The Borate Ester Induced Decomposition of Alkyl Hydroperoxides. The Epoxidation of Olefins by Electrophilic Oxygen

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The decomposition of tetralin, cyclohexyl, cumene, and t-butyl hydroperoxides in the presence of cyclohexyl metaborate is described as a source of electrophilic oxygen. This reaction system efficiently produces epoxides from olefins under relatively mild conditions. This epoxidation reaction is shown to be related in many ways to those reactivity patterns observed with peracetic acid in the epoxidation of olefins. The products from the decomposition of cumene hydroperoxide in the presence of cyclohexyl metaborate are shown to be highly dependent on the presence or absence of a suitable nucleophilic site for the electron-deficient oxygen generated. In an olefinic solvent the products are olefin oxide and 2-phenyl-2-propanol. In a saturated hydrocarbon solvent the products are mainly phenol and acctone with a small amount of α -methylstyrene and 2-methylpropionalde-The cyclohexyl metaborate induced decomposition of tetralin hydroperoxide in tetralin is accelerated hvde. some 125-fold over the homolytic decomposition of tetralin hydroperoxide in tetralin. The nonradical nature of the metaborate ester induced decomposition of alkyl hydroperoxides is implied from an experiment in which a self-sustaining autoxidation of cumene to cumene hydroperoxide, on treatment with cyclohexyl metaborate, almost ceases to take up oxygen, concomitantly with the rapid decomposition of that hydroperoxide already present. Evidence for the generation of a species which can be rationalized as a transient hydroxonium ion, OH+, is presented in the decomposition of a variety of hydroperoxides in the presence of cyclohexyl metaborate in mesitylene, the latter being a strong nucleophile. The oxidation product in these reactions, in high yield, is mesitol (2,4,6-trimethylphenol), a product consistent with the generation of an electrophilic hydroxonium ion.

The rapid epoxidation of carbon-carbon double bonds by peroxy acids is a reaction which has found general application. The subject of oxirane ring formation through the interaction of peroxy acids and olefins has been reviewed.¹

The uncatalyzed reaction of alkyl hydroperoxides with olefins has found less general utility as an epoxidizing system. The slow, thermal decomposition of t-butyl hydroperoxide in a variety of olefins has been reported to be inefficient in producing epoxides.² Hawkins³ discovered that the presence of a trace of vanadium pentoxide in a refluxing solution of cumene hydroperoxide in cyclohexene led to low yields of cyclohexene oxide. This reaction has been extended to the use of the soluble metal acetylacetonates of chromium, vanadium, and molybdenum as catalysts.⁴ Similarly the soluble naphthenates of molybdenum, tungsten, titanium, and vanadium have been shown to be effective catalysts in this reaction.⁵ A kinetic study of the vanadium-catalyzed epoxidation reaction has recently been reported.⁶

We wish to report our findings on a new mode of decomposition of alkyl hydroperoxides which leads to epoxides from olefins (and, less generally, hydroxylation of some substituted aromatic systems). The decomposition of cumene, tetralin, or t-butyl hydroperoxide induced⁷ by cyclohexyl metaborate and in the presence of an olefin, as solvent, or diluted with an appropriate solvent, generally cyclohexane, results in the formation of an oxirane from the olefin and concomitant generation of an alcohol corresponding to the initial hydro-

(1) J. B. Lee and B. C. Uff, Quart. Rev. (London), 21, 429 (1967), and references cited therein.

(2) W. F. Brill and N. Indictor, J. Org. Chem., 29, 710 (1964).

(3) E. G. E. Hawkins, J. Chem. Soc., 2169 (1950).
(4) N. Indictor and W. F. Brill, J. Org. Chem., 30, 2074 (1965).
(5) R. Landau, et al., 7th World Petroleum Congress, Mexico City,

1967, pp 141-152.

