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A Novel Reaction of Xenon Trioxide: Organic π Bond Epoxidation. II. Concerning the Mechanism

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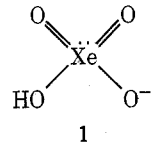
The partially stereoselective epoxidation of alkenes by alkaline xenon trioxide solution was investigated by the employment of reaction quenching techniques, relative reaction rates, and competitive norbornene/cyclohexene product formation ratios. Exclusive peroxide-like attack by the alkaline xenon trioxide reagent toward alkenes was confirmed; no potentially competitive cis-1,2-hydroxylation pathway was detected. Relative rate and product formation ratios, coupled with previously reported stereochemical data, suggest that this epoxidation proceeds via a cyclic, partially bridged three-membered complex that undergoes competitive σ-bond rotation to produce stereoselective epoxide products. The initially formed epoxide product was found to resist direct oxidative attack by the alkaline xenon trioxide reagent. Such resistance to oxidative attack is not found in certain other oxygen containing hydrocarbons, namely, primary and secondary alcohols, aldehydes, and carboxylic acids.

Previously, we reported the epoxidation of alkenes by alkaline xenon trioxide solution.[2] This theoretically intriguing epoxidation proceeded either in a homogeneous aqueous *tert*-butyl alcohol solvent or heterogeneous water emulsion and demonstrated a slight degree of stereoselectivity with pure cis and trans alkenes. Unlike many inorganic oxides that effect cis-1,2-hydroxylation across an olefinic π bond (e.g., OsO_4, MnO_4^-), only epoxide products, or products resulting from in situ hydrolysis of the initially formed epoxides, were isolated from these alkaline xenon trioxide reactions. Hence, this powerful oxidizing reagent chemically reacts like a peroxide in its attack toward organic π bonds. Similar chemical behavior was noted when sodium perxenate and norbornene reacted in an alkaline water emulsion.[2]

This paper describes the employment of reaction-quenching techniques, relative reaction rate measurements, and the well-documented norbornene/cyclohexene reaction rate ratio technique[3-6] to study the reaction mechanism for the epoxidation of alkene hydrocarbons by alkaline xenon trioxide. Additionally, some important experimental procedures are described herein, which were not reported in a previous preliminary communication[2] and are pertinent to the discussion and conclusions drawn in this paper.

Results and Discussion

Reaction Quenching Study. Product isolation from our previous alkaline xenon trioxide oxidations of alkenes produced no derivatives resulting from a cis-1,2-hydroxylation pathway.[2] However, in alkaline xenon trioxide solution, vicinal diol compounds are oxidatively cleaved to generate aldehyde moieties which subsequently are oxidized stepwise, to the corresponding carboxylic acid, and onto carbon dioxide.[7-13] Conceivably, then, a potential competing cis-1,2-hydroxylation reaction pathway could escape detection during product analysis through further in situ oxidation of the initially formed cis vicinal diol derivative. This possibility, coupled with the formal structural similarities of the alkaline xenon trioxide species (1 and 2) to other inorganic oxides that effect cis-1,2-hydroxylation of alkenes (3 and 4), prompted us to investigate the exclusiveness of the observed epoxidation reaction pathway.



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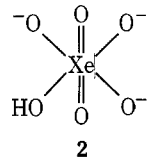

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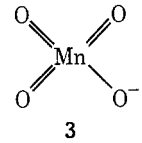

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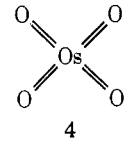

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Under similar reaction conditions employed in the alkaline xenon trioxide epoxidations, the rate of *cis*-1,2-cyclohexanediol oxidation in alkaline xenon trioxide solution was followed by monitoring xenon trioxide consumption through arsenic(III) oxide iodometric titration of aliquoted reaction samples. A sample of *trans*-1,2-cyclohexanediol was also run in parallel with the cis isomer; the initial rates determined for each compound are listed in Table I.

Two experiments between cyclohexene and alkaline xenon trioxide were then conducted under similar reaction conditions employed for the *cis*- and *trans*-1,2-cyclohexanediol oxidation rate study. In the first, after the alkaline xenon trioxide was added dropwise over 33 min, the reaction proceeded for 35 min before the reaction was quenched; the previous oxidation rate data obtained indicated that the total 68-min reaction time corresponded to

Table I
Aqueous Oxidation Rate of Cyclohexanediols with Alkaline XeO_3 at 0° (pH 8)

Species oxidized	Mol/l. min	% reaction monitored
cis-1,2-Cyclohexanediol[a]	8.5×10^{-6}	88.1
trans-1,2-Cyclohexanediol[a]	4.3×10^{-6}	46.3
cis-1,2-Cyclohexanediol[b]	8.3×10^{-6}	79.2

[a] Parallel kinetic run. [b] Later individual kinetic run.

Table II
Aqueous *tert*-Butyl Alcohol Oxidation Rate of Vicinal vs. Nonvicinal Diols by Alkaline Trioxide at 7.5° (pH 9)

Species oxidized	Initial rate, mol/l. hr	% reaction monitored
trans-1,2-Cyclohexanediol	5.0×10^{-5}	83.5
Norbornanediol[16]	1.4×10^{-5}	58.4
Blank alkaline XeO_3	4.7×10^{-6}	27.0

the *cis*-1,2-cyclohexanediol oxidation as proceeding less than 39% toward completion. If cis-1,2-hydroxylation were a significant competitive reaction pathway to epoxidation, some *cis*-1,2-cyclohexanediol would have remained unoxidized after quenching the reaction.

