2; norbornene, 498-66-8; *syn*-2,5-norbornanediol, 21462-09-9; *anti*-2,5-norbornanediol, 21462-10-2; *syn*-2,7-norbornanediol, 17366-25-5; *anti*-2,7-norbornanediol, 17289-99-5; *cis*-stilbene, 645-49-8; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene oxide, 1439-07-2; sodium perxenate, 26304-24-5; *cis*-1,2-cyclohexanediol, 1792-81-0; *m*-chloroperbenzoic acid, 937-14-4.

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Mechanisms of the Borate Ester Induced Decomposition of Alkyl Hydroperoxides

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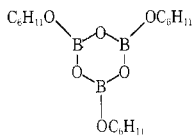
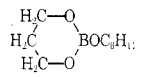
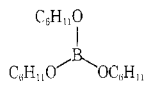
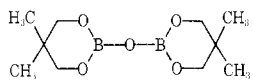
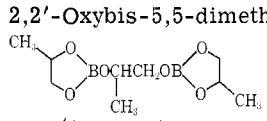
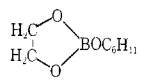
A comparison has been made of the relative rates of tetralin hydroperoxide (THPO) decomposition in *cis*-2-octene, induced by seven different alkyl borate esters. This has demonstrated that the relative acidity of the boron atom, as a result of either the presence of B–O–B bonds or the hybridization of the boron caused by the O–B–O dihedral angle, determines the rate and efficiency of epoxide formation. It is also shown that the highly acidic borate esters, phenyl metaborate, phenyl orthoborate, and triacetyl borate, which decompose THPO approximately 600 times as fast as the most reactive alkyl borate ester, fail to epoxidize olefins but lead to an acid-catalyzed rearrangement of the hydroperoxide producing *o*-(4-hydroxyphenyl)butyraldehyde. The unsaturated borate ester, 2-*n*-butoxy-4,5-diphenyl-1,3,2-dioxaborole (**5**), prepared from *n*-butyl orthoborate and benzoin, reacts rapidly with THPO to give, on hydrolysis, a 4:1 mixture of benzil and benzoic anhydride. Autoxidation of **5** in chlorobenzene produced a 1.2:1 mixture of benzil and benzoic acid. The borate induced decomposition of *tert*-butyl hydroperoxide (*t*-BuOOH) in cyclooctane or *n*-decane is shown to enhance the formation of cyclooctanol and *n*-decanols. This selectivity is interpreted to occur through an induced SH2 (bimolecular homolytic substitution) reaction of solvent alkyl radical on *t*-BuOOH coordinated to borate ester.

We have previously described the generation of a species capable of liberating electrophilic oxygen through the reaction of an alkyl hydroperoxide and a metaborate ester. This intermediate complex has been shown to readily epoxidize olefins or hydroxylate highly nucleophilic aromatic rings and concomitantly produce an alcohol from the hydroperoxide. We have also shown that the presence of a suitable acceptor is critical to efficient consumption of the available nucleophilic oxygen.[1]

Our previous work had shown that the alkyl hydroperoxide–alkyl metaborate system epoxidized olefins in a manner quite similar to that observed with peracetic acid[2] and the hydroperoxide–transition metal system.[3] Thus, more highly substituted olefins are epoxidized more rapidly, stereospecifically, and with no kinetic preference for cis or trans isomers. Unlike peracetic acid, which is relatively stable in hydrocarbons at temperatures at which it readily epoxidizes olefins, the hudroperoxide–metaborate mixture (in hydrocarbon solvent) decomposes at the same rate at which it epoxidizes 1-octene. A unique example of this is the cyclohexyl metaborate induced decomposition at 120° of cumene hydroperoxide in 2-octene and *n*-octane, respectively. In the olefinic solvent, the reaction products are 2-epoxyoctane and 2,2-dimethylbenzyl alcohol. In *n*-octane the reaction gives only acetone and phenol, the products of the well-known acid-catalyzed rearrangement of cumene hydroperoxide.[4] We had previously proposed several related types of metaborate ester–hydroperoxide intermediates to account for the observed reactions.

Recently, Sheldon and VanDoorn[5] have reported studies which expanded the scope of the borate–hydroperoxide system as an epoxidizing agent. These workers have demonstrated that both metaborate esters and the intrinsically less acidic orthoborate esters are capable of acting as catalysts for olefin epoxidation by *tert*-butyl hydroperoxide if sufficiently strong electron-withdrawing groups are at-

Table I
Epoxidation of *cis*-2-Octene by Tetralin Hydroperoxide at 80° Induced by Various Borate Esters

Registry no.	Borate ester[a]	Relative reactivity[b]	Yield of epoxide[c]
		220	100
1172-69-6	Cyclohexyl metaborate (CHMB)		
		1[d]	~20
55089-02-6	2-Cyclohexyloxy-1,3,2-dioxaborinane		
		1[d]	Nil
2467-16-5	Cyclohexyl orthoborate (CHOB)		
		10	83
55089-03-7	2,2′-Oxybis-5,5-dimethyl-1,3,2-dioxaborinane		
		4	50
1216-17-7	Tris(1-methylethylene glycol)biborate		
		4	55
55089-04-8	2-Cyclohexyloxy-1,3,2-dioxaborolane		

[a] The equivalents of borate ester present (measured in gram-atoms of boron) in the reaction solutions is identical with the moles of tetralin hydroperoxide present. [b] Measured as first-order decomposition rate constant for tetralin hydroperoxide. [c] Measured as *cis*-2,3-epoxyoctane. [d] Same absolute decomposition rate constant as for tetralin hydroperoxide with no additive.

tached to boron. It was also noted that bulky substituents about the boron atom extended catalytic lifetimes, apparently owing to steric inhibition of alcoholysis and concurrent catalyst deactivation by the reaction coproduct, *tert*-butyl alcohol. We have now examined additional details relating to borate ester–hydroperoxide intermediates. This paper reports those and related findings.

Results and Discussion

We had previously observed that the decomposition of tetralin hydroperoxide (THPO) at 80° induced by an equimolar quantity of cyclohexyl metaborate (CHMB) (the 1:1 *M* dehydro adduct of cyclohexanol and boric acid) in the presence of *cis*-2-octene is accelerated some 220-fold over that for the noncatalyzed decomposition of THPO in *cis*-2-octene, producing an almost quantitative yield of *cis*-2,3-epoxyoctane and α-tetralol in the former case. In addition, we had observed that cyclohexyl orthoborate (3:1 *M* dehydro adduct of cyclohexanol and boric acid) neither accelerated the decomposition of THPO nor led to epoxide formation.