(6) E. S. Gould, R. R. Hiatt, and K. C. Irwin, J. Amer. Chem. Soc., 90, 4573 (1968).

peroxide. Any alkyl metaborate ester (1:1 M dehydro)adduct of alcohol and boric acid) will function as an effective agent to induce the epoxidation of an olefin by

an alkyl hydroperoxide. The general use of cyclohexyl metaborate rests on its ease of synthesis and solubility in organic solvents. Alkyl orthoborates (3:1 M)dehydro adduct of alcohol and boric acid) are ineffective in producing the epoxidation reaction by alkyl hydroperoxides. The structural and chemical reactivity differences between the two types of borate esters are well documented.⁸ Table I lists some representative olefins and the parameters employed in their epoxidation.

Results and Discussion

The reaction of peroxy acids with olefins has long been recognized to involve the attack of electrophilic oxygen on the double bond resulting, generally, in epoxide formation.¹ This reaction is known to involve a stereospecific, concerted cis addition of oxygen to olefins. In addition, peroxy acids exhibit no preference for cis or trans double bonds in simple olefins and the rate of epoxidation by peroxy acids is little effected by interchanging alkyl and aryl substituents about the double bond. Most significantly the peroxy acid epoxidation reactions of olefins show a high preferential reactivity with the more highly substituted olefins.¹

The epoxidation of olefins by the tetralin hydro-

⁽⁷⁾ The reaction is referred to as induced, rather than catalyzed, since the alkyl metaborate initially present in the reaction is apparently converted into the inactive alkyl orthoborate ester by reaction with the alcohol produced from the hydroperoxide decomposition.

⁽⁸⁾ The hydrolytic stability differences of any related pair of borate esters are generally associated with steric hinderance around the boron atom." Although this difference may be, in part, responsible for the reactivity differences observed with alkyl hydroperoxides, we have reason to believe that more subtle structural differences are responsible for the reactivity pattern observed. Discussion of the role of the borate ester shall be reserved till a later date.

⁽⁹⁾ H. Steinberg, "Organoboron Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1964, pp 840-870.

OLEFIN EPOXIDATION BY 0.08 M TETRALIN HYDROPEROXIDE^a INDUCED BY 0.08 M CYCLOHEXYL METABORATE^b

		of epoxide.
Olefin (concn, mol/l.)	tso ^c , sec	%
None	11800	
1-Octene (0.24)	11600	85
1-Octene (neat)	7000	90
2-Octene ^e (0.24)	3500	98
cis-2-Octene (0.24)	3450	100
cis-2-Octene (0.24) ^f	$7.5 imes10^{5}$	
Cyclohexene (neat)	900	91
Cyclohexene (0.24)	3300	90
1-Methylcyclohexene (0.24)	980	100
Cyclooctene (neat, 90°)	600	100
Cyclooctene (neat, 90°)	9000	90
Cyclooctene (neat, 130°)/	21120	48
Styrene (neat, 90°)	2220	77
Indene (neat, 90°)	720	54

^a Unless otherwise noted reactions were run at 80° in cyclohexane. ^b Cyclohexyl metaborate concentration based on monomeric ester. ^c Time, in seconds, required for 90% decomposition of tetralin hydroperoxide. ^d Epoxide corresponding to parent olefin. ^e Equimolar *cis-trans* isomer mixture. ^f No borate present. ^e t-Butyl hydroperoxide (0.08 M) was used as oxidant.

peroxide¹⁰-cyclohexyl metaborate (THPO-CHMB) system is in the general aspects of its reactivity quite similar to peroxy acids. The epoxidation of *cis*-2octene by THPO-CHMB at 80° produces only *cis*-2,3epoxyoctane in almost quantitative yield. The epoxidation by THPO-CHMB of an equimolar mixture of *cis*- and *trans*-2-octene (in sixfold excess) produced an equimolar mixture of the corresponding epoxides. In addition, olefin epoxidation by THPO-CHMB exhibits a selectivity trend that is in the same direction as peracetic acid.¹¹ Table II lists competitive epoxidation