This first experiment was quenched by adding excess potassium iodide and acidifying the solution to instantly reduce the remaining alkaline xenon trioxide species.[14] Acid hydrolysis ensued and work-up produced a white solid identified as pure *trans*-1,2-cyclohexanediol derived from the hydrolysis of the initially formed cyclohexene oxide. No *cis*-1,2-cyclohexanediol was detected.

The second experiment was run similarly and was quenched by adding excess potassium iodide to reduce any perxenate species. Direct removal of the organic species via chloroform extraction followed. Analysis of the organic extract revealed cyclohexene oxide, but no *cis*-1,2-cyclohexanediol nor any trans isomer.

Because no *cis*-1,2-cyclohexanediol was produced in the two quenched reactions between cyclohexene and alkaline xenon trioxide, cis-1,2-hydroxylation may be ruled out as a potentially significant competitive reaction pathway to the epoxidation reaction mode. In conjunction with this quenching study, it was noted that *cis*-1,2-cyclohexanediol is oxidized significantly more rapidly than its trans isomer (Table I). Subsequent reaction rate studies showed that alkaline xenon trioxide also oxidized nonvicinal diols (Table II);[15] thus, alkaline xenon trioxide does not exhibit the oxidative selectivity toward vicinal diol compounds demonstrated by periodic acid.

Reaction Rate Studies. Xenon trioxide in alkaline solution transforms to the xenate ion ($HXeO_4^-$), which disproportionates to form perxenate ions, oxygen, and elemental xenon (eq 1);[17] once the pH-dependent perxenate ion

$$2HOXeO_3^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O \quad (1)$$

forms, it decomposes to the xenon(VI) species and oxygen.[17] Equation 2 represents the perxenate ion decomposition which at pH 11.5 proceeds about 1% per hour and at pH 8 proceeds about 1% per minute. Once a xenon trioxide solution is brought to an alkaline pH, the xenon oxide species are gradually depleted from solution through the reaction pathways described by eq 1 and 2. For this reason

$$2XeO_6^{4-} + 4H_2O \longrightarrow 2HXeO_4^- + O_2 + 6OH^- \quad (2)$$

all reaction rate data sets presented are comprised of one reaction blank containing only the alkaline xenon trioxide reagent. The inherent rate of xenon trioxide depletion was determined in each data set to verify whether or not reaction between the alkaline xenon trioxide reagent and the organic reactant was proceeding. Each reaction rate data set was obtained under similar but not identical reaction conditions. Stock solutions were prepared and the pH was adjusted separately for each kinetic experiment. Therefore, reaction rate comparisons are valid only within each data set; comparison of reaction rates between two different data sets likely will conjure misconceptions.

Table III
Initial Reaction Rates for Consumption of Xenon Trioxide with Norbornene and Cyclohexene Epoxides at 7.5° (pH 10)

Reactant	Initial rate, mol/l. hr	% reaction monitored
exo-2,3-Norbornene oxide	9.4×10^{-6}	59.0
1,2-Cyclohexene oxide	1.3×10^{-5}	98.0
Blank (alkaline XeO_3)	9.4×10^{-6}	54.0

Certain oxygen-containing organic compounds are readily oxidized by the reagent.[7-13] The oxidative stability of the epoxide product, generated in the alkaline xenon trioxide oxidation of alkenes, was determined utilizing comparative reaction rates. Most epoxides slowly undergo alkaline hydrolysis via a trans opening to produce the corresponding vicinal diol. As discussed, vicinal diols are directly oxidized by xenon trioxide eventually to carbon dioxide. However, unlike most epoxides, *exo*-2,3-norbornene oxide does not hydrolyze in moderately alkaline solution and forms nortricyclanol only in very strong base.[16] Since it does not hydrolyze to the reaction rate complicating oxidizable diol, *exo*-2,3-norbornene oxide was used to test the stability of epoxides toward direct oxidative attack by the alkaline xenon trioxide reagent. A set of reaction rate data was determined with three parallel reactions in a 65% aqueous *tert*-butyl alcohol reaction solution at pH 10. One reaction solution contained *exo*-2,3-norbornene oxide, the second 1,2-cyclohexene oxide in identical concentration, and the third reaction was a blank. All three solutions were thermally equilibrated (7.5°) in a constant-temperature bath before a 2:1 excess of xenon trioxide was introduced into each alkene oxide reaction solution and into the blank solvent solution in equal initial concentrations. The initial reaction rates obtained (Table III) show no appreciable rate difference between the norbornene oxide solution and the alkaline xenon trioxide disproportionation in the blank solution. Thus, *exo*-2,3-norbornene oxide is stable toward direct oxidative attack by alkaline xenon trioxide, even in a 2:1 excess of this reagent, and depletion of the initially formed epoxide products in the alkene epoxidation reaction does not occur through direct oxidative attack by the alkaline xenon trioxide reagent. This suggests that the significantly more rapid consumption of xenon trioxide with the cyclohexene oxide solution must result from the secondary alkaline xenon trioxide diol oxidation initiated from alkaline hydrolysis of the initial cyclohexene oxide to *trans*-1,2-cyclohexanediol. However, the possibility that *exo*-2,3-norbornene oxide's inertness toward direct oxidation by the alkaline xenon trioxide is unique cannot be totally dismissed.