Studies on the hydrolysis of trialkyl-substituted borate esters has shown that the cyclic metaborate esters with bulky substituents are substantially more reactive than the analogous acyclic orthoborates.[6] This has been taken as evidence for steric inhibition of the transient quaternization of boron by coordination with an unshared pair of electrons on the water oxygen in the borate ester. If an analogous interaction is the sole factor in facilitating the epoxidation of olefins by hydroperoxides, then one might anticipate that methyl orthoborate would be an effective catalyst for the epoxidation reaction. Such is not the case; methyl orthoborate exhibits no catalytic activity in the decomposition of THPO in olefinic solvents.

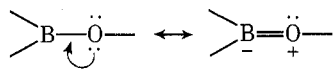
In an effort to determine what structure–reactivity feature is significant in producing an effective catalyst we have synthesized a number of known borate esters and examined their efficacy, at equimolar concentration with the hydroperoxide, in inducing the epoxidation of *cis*-2-octene by THPO. Table I presents the data from that study.

2-Cyclohexyloxy-1,3,2-dioxaborinane is structurally similar to the cyclohexyl metaborate ring system but contains only one boron atom. From a steric point of view the acid–base interaction of the borate ester with a hydroperoxide could occur as readily with 2-cyclohexyloxy-1,3,2-dioxaborinane as with cyclohexyl metaborate. As can be seen, the compound is only modestly active in the epoxidation reaction. The presence of tris(1-methylethylene glycol)biborate accelerates the decomposition of THPO fourfold and leads to a 50% yield of epoxide while 2,2′-oxybis-5,5-dimethyl-1,3,2-dioxaborinane produces a tenfold rate enhancement in THPO decomposition and gives 83% yield of the epoxide.

We had previously considered the possibility that the high reactivity of metaborates was not only due to their ability to coordinate with hydroperoxides but that one of the two remaining free boron atoms in the ring could weakly coordinate with the olefin and thereby facilitate epoxidation. The data presented in Table I are, to a degree, consistent with that idea. The catalytic activity of the various borate esters increases, along with epoxide productivity, as the proximity of two boron atoms in a given molecule increases.

The above data are better explained based on a variation in the reactivity due to the acid hardness of the various borate esters relative to the hydroperoxides as hard bases, where the acidities of the borate ester will vary as a function of the substituents about, and the hybridization of, a given boron atom. This conclusion is consistent with that reported earlier by Sheldon and VanDoorn.[5]

In cyclohexyl metaborate each boron atom of the six-membered ring can draw electron density from a single cyclohexyloxy group through a $p\pi$–$p\pi$ interaction.



This resonance form is stabilized inductively by the cyclohexane ring. On the other hand, the three adjacent B–O bonds in the cyclic system will inductively destabilize the already electron-deficient borons in the presence of the electronegative oxygens. Using CHMB as a benchmark, cyclohexyl orthoborate and 2-cyclohexyloxy-1,3,2-dioxaborinane would have substantially less acidic boron owing to the electron donation from each of three alkoxy linkages. The relative acidity of 2,2′-oxybis-5,5-dimethyl-1,3,2-dioxaborinane, compared to the two above compounds, should be higher owing to the presence of the B–O–B bond.

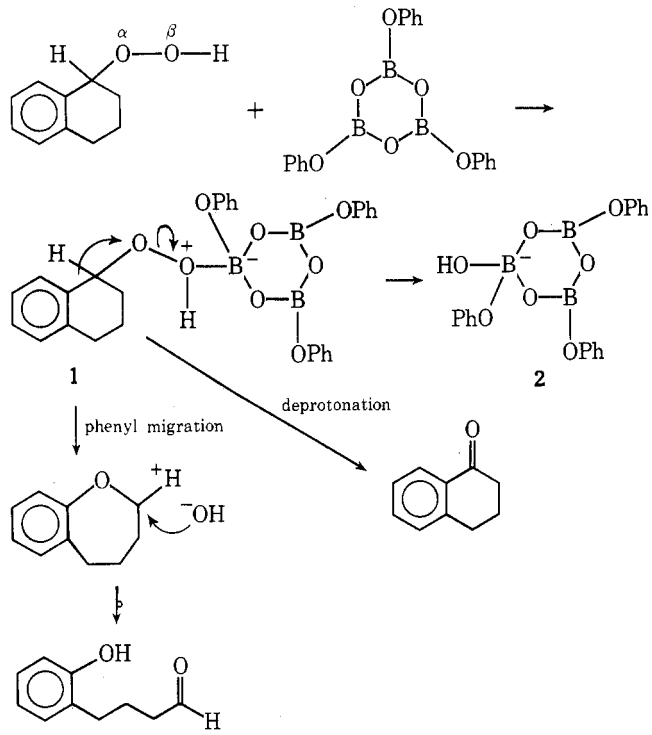
Tris(1-methylethylene glycol)biborate, in which the borons are insulated from each other by a 1,2-dioxoethylene bridge, still accelerates the decomposition of THPO. The enhanced acidity of this biborate is due to the change in hybridization of the boron in a five-membered ring.[7] The O–B–O bond angles about the boron are compressed from the normal trigonal (sp^2) 120° toward the tetrahedral (sp^3) required for quaternization, thereby facilitating coordination with a base. The simpler five-membered ring borate 2-cyclohexyloxy-1,3,2-dioxaborolane produces a rate enhancement and epoxide formation identical with that observed with the five-membered ring biborate.

The effect of even more highly acidic borate esters on the decomposition of THPO can be seen from the following series of experiments. A re-examination of the decomposition of 0.4 *M* THPO in chlorobenzene induced by equimolar CHMB at 120° showed that on completion of the reaction a product distribution of 81 mol % α-tetralol, 8 mol % α-tetralone, and 11 mol % 1,2-dihydronaphthalene was obtained. In a separate experiment it was shown that α-tetralol dehydrates under the reaction conditions to 1,2-dihydronaphthalene at a rate sufficient to produce the amount found after the experiment described above was completed. Hence, the initial α-tetralol selectivity from the THPO–CHMB reaction in chlorobenzene is 92%.