TABLE II

COMPETITIVE EPOXIDATION OF OLEFINS^a

Olefin mixture	Epoxidizing agent	ratio
cis-2-Octene/1-octene	\mathbf{PA}^{b}	35.6
	THPO-CHMB ^c	9.5
cis-2-Octene/2-methyl-1-heptene	PA	1.3
	THPO-CHMB	1.1
2-Methyl-2-heptene/trans-3-octene	PA	13.9
	THPO-CHMB	4.9
1-Methylcyclohexene/cyclohexene	PA	13.6
	THPO-CHMB	3.9

^a Each olefin was present in a threefold excess over the epoxidizing agent in cyclohexane. ^b Peracetic acid (25% in ethyl acetate); decomposition temperature, 25°. ^c Tetralin hydroperoxide-cyclohexyl metaborate system; decomposition temperature, 80°; see footnote 12 of text.

ratios for both peracetic acid in cyclohexane (at 25°) and THPO-CHMB in cyclohexane (at 80°)¹² with a selected series of substituted olefins. As with peroxy acids the THPO-CHMB systems exhibit its highest selectivity ratio between mono- and disubstituted olefins. Between the di- and trisubstituted olefins the differences, though still significant, are lower in magnitude with both systems. In addition, both epoxidizing systems are equally influenced by the additive effect of alkyl groups on either side of the double bond. This last fact has been suggested as evidence for a fairly symmetrical transition state in the epoxidation of olefins by peroxy acids.¹³

It is readily apparent that the magnitude of the effect of increased olefin nucleophilicity (through added alkyl substituents) is less with THPO-CHMB than is seen with peracetic acid. This relatively lower sensitivity by THPO-CHMB is a result of the more energetic ground state of the THPO-CHMB complex in comparison with peracetic acid. This increased energy of the THPO-CHMB system is manifest in the comparatively high rate¹⁴ of decomposition of tetralin hydroperoxide induced by cyclohexyl metaborate in cyclohexane with *no* olefin present (see Table I), being only slightly slower than when a threefold excess of 1-octene is present in the reaction medium.

An especially instructive example of the metaborate induced hydroperoxide decomposition is that of cumene hydroperoxide. The presence or absence of an olefin is critical to the reaction path which this unique hydroperoxide follows. In refluxing (127°) 2-octene (equimolar stereoisomer mixture) the total decomposition of cumene hydroperoxide induced by CHMB requires 37 min. Analysis, by vpc, showed the presence of only cis- and trans-2,3-epoxyoctane and 2-phenyl-2-propanol as the products of the reaction accounting for greater than 95% theoretical yield. In refluxing *n*-octane (127°) the CHMB induced decomposition of cumene hydroperoxide requires 101 min to attain 92% completion. Analysis of the product solution by vpc showed that no 2-phenyl-2-propanol is present, but now four products are obtained. The major products are phenol and acetone along with a small amount of α -methylstyrene and 2-phenylpropionaldehyde. Α mechanistic description of these products origin shall be deferred till further in the discussion.

From the above data it is clear that the presence of an olefin, or some other external nucleophilic reagent, is not necessary, or sufficient, to produce electrophilic oxygen from the decomposition of an alkyl hydroperoxide. The above data are consistent with the fact that the formation (most likely reversible) of a reactive intermediate of alkyl hydroperoxide and metaborate ester with a finite lifetime is energetically close to the transition state for decomposition of the hydroperoxide.

The cyclohexyl metaborate induced decomposition of tetralin and cyclohexyl hydroperoxide in the presence or absence of an olefin produces almost exclusively the alcohol corresponding to starting hydroperoxide. Table III presents data comparing the homolytic decomposition of tetralin and cyclohexyl hydroperoxides with their reaction in the presence of cyclohexyl metaborate. The rate constants for the homolytic decomposition of 0.08 M tetralin hydroperoxide in tetralin from 120.2 to 139.8° produces an Arrhenius expression of $k = 5.38 \times 10^9 e^{-26100/RT} \sec^{-1}$ which extrapolates to a first-order decomposition rate constant of $1.1 \times 10^{-6} \sec^{-1}$ at 90°. The ratio of α -tetralol to

⁽¹⁰⁾ Tetralin hydroperoxide (mp 55-56°) has been used in the major portion of this work owing to its ease of handling and high reactivity. However, all the reactions are generally applicable to all secondary and tertiary alkyl hydroperoxides.