Table IV
Initial Reaction Rates of Concentrated vs. Dilute Cyclohexene with Alkaline XeO_3 at 7.5° (pH 10)

Reactant	Initial rate, mol/l. hr	% reaction monitored
Concentrated cyclohexene	9.1×10^{-5}	91.9
Dilute cyclohexene	3.8×10^{-5}	88.5
Blank (alkaline XeO_3)	2.9×10^{-5}	69.7

A second reaction rate data set was obtained to determine the importance of alkene participation in the epoxidation reaction. Three parallel reactions were employed; one reaction contained "concentrated" cyclohexene (2.97 mmol), a second reaction contained "dilute" cyclohexene (0.297 mmol), and the third reaction was a blank devoid of cyclohexene. The reactions were conducted in a 57% aqueous *tert*-butyl alcohol solution adjusted to pH 10. The initial reaction rates obtained (Table IV) indicate a significant sevenfold rate enhancement for the "concentrated" cyclohexene reactant after substraction of the blank. Such rate enhancement verifies alkene participation in the epoxidation reaction's rate-determining step,[18] and suggests interaction between the alkene's unsaturated bond and the alkaline xenon trioxide species or an oxidizing species generated therefrom.

Relative Norbornene/Cyclohexene Product Formation Ratios. Relative product formation or reaction rate ratios between norbornene and cyclohexene have proved to be valuable chemical tools to decipher the size and nature of suspected cyclic, bimolecular transition states in alkene addition reaction.[3-6] Generally, three-membered transition states provide a ratio on the order of 10 while five-membered ones afford ratios ranging between 10^2 and 10^3. Product formation ratios can be obtained from product yields of a reaction containing equimolar amounts of two competing alkenes and the reagent under evaluation;[6] direct competitive reaction rates obtained with this tested reagent and each alkene in separate reactions offers a second evaluative method.[3-5] The apparent bimolecular interaction between the alkene and the alkaline xenon trioxide or perhaps an epoxidizing species generated therefrom, plus the slight degree of stereoselectiveness exhibited in this epoxidation reaction[2] with pure cis and trans acyclic alkenes, allows consideration of two potential bimolecular, cyclic transition states—a three-membered or five-membered species.

Competitive norbornene/cyclohexene product formation ratios with alkaline xenon trioxide were obtained from competitive reactions conducted in both homogeneous aqueous *tert*-butyl alcohol solvent and heterogeneous water emulsion. Excess but equimolar amounts of norbornene and cyclohexene were stirred in the same reaction solution ($8 < pH < 9$) until all xenon trioxide was consumed. The resulting volatile epoxides were acid hydrolyzed in situ to their respective diols prior to work-up to minimize product loss.[19] After work-up the norbornanediol and cyclohexanediol product mixture was analyzed by gas–liquid chromatography;[16,20] triangulated peak area measurements of each diol product afforded competitive product formation ratios (Table V) that clearly reveal a three-membered transition state species.

Because previous norbornene/cyclohexene reaction rate ratios were accomplished in much less polar solvents than those necessarily employed for the xenon trioxide reagent, duplicate reactions were conducted in our highly polar solvents substituting *m*-chloroperbenzoic acid for the alkaline xenon trioxide.

Table V
Norbornene/Cyclohexene Relative Rate Ratio vs. Cyclic Transition State Size

Reagent	Ref	Cyclic transition state size	Norbornene/cyclohexene rel rate ratio
Perlauric acid	3	3	1.2
Mo(VI) HMPA	6	3	1.94
m-Chloroperbenzoic acid	6	3	2.39
Basic xenon trioxide[a]	This work	?	2.4
Basic xenon trioxide[b]	This work	?	2.7
Cr(VI) oxidation	4	3	5.5
Ag^+ complex formation	21	3	17
OsO_4 in pyridine	22	5	72.3
OsO_4 in ether	6	5	320
Diphenylnitrilimide addition	24	5	283
Benzonitrile oxide addition	24	5	1800
Phenyl azide addition	3, 23, 24	5	6500
Picryl azide addition	3, 23	5	8000

[a] Homogeneous, aqueous *tert*-butyl alcohol solvent. [b] Heterogeneous water solvent.

Table VI
Norbornene/Cyclohexene Product Formation Ratios from Alkaline XeO_3 and *m*-Chloroperbenzoic Acid Epoxidation

Reagent	Product formation ratio
Alkaline XeO_3[a]	2.4
m-Chloroperbenzoic acid[a]	1.8
Alkaline XeO_3[b]	2.7
m-Chloroperbenzoic acid[b]	1.6

[a] Homogeneous aqueous *tert*-butyl alcohol solvent. [b] Heterogeneous water emulsion.

Table VI lists these results and good agreement between the *m*-chloroperbenzoic acid standard and the xenon trioxide epoxidant in both polar solvent systems was obtained. Additionally, the *m*-chloroperbenzoic acid ratios are in line with those formerly reported in the less polar solvents (Table V).

A relative norbornene/cyclohexene reaction rate ratio was secured directly from a parallel reaction rate experiment where equimolar amounts of norbornene and cyclohexene were each treated separately with alkaline xenon trioxide in 65% aqueous *tert*-butyl alcohol (pH 10) at 7.5°. A blank of the alkaline xenon trioxide was also run, and the reaction rate data was secured and treated as previously described. The initial reaction rates (Table VII) provide a norbornene/cyclohexene reaction rate ratio equal to 7.5 after subtraction of the blank xenon trioxide; once again, this value fits well within the range attributed to bimolecular, three-membered transition states (Table V).