Replacing the CHMB with an equivalent amount of phenyl metaborate (PMB) alters the course of this reaction dramatically. Admixture of THPO and PMB in chlorobenzene at room temperature results in a vigorous exothermic reaction (to ~40°) in which over 90% of the active oxygen titer is consumed in 10 min. The final product mixture contains no tetralol, but instead the aldol condensation product of 4-(*o*-hydroxyphenyl)butyraldehyde and a small quantity of α-tetralone. If mesitylene is used as solvent the same result is obtained, giving a 95% yield of the aldol dimer and a 5% yield of α-tetralone. This result is the antithesis of what is observed with CHMB and THPO in mesitylene. This latter reaction is immeasurably slow at room temperature, but at 90° rapidly yields mesitol (2,4,6-trimethylphenol) by hydroxylation of the solvent and concurrently produces α-tetralol on reduction of the THPO.[1]

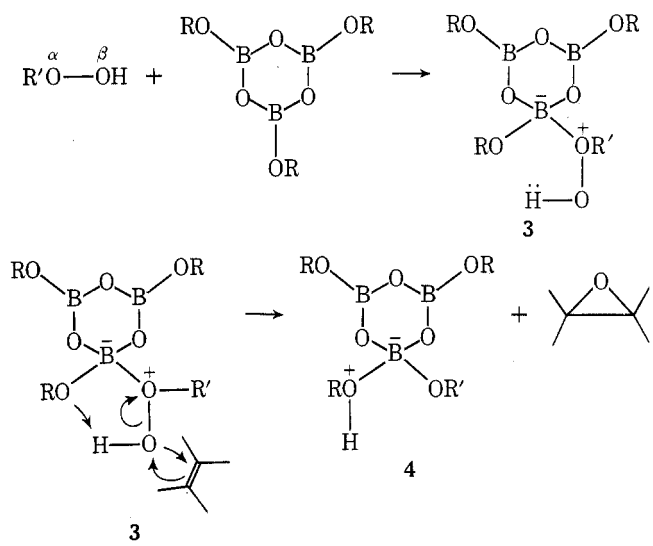
Although the formation of 4-(*o*-hydroxyphenyl)butyraldehyde from THPO in the presence of PMB or triphenyl orthoborate (POB) could be verified by 2,4-DNP[8] formation or titration of its aldol dimer with hydroxylamine hydrochloride,[9] actual isolation of the aldehyde was unsuccessful in the presence of the phenol generated by borate hydrolysis. Successful isolation of 4-(*o*-hydroxyphenyl)-butyraldehyde (see Experimental Section) was achieved from reaction mixtures in which the highly acidic triacetyl borate was used.

Scheme I



The enhanced acidity of PMB compared to CHMB is a result of the phenyl rings acting as electron sinks to generate a high level of electron deficiency at the boron atoms. This is just the opposite effect created by the presence of an aliphatic alkoxy substituent on boron. The observed reaction can be rationalized as shown in Scheme I.

We had previously[1] indicated our preference in the reaction of THPO–CHMB in mesitylene hydroxylation or olefin epoxidation for an intermediate borate–hydroperoxide complex which involved a boron–oxygen interaction at the α oxygen atom of the hydroperoxide as shown below.



In the two mechanisms pictured above, the acidity of the borate ester determines which peroxidic oxygen will develop positive charge and ultimately lead to a O–O bond scission. If, as one would expect, there is a dynamic equilibrium in which the borate ester is forming a reversible complex with either the α or β oxygens of the hydroperoxide, then we must determine the difference in the transient B–O bond formed between a hydroperoxide and PMB (complex 1) from that formed with CHMB (complex 3)

which causes it to proceed to products from those particular complexes.

The collapse of complex **1** to give 4-(*o*-hydroxyphenyl)butyraldehyde or α-tetralone is estimated to be at least 600 times faster than that of complex **3** to produce, for example, epoxide and α-tetralol. The formation of products from complex **1** is unimolecular while that of **3** is clearly bimolecular, requiring an intimate association of the acceptor (i.e., olefin) and the complex.[10] Since in both cases the same bond is breaking, the difference must be in the ability of the two borate esters to stabilize the resulting leaving group. In the transition state where complex **1** leads to O–O bond rupture the leaving group is the anion, phenyl metaborate hydroxide (**2**) having a formal negative charge on the tetrahedral boron atom. The electron-withdrawing phenoxy groups can stabilize this species while the electron-donating cyclohexyloxy group would be destabilizing.

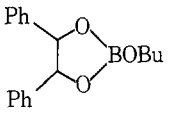
Complex **3**, which also leads to O–O fission, produces a strikingly different and undoubtedly lower energy leaving group. Formation of this species is the result of an intramolecular proton transfer to give **4**, which has an alcohol coordinated to a metaborate ester and will be in equilibrium with the free alcohol and metaborate and thereby require minimal stabilization by the borate ester. This proton transfer step is clearly required for heterolysis of the O–O bond. Cumyl methyl peroxide is unreactive in the presence of CHMB under conditions where cumene hydroperoxide readily epoxidizes olefins.

Hence, there is a spectrum of simple borate esters of varying acidity which include those which are too weak (i.e., acyclic orthoborates and six-membered ring orthoborates) to effectively interact with a hydroperoxide and facilitate a heterolysis of the O–O bond competitive with thermally induced homolysis. This is followed by borate esters of moderate acidity, i.e, five-membered ring orthoborates, biborates, and most effective, alkyl metaborates, which cleave the hydroperoxide O–O bond, generating, in the presence of a suitable acceptor, what may formally be considered a hydroxonium ion, $[HO^+]$.[11] Beyond this are the highly acidic phenyl borate esters and triacetyl borate, which can heterolyze the hydroperoxide so that the electron-deficient center ends up on the oxygen attached to a carbon atom, $[RO^+]$.

This reactivity pattern is obviously dependent on the facility with which the organic moiety of the hydroperoxide can absorb the positive charge. Sheldon and VanDoorn[5] have observed epoxidation of 2-octene by *tert*-butyl hydroperoxide in the presence of PMB in a yield of 26–59%.

This type of selectivity is also consistent with the observations of Sheldon[12] in his study on the metal-catalyzed epoxidation of olefins. The selectivity of Mo(VI), Ti(IV), and V(V) complexes in catalyzing epoxide formation from hydroperoxides is related to their being hard acids. As has been pointed out, in the case of molybdenum catalysis,[12] independent of which oxidation state the metal is initially in, the active species in solution is a Mo(VI) complex. The hardness can be correlated with the ability of an alkyl hydroperoxide, acting as a Lewis base, to coordinate with the metal. Efficient epoxidation in this case requires that the transition metal–hydroperoxide complex not have a favorable internal redox potential for electron transfer. This latter process would lead to radical formation and is the reason why metals such as Cr(VI) are ineffective catalysts. With borate esters no redox processes are possible.