⁽¹¹⁾ The peracetic acid used was 25% by weight in ethyl acetate.

⁽¹²⁾ Competitive epoxidations by THPO-CHMB at 25°, though very slow, gave approximately the same selectivity ratios as at 80°.

⁽¹³⁾ See ref 1, footnote 19.

⁽¹⁴⁾ In the absence of an olefin, or other appropriate nucleophile, peroxy acids are generally very stable at room temperature or below.

Alkyl hydroperoxide (concn. 0.08 mol/l.)	$Solvent^a$	Temp, °C	Cyclohexyl metaborate (concn, (mol/l.)	First-order rate ^b constant \times 10 ⁵ sec ⁻¹
Tetralin hydroperoxide	т	120.2		1.97
Tetralin hydroperoxide	Т	130.0		3.79
Tetralin hydroperoxide	Т	135.2		5.86
Tetralin hydroperoxide	т	139.8		8.42
Tetralin hydroperoxide	Т	90.0	0.04	5.29
Tetralin hydroperoxide	Т	90.0	0.08	8,31
Tetralin hydroperoxide	Т	90.0	0.16	15.70
Tetralin hydroperoxide	м	140.0		1.71
Tetralin hydroperoxide	М	90.0	0.08	36.60
Cyclohexyl hydroperoxide	Т	140.0		4.47
Cyclohexyl hydroperoxide	Т	90.0	0.08	4.96
Cycloheyyl hydroperoyide	м	90.0	0.08	20.89

TABLE III THERMAL DECOMPOSITION OF ALKYL HYDROPEROXIDES

^a Solvents are designated T, tetralin, M, mesitylene. ^b Rate constants and half-lives reported are for those segments of the kinetic plots which are linear with respect to $\log C/C_0 vs$. time.

 α -tetralone produced at 139.8° from the homolytic decomposition of tetralin hydroperoxide is 6:1.

The cyclohexyl metaborate induced decomposition of 0.08 M tetralin hydroperoxide in tetralin at 90° increases in rate as the concentration of the borate ester is increased. As can be seen in Figure 1 the kinetics of the decomposition approach first order in tetralin hydroperoxide over the entire course of the reaction as the concentration of cyclohexyl metaborate is increased. The relative rates for the homolytic decomposition of tetralin hydroperoxide and the decomposition of tetralin hydroperoxide in the presence of a twofold excess of cyclohexyl metaborate are 1 to 143. In addition, the product of the latter reaction has no α -tetralone present but gives only α -tetralol.

This rapid decomposition and specific production to secondary alcohol from secondary hydroperoxide in the presence of cyclohexyl metaborate indicates the existence of a species other than the simple secondary alkoxy radical, a species which is known to be less specific in its product-forming steps. The overwhelming preference for alcohol formation in the metaborate induced decomposition does in fact suggest the presence of a species electronically close to an alkoxide ion, RO-, rather than an electron-deficient alkoxonium ion RO+. If the latter species were derived from a secondary hydroperoxide it would produce ketonic materials by deprotonation. If a species close to RO- is generated by the action of a metaborate ester on an alkyl hydroperoxide, then the other moiety generated should be akin to the electropositive hydroxonium ion, OH+. The transient existence of an electrophilic hydroxylating agent has been postulated to occur through the decomposition of peroxy acids.¹⁵ Recently Hart¹⁶ has suggested that the boron trifluoride catalyzed decomposition of peroxytrifluoroacetic acid in polyalkylated aromatic solvents (i.e., mesitylene) is a source of transient hydroxonium ions. The facile heterolysis of peroxytrifluoroacetic acid in the direction required has been attributed to the weakly basic trifluoroacetate ion being a good leaving group.

$$CF_{3}CO_{2}-OH \xrightarrow{BF_{3}} CF_{3}CO_{2}^{-}+OH^{+}$$



Figure 1.—Decomposition of 0.08 M tetralin hydroperoxide in tetralin at 90°. Concentration effect of cyclohexyl metaborate.