Table VII
Initial Reaction Rates of Norbornene and Cyclohexene with Alkaline XeO_3 at 7.5° (pH 10)

Reactant	Initial rate, mol/l. hr	% reaction monitored
Norbornene	2.9×10^{-5}	66.2
Cyclohexene	1.6×10^{-5}	61.6
Blank (alk XeO_3)	1.4×10^{-5}	41.4

Conclusions

Chemical reaction between alkene hydrocarbons and alkaline xenon trioxide solution initiates a peroxide-type attack upon the alkene π electrons to produce epoxide derivatives. Epoxidation is the only significant reaction mode detected with alkenes. While some of the initially formed epoxide product is lost during the reaction, through alkaline hydrolysis to diol compounds and subsequent alkaline XeO_3 oxidation of these diols to carbon dioxide, the epoxide product itself is apparently stable toward direct oxidative attack by the alkaline xenon trioxide reagent, and no epoxide is probably lost via direct secondary oxidations.

Previous epoxidations of pure *cis*- and *trans*-stilbene plus *cis*- and *trans*-2-octene in alkaline XeO_3 solution demonstrated a slight degree of stereoselectivity in the isomeric epoxide products.[2] Therefore, some structural rigidity must exist in this reaction's rate-determining step to account for such results. The alkene does interact with the epoxidizing species during the course of reaction as reflected in the concentrated/dilute cyclohexene reaction rates. The competitive norbornene/cyclohexene ratios verify the epoxidation as proceeding via a cyclic three-membered species involving alkene π bond and the oxidant.

The experimental results obtained to date for the alkaline XeO_3 epoxidation of alkenes are consistent with the formation of a weakly bridged, cyclic three-membered complex in the epoxidation's rate-determining step. This intermediate complex forms from an interaction between the alkene and either the alkaline xenon trioxide species or an oxidizing species generated therefrom. This weakly bridged, three-membered cyclic complex, once formed, undergoes significant competitive σ bond rotation about the carbon–carbon single bond to form the nonstereospecific cis/trans epoxide mixture. In the highly polar solvents, as required by the alkaline xenon trioxide reagent, charge localization would be favored over charge dispersal in the partially bridged intermediate species. Charge localization would tend to weaken the cyclic bridging in the intermediate complex and allow significant, competitive σ bond rotation that would result in the low degree of stereoselectivity observed[2] in the epoxidation of acyclic cis/trans alkenes.

Experimental Section

General Procedures. All common reagents and extraction solvents employed were Mallinckrodt AR, Matheson Coleman and Bell AR, or Baker Analyzed. The water used in all reactions and in the dilution of xenon trioxide solution was taken directly from a deionized water line in the laboratory; the *tert*-butyl alcohol solvent was Mallinckrodt AR that had been triply distilled. All glassware and Teflon-coated stirring bars were soaked in a clean, steam-heated, deionized water bath containing a small amount of Alconox soap. The equipment was then thoroughly rinsed with deionized water followed by one rinse with distilled Mallinckrodt AR acetone that was stored over 4A molecular seieves. The cyclohexene (Mallinckrodt AR Grade) was distilled once and the norbornene (MCB Practical) was twice distilled unless stated otherwise. *cis*-Stilbene was synthesized by previously described methods;[25] GLC analysis showed it to be 99.3% isomerically pure.

Glassware joints were treated with vacuum grease or were wrapped with Teflon tape to avoid trapping any xenon trioxide solution in the joints. (*Dry xenon trioxide is explosive and detonates very easily!*)[26] Reactions were stoppered because most alkenes employed were rather volatile. Both the homogeneous and heterogeneous xenon trioxide–alkene reactions were stirred with Teflon coated bars, and unless stated otherwise, all pH adjustments were made with 1% sodium hydroxide or 2 *N* sulfuric acid. The pH measurements were taken with wide-range pH hydrion paper, and organic extracts were dried over anhydrous magnesium sulfate or sodium sulfate.

Table VIII
Gas Chromatography Columns Employed in Experiments with the Compounds Listed

9 ft × 0.25 in. 20% Carbowax 20M on 70/80 Mesh Anakrom ABS

cis- and *trans*-1,2-cyclohexanediol, cyclohexene oxide, *cis*- and *trans*-1,2-cyclopentanediol, cyclopentene oxide, *exo*-2,3-norbornene oxide, bicyclo[2.2.2]oct-2-ene oxide

1.45 m × 0.25 in. 5% SE-30 on 70/80 Mesh Anakrom ABS

syn- and *anti*-2,7-norbornanediol and *syn*- and *anti*-2,5-norbornanediol mixture (single peak), *trans*-1,2-cyclohexanediol

6 ft × 0.05 in. 5% QF-1 on 100/120 Mesh Varaport 30

cis-Stilbene, *cis*-stilbene oxide, *trans*-stilbene, *trans*-stilbene oxide

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. Mass spectra were determined on an Atlas CH-4B mass spectrometer; nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument, and all infrared plots were secured on a Beckman IR-33 in potassium bromide pellets or as a thin film between sodium chloride or silver chloride disks. Gas–liquid partition chromatograms were obtained on an Aerograph Dual Column Model A-350-B chromatograph; Table VIII records the columns employed to identify, separate, and isolate the compounds listed. Isomeric percent analyses obtained by GLC were determined by triangulation. In several cases where interfering peaks made direct measurement of peak width at one-half the peak's height impossible, a standard peak of equal size obtained from a pure sample was used to gain this necessary measurement. All reported product yields were calculated as quantitative theoretical yields assuming a 3:1 alkene to XeO_3 reaction stoichiometry and are not corrected for work-up losses.

In all reaction rate studies, where iodometric titration analysis was employed, starch indicator was added near the end point to sharpen detection. The xenon trioxide was purchased from PCR in 100-ml quantities as 0.1 *N* solution.