In the course of these studies we had the opportunity to examine the reactivity of the unsaturated borate ester 2-*n*-butoxy-4,5-diphenyl-1,3,2-dioxaborole (**5**). This compound, described by Bolban et al.,[13] is readily synthesized by heating an equimolar mixture of benzoin and tributyl borate at 100° and 2 mmHg pressure and distilling off butanol as **5**, an orange, viscous liquid, is formed. Compound **5** is unstable in water or air. Based on our previous discussion the Lewis acid acidity of **5** should be greater than that of a simple five-membered ring borate but probably less than that of PMB. The purity of **5** as synthesized above is no greater than 80%, as attested to by the ratio of the aromatic and aliphatic proton in the NMR spectrum of this residue product (see Experimental Section). The titer for boron is also high by approximately 20% based on that required for **5**.

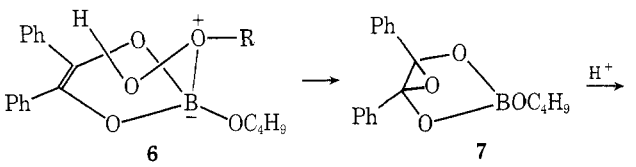


5

The reactivity of dioxaborole **5** with THPO was indeed dramatic. In cyclohexane the presence of an equimolar amount of **5** caused THPO to completely disappear in the time required to bring the solution to reflux (81°). At 25°, in cyclohexane or in *cis*-2-octene, 75% of the active oxygen titer disappeared within 1 min of mixing the reactants. In the latter solvent only a trace of *cis*-2-epoxyoctane was observed by VPC analysis. Hydrolysis of a number of reaction mixtures, separation and drying of the organic phase, and removal of the volatile components from the reaction products always gave the same results.

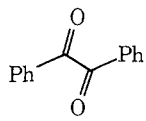
The residue, a yellow oil mixed with some solid in 70% yield, was a mixture readily analyzed by infrared and identified through comparison with the spectra of authentic materials. The characteristic infrared bands of benzil (approximately 80% of the total oxidation product) and α-tetralol were readily identified as the major products of the reaction, and only a trace of unreacted benzoin could be identified. However, an additional and unexpected minor product (approximately 20% of the total oxidation product), benzoic anhydride, was shown to be present by its characteristic carbonyl doublet in the infrared at 1785 and 1725 cm^{-1}. The starting dioxaborole (**5**) produced only benzoin when hydrolyzed in aqueous ethanol. Separation and individual characterization of the products of the THPO–dioxaborole reaction prior to hydrolysis proved impractical and was abandoned.

The presence of benzil as the major oxidation product from the reaction of dioxaborole **5** and THPO is explicable by the scheme presented below. In addition the formation



6
R = tetralyl

7
+ ROH

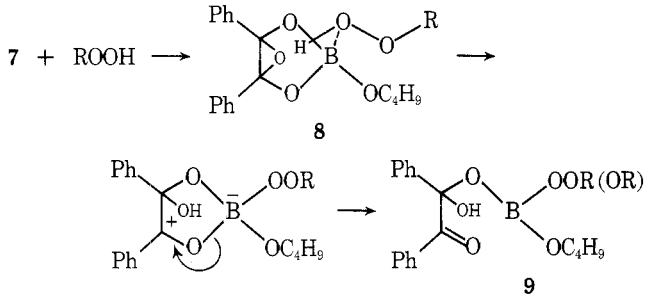


+ C_4H_9OH

of benzil is consistent with the thesis that the electron-deficient oxygen (incipient or fully formed) requires a nucleophilic site (i.e., an olefinic linkage in close proximity to the developing oxidizing species). The intermediate **6** is structurally analogous to that postulated in the vanadium-catalyzed epoxidation of allylic alcohols.[14]

The oxidation to benzoic anhydride can be rationalized in the following way. Complex **8** formed from a second mole

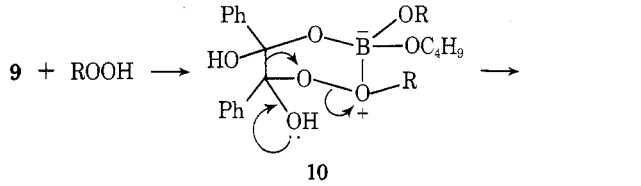
of tetralin hydroperoxide reacting with **7** will provide a source of protons to open the oxirane ring. The resultant 1,3-dipolar species can then open the dioxaborole ring to a borated α-ketal ketone (**9**). The carbonyl in this species could, in turn, convert to a hydroxy peroxide (**10**), which would be uniquely arranged to facilitate a Baeyer–Villiger rearrangement through a six-membered ring coordination of the peroxide α oxygen and the pendant borate group.



8

9

A sequence could be pictured in which the major reaction product, benzil, reacts further with THPO to form a hydroxy hydroperoxide. This intermediate could then decompose, directly or by assistance from the borate ester. This alternative does not seem valid. The decomposition of 0.1 *M* THPO in cyclohexane in the presence of equimolar benzil at 24° is approximately 5×10^3 times slower than observed for THPO in the presence of dioxaborole **5**. In the course of this decomposition ~60% of benzil is consumed and benzoic acid is identified as the major product. When 1 equiv of the weakly acidic borate ester, 2-butoxy-1,3,2-dioxaborinone, is added to a cyclohexane solution 0.1 *M* each in THPO and benzil, the hydroperoxide decomposition is slightly accelerated and only 10% of the benzil initially present is consumed. Finally, when CHMB is the borate ester added the THPO decomposition is further accelerated and only a trace of benzil is consumed.



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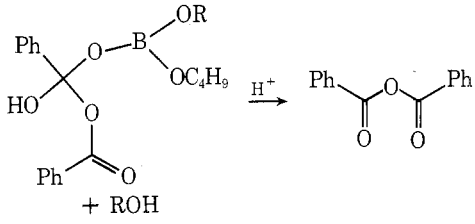


+ ROH

The ability of a hydroperoxide–borate complex, such as **8**, to function as an acid of sufficient strength to open an epoxide ring has been demonstrated in the epoxidation of 2-methyl-1-heptene with THPO and CHMB at 60°. In addition to 1,2-epoxy-2-methylheptane a small amount (~5 mol%) of 2-methylheptaldehyde is formed. After the tetralin hydroperoxide is consumed the resultant mixture is stable. Under reaction conditions a mixture of 1,2-epoxy-2-methylheptane is stable in the presence of either CHMB or THPO alone. However, a solution of 1,2-epoxy-2-methylheptane in cyclohexane at 60° in the presence of an equimolar mixture of both THPO and CHMB rapidly converts the epoxide to the isomeric aldehyde and concomitantly depresses the rate of THPO decomposition 150-fold. This phenomenon is dependent on the presence of groups in the epoxide capable of stabilizing a positive charge as the oxirane ring opens prior to hydride transfer and aldehyde formation, i.e., 1,2-epoxyoctane is stable under the above reaction conditions.