The first-order rate constant for the homolytic decomposition of 0.08 M tetralin hydroperoxide in mesitylene at 140° is 1.71×10^{-4} sec⁻¹; approximately five times as slow as the homolysis of tetralin hydroperoxide in tetralin. The tetralol to tetralone ratio in the former reaction is 1.8:1.0. The metaborate (0.08 M) induced decomposition of tetralin hydroperoxide in mesitylene at 90° is 4.4 times as fast as the metaborate induced decomposition of tetralin hydroperoxide in tetralin. As in tetralin the sole reduction product in mesitylene is tetralol. More significantly, and in agreement with the postulation of the generation of an electron-deficient oxidizing agent, 2,4,6-trimethylphenol (mesitol) is obtained as the oxidation product in quantitative yield. Similarly the decomposition of cyclohexyl and t-butyl hydroperoxides in mesitylene

⁽¹⁵⁾ D. Swern, Org. Reactions, 7, 378 (1958).

⁽¹⁶⁾ H. Hart, C. A. Buehler, and A. J. Waring in "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1965, p 1.

produced greater than 90% yields of mesitol. Attempts to hydroxylate benzene and toluene under these conditions failed to produce phenolic products.¹⁷



Similarly Hart¹⁶ has found that passing boron trifluoride through a solution of peroxytrifluoracetic acid in mesitylene at -40° results in a quantitative yield (based on peroxy acid decomposed) of mesitol (2,4,6trimethylphenol). Here too the alternating arrangement of the three methyl substituents, which allows the positive charge of the hydroxonium ion to be distributed efficiently over the aromatic ring, undoubtedly is necessary since benzene and toluene produce no significant quantities of phenolic materials.

The dramatic differences in the rates and products from the decomposition of alkyl hydroperoxides in the presence or absence of cyclohexyl metaborate can be related to a nonradical and radical scission of the hydroperoxide oxygen-oxygen bond, respectively. The fact that the metaborate induced decomposition of an alkyl hydroperoxide is nonradical can be implied, in addition to the above data, from the following observation. A self-sustaining free-radical autoxidation of cumene in the absence of initiators at 135° and 1-atm oxygen pressure, which has consumed 0.35 mol/l. of oxygen, having attained a hydroperoxide level of approximately the same magnitude and achieved a steady rate of oxidation will, on the addition of a slight molar excess of cyclohexyl metaborate, almost cease to consume oxygen. At the same time the hydroperoxide titer will rapidly decrease to zero. The metaborate ester through its rapid nonradical reaction with cumene hydroperoxide thus substantially depletes the concentration of $RO \cdot$ and $HO \cdot$ from the normal homolytic decomposition of the hydroperoxide, and the normal initiating species of the autoxidation chain are destroyed.18

If, as proposed, the alkyl hydroperoxide suffers a heterolytic cleavage in the presence of a metaborate ester, it is necessary to define the nature of the intermediate which results in oxygen-oxygen bond fission. Since the two oxygen atoms which make up a hydroperoxide are nonequivalent, there are several possible modes of boron-oxygen interaction. If the β oxygen of the hydroperoxide acts as a nucleophile for the metaborate then an intermediate of type a will result, while

(17) The oxidation products obtained in the metaborate induced decomposition of alkyl hydroperoxides in solvents which are not nucleophilic enough to react efficiently with the electron-deficient oxygen are not totally understood and are presently under investigation.