***trans*-1,2-Cyclohexanediol from Cyclohexene and Xenon Trioxide.** A 100-ml water solution containing 0.12335 g (1.508 mmol) of cyclohexene was rapidly stirred and cooled while submerged in an ice–salt bath. One milliliter of 0.28 *M* (0.28 mmol) XeO_3 was diluted with 60 ml of H_2O and brought to pH 9–10 by the dropwise addition of 10% NaOH. Over 1.25 hr the XeO_3 solution was added to the stirred cyclohexene emulsion. The reaction mixture was maintained at ice bath temperature for an additional 3.5 hr, then was allowed to gradually equilibrate to room temperature over the next 44 hr. The solution was brought to pH 3 by dropwise addition of 6 *N* H_2SO_4 and left at room temperature for 141.5 hr. The aqueous reaction solution was concentrated to 50 ml over a Bunsen burner, and the concentrate was extracted 12 times with ~50 ml of $CHCl_3$. The combined $CHCl_3$ extracts were concentrated to 50 ml and dried. In vacuo solvent removal gave 0.0152 g (15.6%) of crude white solid: ir (KBr) 3400 (OH), 2950 and 2880 (CH), 1040, 930, and 670 cm^{-1} (characteristic trans isomer fingerprint absorptions); micro-NMR ($DCCl_3$) δ 4.48 (2 H, m, methine), 3.38 (2 H, s, hydroxy), 2.25–1.00 (8 H, m, cyclohexyl); GLC on the Carbowax 20M column (210°) D_r' 11.25 cm only (commercial *trans*-1,2-cyclohexanediol D_r' 11.25 cm and *cis*-1,2-cyclohexanediol D_r' 10.10 cm).

***exo*-2,3-Norbornene Oxide from Norbornene and Xenon Trioxide.** A 15-ml H_2O solution containing 0.1570 g (1.67 mmol) of once-distilled norbornene was stirred and cooled in an ice–salt bath for 1.5 hr. Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 was adjusted to pH 9 and added dropwise over 15 min to the stirred norbornene solution. The reaction solution and ice bath were placed into a cold room (3°) for 3 hr. Then the reaction vessel was re-

moved from the cold room and packed into a fresh ice bath, which was allowed to melt and equilibrate to room temperature. After 22.25 hr reaction time, the solution was yellow and at a neutral pH. The pH was adjusted to 8; the same pH adjustment was necessary after an additional 8 hr. All XeO_3 was consumed after a total of 54.5 hr; the solution was saturated with NaCl and extracted four times with diethyl ether. The combined extracts were concentrated to 50 ml, then dried, filtered, and concentrated further by rotary evaporation to 0.1 ml for GLC analysis; GLC on the Carbowax 20M column (163°) D_r' 5.74 cm only (*exo*-2,3-norbornene oxide D_r' 5.74 cm); mass spectrum M^+ 110 from a sample collected off the Carbowax column at 187° that gave a fragmentation pattern identical with known *exo*-2,3-norbornene oxide that was also collected off the same column (187°); ir (neat) 3010–2880 (CH), 845 cm^{-1} (oxide); the reaction sample was subjected to a second GLC analysis on the Xe-60 column (150°) D_r' no peaks at 5.02–5.20 or at 4.10–4.20 cm (known *exo-cis*-2,3-norbornane diol D_r' 4.12 cm and known *syn*- and *anti*-2,5- and -2,7-norbornanediol mixture (single peak) D_r' 5.06 cm).

***syn*- and *anti*-2,5- and -2,7-Norbornanediol Mixture from Norbornene and Xenon Trioxide.** A 15-ml H_2O solution containing 0.1560 g (1.66 mmol) of norbornene was cooled with stirring for 1.5 hr in an ice–salt bath. Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 was adjusted to pH 9 and added dropwise over 6 min to the stirred norbornene solution. The ice bath was allowed to equilibrate to room temperature environment; after 12 hr the solution pH was neutral and was adjusted to pH 8. After 23.5 hr of reaction, the pH was again adjusted to 8; the same adjustment was made 6.25 hr later. After a total reaction time of 38 hr, all xenon trioxide was spent; the yellow solution was adjusted to pH 3 and left for 108 hr at room temperature. Then the aqueous solution was concentrated to 20 ml, adjusted to pH 11, and extracted six times with ~50 ml of diethyl ether. The aqueous layer was saturated with NaCl and six additional ethereal extractions were accomplished. The combined extracts were concentrated to 30 ml, dried, and filtered. In vacuo solvent removal left a crude brownish oil weighing 0.0254 g. The oil was redissolved in 0.2 ml of ether. It was then analyzed and purified by preparative GLC to yield 0.0080 g (12.5%) of white solid: ir (KBr) 3390 (OH), 2970 and 2890 cm^{-1} (CH); mass spectrum M^+ 128; GLC on the Xe-60 column (152°) D_r' 5.06 cm only [*syn*- and *anti*-2,5- and -2,7-norbornanediol mixture (single peak) D_r' 5.02 cm and *exo-cis*-2,3-norbornanediol D_r' 4.06 cm].