In the terse published description on the preparation of 2-*n*-butoxy-4,5-diphenyl-1,3,2-dioxaborole (**5**) the only physical property mentioned was the compounds sensitivity to air.[13] This is readily observable since the orange solutions of **5** produce dark "Schlieren" lines on exposure to the air.

The autoxidation of the dioxaborole **5** by pure oxygen, in the absence of initiators, at 80° in chlorobenzene is very rapid. The uptake of oxygen by **5** begins, with no observable induction period, at a rate of approximately 7.2×10^{-3} mol oxygen/mol min and maintains that rate throughout the course of the oxidation. Approximately 0.85 molar equiv of oxygen is absorbed based on the estimated purity of the dioxaborole. By comparison there is no observable consumption of oxygen by tetralin under identical conditions for a 2-hr period. At 120°, after an approximately 400-sec induction period, tetralin is oxidized at a maximum rate of 3×10^{-5} mol oxygen/mol min.

The products in the crude reaction mixture, accounting for a quantitative material balance based on the estimated real initial concentration of **5** were characterized by ir, NMR, and product isolation with individual characterization. The products identified were benzil, benzoic acid, and, again, benzoic anhydride. Benzil and benzoic acid were the major isolated products in a ratio of 1.2:1.0. Benzoic anhydride was identified spectroscopically as a trace reaction product.

In the presence of 4 mol % *p*-hydroquinone an autoxidation of dioxaborole **6** run identically with the one above absorbed oxygen at the same rate and gave the same products, benzil, benzoic acid, and benzoic anhydride, in identical product ratios. By comparison, tetralin in the presence of 4 mol % *p*-hydroquinone fails to consume any oxygen within a 5100-sec period at 120°.

The mechanism of borane autoxidation has been studied in detail by Davies.[15] It was originally believed, on the basis of inhibitor studies, that the reaction of O_2 and a trialkylborane (R_3B) proceeded through a polar intermediate, $R_3\bar{B}$–O–O^+, followed by alkyl migration to give isolable peroxyboranes, R_2BOOR. From more recent work using galvinoxyl as an inhibitor and optically active 1-phenylethylboronic acid and epimeric norborn-2-yl boranes in various autoxidation experiments, evidence has been presented which is consistent with a free-radical chain reaction in which the boron atom acts as an extremely active scavenger for peroxy radicals.

The question of the intermediacy of radicals or charged species in the reaction of **5** with oxygen is, as yet, unanswered. If a boron–oxygen intermediate complex is formed then some polar contribution to this species is possible. Davies and Ingold[16] have examined the reactions of various peroxy radicals with several organoboranes. A progressively decreasing rate of reaction of alkyl peroxy radicals with the boranes was noted as the number of B–O bonds in the molecules increased. This decreasing rate of substitution on boron by peroxy radical was ascribed to a decrease in boron atom acidity due to a pπ–pπ interaction with the lone pairs on oxygen and hence the resonance contribution of $\bar{B}$=O^+. This observation, coupled with the lack of a ready source of alkyl radicals, suggests that an alternate mechanism is operative with borates. Equivalent intermediates for product formation can be rationalized through oxygen addition to either boron or the double bond. It would appear that benzil is formed in a process involving 2 mol of **5** and 1 mol of oxygen. This comes from the stoichiometry of the reaction

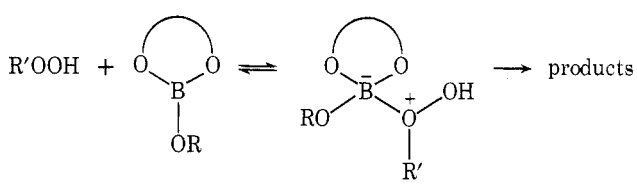
Table II
First-Order Decomposition of 0.350 *M tert*-butyl Hydroperoxide in Hydrocarbon Solvents at 120°

Rxn no.	Solvent[a]	Borate (*M*/1)	k_1, hr^{-1} [b]	Products: Alcohol, *M*/1	Products: Ketone, *M*/1	Total available oxygen as ol + one, %	Ol/one
1	C		0.027	0.077	0.029	30.3	2.7
2	C	CHMB (0.38)[c]	0.032	0.247	0.035	80.6	7.1
3	C	CHOB[d] (0.35)	0.031	0.167	0.036	58.0	4.6
4	C	*n*-BuOB[e] (0.35)	0.031	0.159	0.040	56.9	4.0
5	D		0.004	0.050	0.062	32.0	0.8
6	D	CHMB (0.38)[c]	0.029	0.110	0.015	34.7	7.3

[a] C, cyclooctane; D, *n*-decane. [b] First-order kinetics were observed for at least 3 half-lives for all reactions. [c] Concentrations of CHMB (cyclohexyl metaborate) were based on molecular weight of monomer, $C_6H_{11}OBO$. [d] CHOB = cyclohexyl orthoborate. [e] *n*-BuOB = *n*-butyl orthoborate (registry no., 688-74-4).

as well as the fact that hydrogen peroxide, which is stable under these reaction conditions, is not found in the aqueous fraction after hydrolysis of the crude product.

One of the most striking features of the CHMB-catalyzed decomposition of alkyl hydroperoxides is that the loss of active oxygen is accelerated even if a nucleophile, such as an olefin or mesitylene, is not present to scavenge the incipient hydroxonium ion. Thus the decomposition of 0.08 *M* THPO in the presence of 0.08 *M* CHMB in cyclohexane at 80° is 63 times faster than for the uncatalyzed decomposition of THPO in cyclohexane.



It is unlikely that a highly energetic species such as [OH^+] would form in cyclohexane. No hydride abstraction by THPO–CHMB in cumene to give α-methylstyrene or products thereof was observed. This is in spite of the fact that hydroxylation of the aromatic ring in cumene to give isopropyl phenols is only a minor reaction. Neither is oxygen evolution observed in the above reaction media.