(18) It would appear that autoxidation propagation steps are not inhibited by metaborate esters. The autoxidation of saturated hydrocarbons, which have very short chain lengths, are totally stopped by the presence of metaborate esters. However, in the presence of radical initiators without hydroperoxy linkages, the autoxidation will proceed in the presence of metaborate ester almost as efficiently as they do in the latter's absence, but with no buildup of hydroperoxide titer. if the α oxygen reacts then type-b intermediate will result.¹⁹ Finally, an intermediate c in which both oxygens of the alkyl hydroperoxide are coordinated with two boron atoms of the metaborate is possible.

Fragmentation of the peroxy linkage in a will result in the expulsion of a secondary alkoxonium ion (*i.e.*, from tetralin hydroperoxide), $R'O^+$, which through the loss of a proton would produce a ketone in addition to a



hydroxylated ester. This is contrary to the observed effect exerted by a metaborate ester. If proton migration occurs from the β to the α oxygen, an intermediate of the type a' can be generated, and this could collapse to an active (electron deficient) oxygen betaine and an alcohol.



Fragmentation of the peroxy linkage in b results in the expulsion of what can be formalized as an electrophilic hydroxyl (hydroxonium ion), OH^+ . The other half of the original hydroperoxide is incorporated into the borate ester as an alkoxide moiety, a precursor to the alcohol R'OH which is the only product observed from tetralin hydroperoxide decomposition in the presence of a metaborate ester. Intermediate c can either collapse to a or b or decompose directly in the presence of a nucleophilic reagent to give the type of products observed.

Either of the intermediates a', b, or c can be responsible for the preferential formation of alcohols from alkyl hydroperoxides, epoxidation of olefins, and the hydroxylation of mesitylene. The stereochemical and kinetic similarities of the peroxy acid and THPO-CHMB epoxidation reactions with olefins may possibly



⁽¹⁹⁾ The two nonequivalent oxygens of the alkyl hydroperoxide are designated α and β , with the α oxygen juxtaposed to the alkyl group and the β oxygen bound to the hydroperoxy hydrogen.

reflect similar mechanisms for the two reactants. Intermediate b would seem better able to accommodate such a mechanism. Intermediates b and c, rather than intermediate a', could better accommodate, on the basis of steric hindrance to intermediate formation, the fact that tertiary hydroperoxides are some 10 to 15 times less reactive than secondary hydroperoxides.

The major products from the previously discussed decomposition of cumene hydroperoxide in the absence of a nucleophilic solvent can be rationalized from intermediate a'. Intermediate a from cumene hydroperoxide is analogous to the proposed intermediate in



the mineral acid catalyzed decomposition of cumene hydroperoxide to acetone and phenol.²⁰ Intermediate b can also lead to phenol and acetone through a 1,3 shift of the phenyl group to the β oxygen of the cumene hydroperoxide-metaborate intermediate. At this time the evidence available does not allow for a definitive choice between the proposed intermediates.

Work on the effect of borate ester structure and other ramifications of the induced decomposition of alkyl hydroperoxides are presently being completed.

Experimental Section

Materials.—Tetralin (Union Carbide Corp.) was purified by distillation (bp 204-205°, $n^{20}_D 1.5426$) and tetralin hydroperoxide (a colorless crystalline solid, mp 55-56°) was prepared according to the procedure described by Knight and Swern,²¹ and gave a 99% of theoretical active oxygen titer. Olefins used were supplied by Aldrich Chemical Co., Inc., and were purified by distillation. Mesitylene, cumene, *t*-butyl hydroperoxide, and cumene hydroperoxide (a colorless liquid, bp 42-45° (1.1 mm), $n^{21}_D 1.4634$] was prepared by the method of Walling and Buckler²² and titrated for 98.05% theoretical active oxygen. Cyclohexyl metaborate (a colorless solid, mp 163-166°) was prepared according to the procedure of O'Connor and Nace.²³ Cyclohexyl orthoborate [a colorless waxy solid, mp 65-67°, bp 90° (2 mm)] was prepared by the method of O'Brien.²⁴ Tetralol [bp 128-129° (10 mm)]

(20) F. H. Seubold, Jr., and W. E. Vaughan, J. Amer. Chem. Soc., 75, 3790 (1953).