Stilbene Oxide from *cis*-Stilbene and Xenon Trioxide (Heterogeneous Reaction at 3°). A solution containing 2 ml of H_2O and 0.06055 g (0.336 mmol) of 99.3% *cis*-stilbene was cooled with stirring in a cold room (3°) for 35 min. Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 at pH 9 was added over a 5-min period to the stilbene–H_2O solution. For the next 280 hr, the reaction proceeded until all xenon trioxide was depleted; at 24-, 51-, 72-, and 122-hr reaction intervals, the solution was adjusted from near neutral pH to pH 8. The reaction solution was extracted once with diethyl ether; the aqueous layer was then saturated with NaCl. Three more ethereal extracts were taken; the combined ether extracts were dried, filtered, and concentrated to about 0.2 ml. Preparative GLC on the QF-1 column (139°) allowed the identification and isolation of four compounds: unreacted *cis*-stilbene, *cis*-stilbene oxide, *trans*-stilbene, and *trans*-stilbene oxide was the elution order on the QF-1 column. The GLC results showed that 1.4% of the initial *cis*-stilbene was converted to the cis oxide; GLC results of a blank indicated only 2.8% isomerization of the *cis*-stilbene to the trans isomer under the reaction conditions described. Peak 1: ir (neat) 3100, 3080, and 3040 (CH), 1600, 1575, 1495, and 1450 cm^{-1} (phenyl); mass spectrum M^+ 180. Peak 2: mass spectrum M^+ 196, characteristic stilbene oxide peaks *m/e* 167 and 105. Peak 3: ir (KBr) 3100, 3080, and 3040 (CH), 1600, 1580, 1495, and 1450 cm^{-1} (phenyl); mass spectrum M^+ 180. Peak 4: mass spectrum, M^+ 196, characteristic stilbene oxide peaks *m/e* 167 and 105.

Stilbene Oxide from *cis*-Stilbene and Xenon Trioxide (Homogeneous Reaction at 25°). Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 was cooled in a cold room (3°) for 1.25 hr. A solution containing 20 ml of *tert*-butyl alcohol and 0.06047 g (0.336 mmol) of 99.3% *cis*-stilbene was taken into the cold room. After the xenon trioxide solution was adjusted to pH 9, it was added over 3 min to the stirred *cis*-stilbene solution. When the solution showed $7 < pH < 8$, it was adjusted to pH 8. The reaction proceeded for 0.25 hr in the cold room and was then removed to a room temperature environment. During the reaction, adjustments to pH 8 were made at 3.0-, 8,0-, 31.5-, 36.5-, and 46.5-hr intervals. After 57.75 hr, all XeO_3 was consumed and a yellowish solution remained. The reaction solution was saturated with NaCl and extracted three times with diethyl ether. The combined extracts were concentrated to 75 ml, dried, and filtered. The solution was concentrated to about 0.2 ml. Analysis by GLC on the QF-1 column (139°) identified and isolated four compounds that eluted from the column in the order *cis*-stilbene, *cis*-stilbene oxide, *trans*-stilbene, and *trans*-stilbene oxide; GLC results of a blank indicated only 6.4% isomerization of the *cis*-stilbene to the trans isomer under the reaction condition described. Peak 1: ir (neat) 3100, 3070, and 3040 (CH), 1600, 1575, 1495, and 1450 cm^{-1} (phenyl). Peak 2: mass spectrum M^+ 196, characteristic stilbene oxide peak *m/e* 167. Peak 3: ir (KBr) 3100, 3070, and 3040 (CH), 1600, 1575, 1495, and 1450 cm^{-1} Peak 4: mass spectrum M^+ 196, characteristic stilbene oxide peaks *m/e* 167 and 105.

***exo*-2,3-Norbornene Oxide from Norbornene and Sodium Perxenate.** A solution containing 5 ml of water and 0.15700 g (1.67 mmol) of norbornene was cooled for 20 min in an ice–salt bath; it was then placed into a cold room (3°) and stirred for another 45 min. Next, 0.05250 g (0.167 mmol) of Na_4XeO_6 was added to the stirred solution and a very high solution pH (ca. 12) resulted. After 5 hr the yellow reaction solution was removed from the cold room, placed into an ice bath, and equilibrated to room temperature. After a total reaction time of 33.25 hr, all Xe species were spent. The solution was saturated with NaCl and was extracted three times with diethyl ether. The combined extracts were dried, filtered, and concentrated to about 0.3 ml. The concentrate was analyzed by GLC, and the products were isolated: GLC on the Carbowax 20M column (174°) D_r' 3.48 and 6.80 cm (*exo*-2,3-norbornene oxide D_r' 3.48); mass spectrum M^+ 110, the smaller peak at D_r' 6.80 cm remained unidentified but gave a mass spectrum, parent peak *m/e* 124, and a fragmentation pattern similar to, but different from, that of *exo*-2,3-norbornene oxide.

***cis*- and *trans*-1,2-Cyclohexanediol Oxidation Rates with Xenon Trioxide.** Two 20-ml H_2O solutions, one containing 0.0334 mmol of *cis*-1,2-cyclohexanediol and the other containing an identical concentration of *trans*-1,2-cyclohexanediol, were submerged into a constant-temperature ice bath (0°). The solutions were allowed to temperature equilibrate. Next, 5% NaOH was added to 6 ml of 0.1 *N* XeO_3 solution until a pH 9 was reached. Into each homogeneous diol solution was pipetted 2 ml (0.0334 mmol) of the alkaline XeO_3; an oxidation reaction at pH 8 resulted. At appropriate intervals, 2-ml aliquots were pipetted from the reaction solutions and were each transferred into an erlenmeyer flask that contained 1.5 g of KI. Two milliliters of 2 *N* H_2SO_4 were added to liberate iodine. Thirty seconds later, 1.5 g of $NaHCO_3$ was added to the flask which was then swirled and allowed to stand for 5 min. Iodometric titration with 0.002 *N* arsenic(III) oxide with starch indicator determined the concentration of unreacted XeO_3. A titer to determine initial XeO_3 concentration at time zero was obtained by placing 1 ml of the freshly prepared alkaline XeO_3 into 10 ml of water. A 1-ml aliquot was pipetted, treated, and titrated as described above. The individual *cis*-1,2-cyclohexanediol rate study was set up and analyzed in an identical manner.