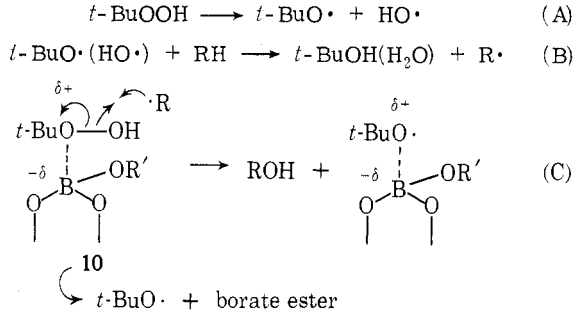
For a probe of the borate induced decomposition of alkyl hydroperoxides in aliphatic hydrocarbon solvents we chose to use a hydroperoxide which was relatively unreactive and would have limited prerogatives in product formation: *tert*-butyl hydroperoxide (*t*-BuOOH). Cyclooctane and *n*-decane, each with eight methylene groups, were chosen as hydrocarbon solvents.

On a per-hydrogen basis cyclooctane has been shown to be about twice as susceptible to hydrogen abstraction by moderately reactive radicals[17] than are typical acyclic secondary hydrogens or cyclohexane ring hydrogens. No data comparing solvent hydrogen selectivities of *tert*-butoxy or *tert*-butylperoxy radicals for cyclooctane vs. other hydrocarbons are presently available.

The decomposition of 0.35 *M* *t*-BuOOH at 120° in cyclooctane, as shown in Table II, is more than six times as fast as that in *n*-decane as measured by first-order rate constants (k_1) (0.027 hr^{-1} vs. 0.004 hr^{-1}). In cyclooctane 30.3% of the consumed *t*-BuOOH is accounted for as cyclooctanol (COL) and cyclooctanone (CON) present in a 2.7:1 ratio. In *n*-decane 32% of the consumed *t*-BuOOH is accounted for as *n*-decanols and *n*-decanones in a 0.8:1 ratio.

When *t*-BuOOH is decomposed at 120° in cyclooctane in the presence of 1 equivalent of CHMB a modest increase in the first-order rate constant of 0.032 hr^{-1} is observed. More significantly, 80.6% of the consumed *t*-BuOOH is converted to COL and CON in a 7.1:1 ratio. Replacing CHMB with cyclohexyl orthoborate or *n*-butyl orthoborate, two borates which would not induce the heterolysis of a hydroperoxide O–O bond, resulted in approximately the same modest rate enhancement. A product accountability of nearly 60% based on *t*-BuOOH was obtained with COL to CON ratios of 4.6:1 and 4.0:1, respectively. Finally, the presence of equimolar CHMB and *t*-BuOOH in *n*-decane accelerates the first-order rate of decomposition of *t*-BuOOH sevenfold to k_1 = 0.029 hr^{-1} and the 34.7% accountability of active oxygen gives a decanol to decanone ratio of 7.3:1. No evidence of oxygen evolution was observed in any of these reactions and *tert*-butyl alcohol was the only observed product from *t*-BuOOH.[18]

These data are consistent with the following chain reaction sequence, which can be considered a borate induced



SH2 (bimolecular homolytic substitution[19]) reaction. The SH2 reaction has been well documented in homolytic peracid decompositions.[20,21] Since the complex of a hydroperoxide coordinated to a borate ester has electron distribution similar to peracids and similar nonradical reaction characteristics,[1] the occurrence of SH2 reactions can be considered another extension of the previously observed analogies. A possible termination step for this reaction in cyclooctane, which has good active oxygen accountability, might be either cyclooctyl radical coupling to bicyclooctyl or *tert*-butoxy–cyclooctyl radical coupling to the ether. Neither of these products has been identified in reaction residues.

In cyclooctane solvent the amount of CON produced by *t*-BuOOH decomposition increases about the same small amount over that observed in the uncatalyzed reaction as do the reaction rates when borate esters are added. Thus, essentially *all* the new product formed as a result of *t*-BuOOH coordination with borate ester is cyclooctanol. In the presence of borate esters there are two parallel reactions taking place: the normal decomposition of *t*-BuOOH which leads to cyclooctyl radicals which are only 30% efficient in giving COL and CON on reacting with *t*-BuOOH and the borate induced SH2 decomposition of *t*-BuOOH via intermediate **10** which scavenges cyclooctyl radicals with an extremely high efficiency to give *only* cyclooctanol.

In *n*-decane the situation is quite different. The CHMB accelerated decomposition of *t*-BuOOH not only increases the amount of *n*-decanols produced but substantially decreases the amount of decanones formed. In this case, secondary decyl radicals (see Experimental Section) are generated more rapidly in the presence of CHMB. Thus, the lower energy borate induced decomposition pathway diverts radicals from the noncatalytic reaction routes to follow the more favorable SH2 reaction. This results in the formation of alcohol at the expense of ketone, as seen in the last entry in Table II.

That portion of alcohol and ketone formed in both solvents by more classical routes has been suggested to involve[22] coupling of alkyl radicals and *tert*-butylperoxy radicals, followed by homolysis of the *tert*-butyl alkyl peroxide and disproportionation of, or hydrogen abstraction by, the resulting alkoxy radicals.

$$R\cdot + t\text{-BuOO}\cdot \longrightarrow t\text{-BuOOR}$$

$$t\text{-BuOOR} \longrightarrow t\text{-BuO}\cdot + \cdot OR$$

$$2RO\cdot \longrightarrow ROH + R{=}O$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot$$

Conclusions

The results of the above observations coupled with those previously reported[1,3] indicate that a broad spectrum of hydroperoxide–borate–substrate interactions are possible. The course of a given reaction is generally determined by one of the three reacting compounds. The major variations of this system are presented below.

1. With an alkyl metaborate or alkyl orthoborate of appropriate acidity all hydroperoxides coordinate with boron to produce a species similar to a peracid which can either epoxidize olefins or hydroxylate highly nucleophilic aromatics.

2. With phenyl borates or other highly acidic borates *t*-BuOOH will epoxidize olefins[3] but aralkyl hydroperoxides will preferentially undergo a Baeyer–Villiger-type rearrangement.