(21) H. B. Knight and D. Swern in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 895.

(22) C. Walling and S. A. Buckler, J. Amer. Chem. Soc., 77, 6032 (1955).

(23) G. L. O'Connor and H. R. Nace, *ibid.*, **77**, 1578 (1955).

(24) K. G. O'Brien, Aust. J. Chem., 10, 91 (1957).

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.—An authentic sample of mesitol was prepared from the decomposition of 2.64 g (0.016 mol) of tetralin hydroperoxide in the presence of 2.015 g (0.016 mol) of cyclohexyl metaborate in 200 cc of mesitylene heated at 90°. The reaction was complete in 4 hr. Extraction of this crude reaction mixture with aqueous sodium hydroxide and acidification of the aqueous extract, followed by extraction of the acidic solution with ether, afforded, on evaporation of the dried ether solution, crude mesitol. Recrystallization from pentane produced a colorless crystalline material, mp 70–71° (lit.¹⁶ mp 69–70°). The nmr spectrum²⁶ exhibited three "broad" singlets, a nine-proton resonance at τ 7.68 (methyl hydrogens), a one-proton resonance at 5.51 (phenolic hydrogen), and a two-proton resonance at 3.28 (aromatic hydrogens). The ir spectrum exhibited maxima (1% KBr) at 2.94, 3.31, 3.37, 3.45, 3.54, 6.70, 8.30, 8.65, 11.68, and 13.05 μ .

cis-2,3-Epoxyoctane.—The following is a representative epoxidation reaction. Tetralin hydroperoxide, 0.410 g (0.0025 mol), and cyclohexyl metaborate, 0.315 g (0.0025 mol), were placed in a 100-cc, round-bottom, three-necked flask fitted with a thermometer, reflux condenser, serum cap, and a magnetic stirrer. To this 0.842 g (0.0075 mol) of cis-2-octene in 20 cc of cyclohexane was added in one portion. The reaction mixture was heated to reflux.²⁶ Samples were removed periodically and titrated iodometrically²⁷ for unreacted hydroperoxide. After the disappearance of all of the hydroperoxide the product solution was washed with water to hydrolyze the borate ester, and the organic phase was analyzed by vpc.²⁸

Authentic samples of the epoxides produced were synthesized from the appropriate olefin and peracetic acid (25%) in ethyl acetate). The purity of distilled epoxides was confirmed by gas chromatography, infrared spectroscopy, and refractive indices.

Kinetic Measurements.—The decomposition of tetralin and cyclohexyl hydroperoxides in tetralin and mesitylene were run under nitrogen in a flask equipped with a serum cap to facilitate sample removal. Aliquots were removed periodically and titrated for unreacted hydroperoxide iodometrically. Cumene oxidations were performed in a closed system in which oxygen absorption could be followed quantitatively.

Product Determinations.—Analyses were performed by vpc on an F & M 810 and an F & M 5750 using a 6-ft column of XE-60 on Chromosorb G and a 10-ft column of Carbowax 20M on Chromosorb W. Known concentrations of tetralol and mesitol in tetralin were used as calibration standards for product analysis.

Registry No.—Cyclohexyl metaborate, 10534-18-6; mesitol, 527-60-6; tetralin hydroperoxide, 771-29-9; cyclohexyl hydroperoxide, 766-07-4; cumene hydroperoxide, 80-15-9; *t*-butyl hydroperoxide, 75-91-2.

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(27) J. P. Wibaut, Rec. Trav. Chem. Pays-Bas, 73, 1033 (1954).

 $(28)\,$ The competitive epoxidations were run in an identical fashion with 0.075 mol of each olefin present in the initial reaction mixture.

⁽²⁵⁾ The nmr spectrum was taken in deuteriochloroform on a Varian A-60.(26) Reactions in which the olefin to be epoxidized was used as the solvent were run in constant-temperature baths.