Direct *cis*-1,2-Cyclohexanediol Formation Check in Alkaline XeO_3 Epoxidation of Alkenes. A 100-ml H_2O emulsion containing 0.1187 g (1.45 mmol) of cyclohexene was cooled via stirring while submerged in an ice–salt bath. Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 was diluted with 50 ml of H_2O and adjusted to pH 9 with 1% NaOH. The alkaline XeO_3 was added dropwise to the stirred cyclohexene emulsion over 33 min. Reaction proceeded for an additional 35 min before quenching by the introduction of 70 mg of KI. After dropwise addition of 2 *N* H_2SO_4 followed until pH 3 was reached,[14] the acidified reaction solution was left for 97.5 hr at room temperature. The solution was then made alkaline (pH 9) and was extracted 12 times with ~50-ml $CHCl_3$ portions. The combined $CHCl_3$ extracts were concentrated to 50 ml, dried, and filtered. The remaining solvent was removed in vacuo to yield 8.8 mg (15.1%) of crude off-white solid; GLC on a 9 ft × 0.25 in. 20% Carbowax 20M column (211°) produced only one peak with a retention time identical with that of commercial *trans*-1,2-cyclohexanediol, mass spectrum M^+ 116. Another sample of cyclohexene (0.1218 g, 1.49 mmol) was added to a stirred 100-ml H_2O solution, and the solution was cooled for 2.25 hr in an ice–salt bath in a cold room. Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 were pipetted into 50 ml of H_2O; the solution was adjusted to pH 9. The alkaline XeO_3 was added dropwise to the stirred cyclohexene over 32 min and the reaction was then continued for an additional 36 min. KI (0.100 g) was introduced into the reaction; immediately 5 ml of $NaHCO_3$ buffered 0.2 *N* arsenic(III) trioxide was added. Nine $CHCl_3$ extractions followed; the combined extracts were dried, fil-

tered, and concentrated via rotary evaporation to 0.3 ml; GLC on the Carbowax 20M column (160 and 220°) showed cyclohexene oxide in low concentration; no *cis*- or *trans*-1,2-cyclohexanediol was detected.

General. Relative Reaction Rate Data Sets. The various sets of comparative reaction rates were monitored at specific time intervals by direct iodometric titration of the unconsumed alkaline xenon trioxide present in the reaction aliquots. The concentration of unconsumed xenon trioxide was plotted against time, and initial reaction rates were obtained. All reaction rate data sets were conducted in alkaline aqueous *tert*-butyl alcohol solution with three parallel reactions being run in each data set; one reaction was always the blank alkaline xenon trioxide reagent previously described in the Results and Discussion.

Competitive *exo*-2,3-Norbornene Oxide vs. 1,2-Cyclohexene Oxide Reaction Rate Determination. A stock solution containing 77 ml of *tert*-butyl alcohol and 143 ml of H_2O was prepared and adjusted to pH 10 with 10% NaOH. Into a 100-ml volumetric flask was weighed 0.00918 g (0.0835 mmol) of norbornene oxide; the volumetric flask was then filled to its mark with the stock solution. Twenty milliliters (0.0167 mmol) of norbornene oxide solution was pipetted into a 35-ml round-bottom flask which was then stoppered, placed into a constant-temperature bath in a cold room, and stirred. Into another 100-ml volumetric flask was placed 0.00812 g (0.0830 mmol) of cyclohexene oxide which was diluted with the stock solution to the mark. Twenty milliliters (0.0166 mmol) of cyclohexene oxide solution was pipetted into a second 35-ml, single-necked, round-bottom flask which was stoppered, placed into the constant-temperature bath in the cold room, and stirred. Ten milliliters of the stock solution was pipetted into a 10-ml pear-shaped flask; it was stoppered and placed into the same constant-temperature bath. All three solutions were temperature equilibrated; the two epoxide solutions were stirred. Into each 35-ml flask was pipetted 2 ml of 0.1 *N* (0.0334 mmol) XeO_3, and into the 10-ml flask was pipetted 1 ml (0.0167 mmol) of XeO_3; the 10-ml flask was stirred with a glass rod to effect a homogeneous solution. Aliquot removal and analysis were accomplished as previously described.

Concentrated vs. Dilute Cyclohexene Reaction Rate Determination. A stock solvent solution for all three kinetic reactions was prepared by mixing 29 ml of *tert*-butyl alcohol with 39 ml of H_2O and was adjusted to pH 10. Into two 35-ml, single-neck, round-bottom flasks was pipetted 20 ml of the stock solution, and into a 10-ml, single-neck, pear-shaped flask was pipetted 10 ml of the stock solution. The three flasks were placed into a constant-temperature bath (7.5°) and equilibrated. To one 35-ml flask were added 30 μl (0.297 mmol) of cyclohexene, and to the other 3 μl (0.0297 mmol) of cyclohexene; in both cases the cyclohexene was injected directly into the stirred solutions with a syringe. Into each cyclohexene solution were pipetted 2 ml of 0.1 *N* (0.0334 mmol) XeO_3 and into the 10-ml pear-shaped titer flask was placed 1 ml of 0.1 *N* (0.0167 mmol) XeO_3. The titer solution was initially stirred with a glass stirring rod to effect a homogeneous solution. At appropriate intervals, 2-ml aliquots were pipetted from the cyclohexene solutions, and 1-ml aliquots were pipetted from the titer solution. A 1-ml aliquot was taken immediately upon mixing the titer solution and represented the initial molar concentration of xenon trioxide in all three reactions. The 2-ml cyclohexene solution aliquots were placed onto 1.5 g of KI in a 125-ml erlenmeyer flask; the aliquot was acidified with 2 ml of 2 *N* H_2SO_4 acid and was then swirled. Thirty seconds after the acid addition, the aliquot solution was buffered with 1 g of $NaHCO_3$ and the inner walls of the flask were washed with a water bottle. The solution was swirled and left to stand at room temperature for 5 min. It was then titrated with $NaHCO_3$-buffered 0.002 *N* arsenic(III) oxide.