3. In the absence of a suitable acceptor (i.e., in an aliphatic hydrocarbon) *t*-BuOOH will undergo an SH2 reaction induced through coordination with boron, while the tertiary aralkyl hydroperoxide, cumene hydroperoxide, will rearrange to acetone and phenol.[1]

Experimental Section

Chlorobenzene, 1,2-dichloroethane, cyclooctane, cyclohexane, *n*-decane, and mesitylene were obtained from Aldrich Chemical Co. and purified by standard procedures. Benzoin and *n*-butyl borate obtained from the same source were used as received. *cis*-2-Octene (99.9%) obtained from Chemical Samples Co. was used as received. The *tert*-butyl hydroperoxide obtained from Lucidol initially at 90% active oxygen titer afforded on reduced pressure distillation material which gave a greater than 99% titer for active oxygen.

Tetralin hydroperoxide, a colorless, crystalline solid, mp 55–56°, was prepared according to the procedure described by Knight and Swern,[23] and gave a 99% titer for active oxygen. Tetralol, bp 128–129° (10 mm), was prepared by the lithium aluminum hydride reduction of a tetralone–tetralol mixture (approximately 50:50) obtained from Union Carbide Corp. Tetralone was obtained from Eastman Chemical Co. Mesitol was synthesized as previously described.[1]

Borate Syntheses. Cyclohexyl metaborate, a colorless solid, mp 163–166°, was prepared according to the procedure of O'Connor and Nace.[24] Cyclohexyl orthoborate, a colorless, waxy solid,[24] mp 65–67°, bp 90° (2 mm), was prepared by the method of O'Brien.[25]

The several borates prepared from diols were all synthesized in the same fashion. A mixture of boric acid or boric anhydride and diol in a molar proportion calculated to produce the desired derivative was added to benzene. The mixture was heated to reflux and the stoichiometric amount of water was collected in a Dean-Stark trap. The resulting product was either distilled or allowed to crystallize from the benzene solution. All products gave the appropriate titers for boron using the mannitol method.[26] The colorless liquids, 2-cyclohexyloxy-1,3,2-dioxaborinane, bp 132–133° (10 mm) [reported bp 87–91° (0.8 mm)],[27] 2-cyclohexyloxy-1,3,2-dioxaborolane, bp 116° (10 mm) [reported bp 119–120° (10 mm)],[28] and 2,2′-oxybis-5,5-dimethyl-1,3,2-dioxaborinane, bp 120–125° (0.05 mm) [reported bp 134–140° (0.5 mm)],[29] were stored, after distillation, in a drybox and transferred into reaction mixtures under anhydrous conditions. Tris(1-methylethylene glycol)biborate was obtained as a viscous oil.[30]

Phenyl metaborate and phenyl orthoborate were synthesized from phenol and boric acid (1:1 and 3:1 mole ratios, respectively) by azeotropic removal of water from refluxing toluene. Upon distillation of the toluene a crystalline residue product was obtained which was used without further purification. Triacetyl borate synthesis has recently been described by Ritscher.[31]

Reaction Kinetics and Epoxide Analysis. Hydroperoxide consumption was followed iodometrically by the method of Wibaut.[32] Analyses for 2,3-epoxyoctanes were performed by VPC on a 6 ft × 0.25 in. Carbowax 20M on Chromosorb T column programmed at 6°/min from 80 to 150° with a He gas flow rate of 50 ml/min. The retention time for *trans*-2,3-epoxyoctane is 4.76 min and for *cis*-2,3-epoxyoctane is 5.28 min.

Isolation and Characterization of 4-(*o*-Hydroxyphenyl)-butyraldehyde.[33] Triacetyl borate (9.4 g, 0.05 mol) in 100 ml of 1,2-dichlorethane was added to a room temperature solution of 8.2 g (0.05 mol) of THPO in 50 ml of dichloroethane in a 500-ml three-necked round-bottom flask fitted with mechanical stirrer, thermometer, and reflux condenser. Within 1 min after mixing the reaction temperature rose to ~60° and the active oxygen titer dropped to zero. The resulting solution was washed with water, dilute bicarbonate, and saturated salt and dried over magnesium sulfate.

Removal of the solvent gave 8 g of material which was passed down a chromatography column containing 100 g of silica gel. After extensive elution with benzene several fractions were collected. On evaporation of solvent these gave a yellow oil exhibiting carbonyl, hydroxyl, aliphatic, and aromatic C–H stretching vibrations in the infrared.

Isolation of this compound by preparative VPC on Carbowax 20M on Chromosorb W gave an oil which was identified by the ir and NMR spectra to be 4-(*o*-hydroxyphenyl)butyraldehyde: ir (KBr) 3420, 2930, 1720, 1240, and 750 cm^{-1}; NMR ($CDCl_3$) δ 1.97 (m, 2 H), 2.53 (t, J = 6 Hz, 2 H), 2.68 (m, 2 H), 6.99 (m, 4 H), 9.78 (t, J = 1.2 Hz, 1 H). No phenolic proton was identified in this sample, possibly owing to the presence of volatile liquid-phase components from the VPC column which blocked out the δ 4–5 region of the NMR.

Synthesis of 2-*n*-Butoxy-4,5-diphenyl-1,3,2-dioxaborole (5). A predried, 250-ml flat-bottomed three-necked flask equipped with magnetic stirrer, thermometer, and serum cap was charged with 5.31 g (0.025 mol) of benzoin (oven dried, 100°) and 13.50 ml (0.050 mol) of *n*-butyl borate. This reaction system was attached to a short-path (gooseneck) distillation system connected to a vacuum pump. The system was purged with dry nitrogen by means of a syringe needle through the serum cap. The stirred reaction vessel was immersed into an oil bath whose temperature was gradually raised from 75 to 100° during the course of the reaction. The pressure was maintained at 2–5 mmHg. Upon heating, the initially colorless heterogeneous reaction mixture turned light orange, and then suddenly a vigorous ebullation took place. At this time, the reaction became homogeneous and *n*-butyl alcohol was distilled through the short path system into a receiver. After the reaction was over the excess *n*-butyl borate was removed by distillation at 100° (0.05 mmHg). The resulting thick orange liquid was used without further purification: ir (neat) 2960, 1852, 1473, 1390, 1260, 1065, 1027, 763, and 687 cm^{-1}; NMR ($CDCl_3$) 0.95 (t, J = 6 Hz, 3 H), 1.54 (m, 4 H), 4.12 (t, J = 6 Hz, 2 H), 7.48 ppm (m, <10 H). The ratio of the aromatic to butyl protons in several spectra was always less than the theoretical 10:9. This ratio did, however, vary, and the low proton count in the aromatic region was apparently due to excess *n*-butyl borate present in the product. Consistent with this is the observation that hydrolyzed samples of dioxaborole 5 give high boron titers.

On hydrogenation at 1 atm, a 1-g sample of 5 in 25 ml of ethyl acetate containing 0.049 g of PtO_2 absorbed 1.09 molar equiv of hydrogen. Filtration gave a colorless solution, which on evaporation of the solvent left an oily residue. One recrystallization from

ethanol–water gave the solid *meso*-1,2-diphenyl-1,2-ethanediol, mp 135–137° (reported[34] mp 136–137°).

Reaction of 5 with Tetralin Hydroperoxide. To 0.735 g (0.0025 mol) of dioxaborole (1) in a 125-ml erlenmeyer flask, 0.410 g (0.0025 mol) of tetralin hydroperoxide in 25 ml of cyclohexane was added. Within 30 min at room temperature in the drybox, the solution had turned from bright orange to yellow and the hydroperoxide titer was only 7% of the original value. The solution was allowed to stand overnight after which time the titer for hydroperoxide was zero. The cyclohexane solution was washed three times with 25-ml portions of water and once with a saturated salt solution and dried over sodium sulfate. Removal of the solvent left 0.54 g of a yellow oil mixed with some crystals. The infrared spectrum (neat) of this residue exhibited the characteristic bands of benzil (1675 and 873 cm^{-1}) and tetralol (3330, 774, and 739 cm^{-1}) as the major products. Analysis by VPC on a 6 ft × 0.25 in. Carbowax 20M on Chromosorb T column programmed at 6° from 80 to 220° with an upper limit hold and a He gas flow of 50 ml/min showed the major products of the reaction to be an approximately 1:1 mixture of tetralol (retention time 22.35 min) and benzil (37.95 min) with a trace of tetralone (20.75 min) present. A second product of benzoin oxidation present in ~20% yield was shown to be benzoic anhydride by the characteristic carbonyl doublet at 1785 and 1725 cm^{-1}. A trace amount of benzoic acid was also shown to be present by ir and VPC analyses.

Autoxidation of Dioxaborole 5. A 25-ml chlorobenzene solution in a 100-ml two-necked flat-bottom flask containing approximately 0.025 mol of the dioxaborole was brought to 80° under 1 atm of oxygen. Upon commencement of stirring oxygen uptake began. Within 80 min the oxidation ceased and 0.85 mol of oxygen per mole of dioxaborole was absorbed. A similar reaction containing 0.11 g of *p*-hydroquinone required 70 min to reach completion having absorbent 0.67 mol of oxygen per mole of dioxaborole. After most of the chlorobenzene was distilled off, the residue (4.69 g) was dissolved in 30 ml of ether washed three times with 25 ml of water and once with 25 ml of saturated salt solution, and dried over sodium sulfate. Evaporation of the ether left a solid residue. The infrared spectrum of these residues had the characteristic bands of benzil, benzoic acid, and a small amount of benzoic anhydride. The NMR of these residues exhibited only aromatic protons, δ 7.30–8.43, and a single acid proton, δ 12.27. The ratio of benzoic acid to benzil was established as 1.0:1.2. Pure samples of benzil (mp 95–96°) and benzoic acid (mp 120–122°) could be isolated from these and other autoxidations of dioxaborole **5**.

Decomposition of *t*-BuOOH in Saturated Hydrocarbon Solvents. A typical reaction was run by charging a 20-ml spherical reactor equipped with a pressure stopcock with 10 ml of hydrocarbon solvent and the appropriate amount of borate ester (when used). This solution was purged with dry nitrogen for 10 min and the stopcock was then closed. A serum cap was placed over the stopcock extension and a nitrogen head was maintained in this region above the stopcock by inserting a syringe needle attached to the dry nitrogen line with ~5 lb positive pressure. The reactor was placed in the constant-temperature bath at 120° and heated for 5 min. The addition of 0.8 ml of *t*-BuOOH followed directly. This was considered as time zero. The progress of the reaction was followed iodometrically and was run for 10 half-lives prior to product analysis.

Product analyses of the reaction in cyclooctane were performed by vapor phase chromatography on a 5% Carbowax 20M on Chromosorb T column, 0.25 in. × 11.5 ft. The separation was performed using a temperature program of 80–170° at 10°/min. followed by a hold at 170°, with a He gas flow of 50 ml/min. Under these conditions the retention times (minutes) follow: cyclooctanone (18.5), cyclooctanol (23.2), cyclohexanol (13.5), cyclohexanone (12.2) and the internal standard, chlorobenzene (10.5).

Analysis for the products in decane was performed on a 12 ft × 0.25 in., 5% DEGS on Chromosorb G column. All the other parameters were as reported for the cyclooctane reaction analyses. Under these conditions the observed retention times (minutes) follow: 4- and 5-decanone (15.0), 3-decanone (15.8), 2-decanone (16.6), 4- and 5-decanol (18.0), 3-decanol (18.5), and 2-decanol (19.3). No 1-decanol or *n*-decanal was observed in either reaction. Quantitatively, the 2, 4, and 5 isomers of both alcoholic and ketonic products appeared in equal amounts while the 3 isomers appeared in an amount which was 50–75% that of the other isomers. The retention times (minutes) follow: cyclohexanone (12.3), cyclohexanol (13.6), and for the internal standard, 1,2,4-trichlorobenzene (21.6). In neither the cyclooctane nor the decane system was it possible to separate the small quantities of olefinic products of solvent dehydrogenation possibly present.

In order to reproducibly analyze by VPC it was necessary to free any potential products from boron in those solutions containing borate esters. Initial attempts to add a large excess of methanol and thereby convert all the available borated material to trimethyl borate failed, apparently owing to deposition of boron on the VPC column. This ultimately led to low analyses for alcohols based on established internal standard factors. Satisfactory reproducibility of analyses was obtained by adding an equal volume of aqueous mannitol solution just prior to injection to those reaction solutions containing borate esters. All factors were redetermined under the identical two-phase conditions and no loss of any of the organic products of interest from the hydrocarbon phase to the aqueous mannitol phase was observed.

Acknowledgment. We would like to express our gratitude to Drs. N. A. Clinton and J. S. Ritscher for their many helpful comments.

Registry No.—**5**, 55089-01-5; 4-(*o*-hydroxyphenyl)butyraldehyde, 55089-05-9; triacetyl borate, 4877-24-5; tetralin hydroperoxide, 771-29-9; benzoin, 119-53-9.

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