Norbornene–Cyclohexene Competitive Reaction with Xenon Trioxide (Heterogeneous). Into the same reaction vessel was weighed 0.07828 g (8.33 mmol) of norbornene and 0.06789 g (8.29 mmol) of cyclohexene; the cyclohexene dissolved the norbornene. The stoppered reaction flask was placed into a cold room and packed into an ice bath; then 5 ml of H_2O was added to the reaction flask. Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 was adjusted to pH 9 and added to the stirred mixed olefin emulsion over a 2-min period. The ice bath was removed, and the reaction was stirred for 145 hr in the cold room; adjustments to maintain a solution pH of 8 were made at 11, 48, 59, 74, and 116 hr into the reaction. After 145 hr the XeO_3 was depleted, and the reaction solution was acidified to pH 3 and left for 144 hr at room temperature. The pH was then adjusted to 8, and the solution was saturated with NaCl. Six $CHCl_3$ extractions were accomplished; the combined extracts were dried, filtered, and concentrated to about 0.2 ml. Analysis for the percentage of each diol product was made by GLC, and each diol was isolated from the XE-60 column (148°): D_r' 1.10, 1.62, 1.90, 2.40, and 4.46 cm [*trans*-1,2-cyclohexanediol D_r' 1.90 cm and norbornanediols mixture (single peak) D_r' 4.46 cm]. Peak 3: mass spectrum M^+ 116; ir (KBr) 3400 (OH), 2950 and 2880 (CH), 1040, 930, and 670 cm^{-1} (characteristic *trans*-1,2-cyclohexanediol fingerprint absorptions). Peak 5: mass spectrum M^+ 129 with the remaining fragmentation pattern identical with those of known norbornanediols;[16] ir (KBr) 3400 (OH), 2970 and 2890 cm^{-1} (CH).

Norbornene–Cyclohexene Competitive Reaction with *m*-Chloroperbenzoic Acid (Heterogeneous). The reaction was conducted as previous described except that 0.06800 g (0.334 mmol) of 85% *m*-chloroperbenzoic acid (MCPBA) was substituted for the XeO_3 without any initial pH adjustments. After an identical work-up, the amount of each diol product was determined by GLC and isolated from the XE-60 column (144°): D_r' 2.16 and 5.62 cm [*trans*-1,2-cyclohexanediol D_r' 2.12 cm and norbornanediol mixture (single peak) D_r' 5.62 cm]. Peak 1: ir (KBr) 3400 (OH), 2940 and 2870 (CH), 1040, 830, and 670 cm^{-1} (characteristic *trans*-1,2-cyclohexanediol fingerprint absorptions). Peak 2: ir (KBr) 3400 (OH), 2970 and 2880 cm^{-1} (CH).

Norbornene–Cyclohexene Competitive Reaction with Xenon Trioxide (Homogeneous). Ten milliliters of 0.1 *N* (0.167 mmol) XeO_3 was cooled in a cold room for 1.25 hr. A solution containing 0.05780 g (0.616 mmol) of norbornene, 0.05172 g (0.631 mmol) of cyclohexene, and 15 ml of *tert*-butyl alcohol, was prepared and placed in the cold room. The xenon trioxide solution was adjusted to pH 9 and was added to the stirred *tert*-butyl alcohol solution over 2.5 min. After 15 min, the entire solution was adjusted to pH 8 and left to stir in the cold room. Adjustments to pH 8 were made at 21.75, 48.0, 67.75, 72.75, 88.25, and 96.25 hr after reaction was initiated. After a total of 111 hr, XeO_3 was absent; the solution was brought to pH 3 and left at room temperature for 145 hr. The solution was adjusted to pH 9, saturated with NaCl, and then extracted six times with $CHCl_3$. The combined $CHCl_3$ extracts were dried, filtered, and concentrated to about 0.2 ml. Analysis by GLC followed to identify, isolate, and determine the percentage of each diol product formed: GLC on the XE-60 column (144°) D_r' 1.52, 1.98, 2.28, 2.72, 3.16, and 5.92 cm (norbornanediols mixture D_r' 5.60 cm and *trans*-1,2-cyclohexanediol D_r' 2.50 cm). Peak 6: mass spectrum M^+ 128; ir (KBr) 3400 (OH), 2970 and 2890 cm^{-1} (CH). Peak 4: mass spectrum M^+ 116 detected among other characteristic *trans*-1,2-cyclohexanediol fragmentations.

Norbornene–Cyclohexene Competitive Reaction with *m*-Chloroperbenzoic Acid (Homogeneous). The reaction was conducted as previously described except that 0.03400 g (0.167 mmol) of 85% MCPBA was substituted for the XeO_3 without any initial pH adjustments. After an identical work-up, the diol percentage was determined by GLC analysis, which was also used to preparatively isolate and purify the reaction products: GLC on the XE-60 column (145°) D_r' 0.80, 1.36, 1.80, 2.38, 2.58, 3.02, and 6.42 cm (norbornanediols mixture D_r' 5.20 cm and *trans*-1,2-cycohexanediol D_r' 2.88 cm). Peak 5: mass spectrum M^+ 116. Peak 7: mass spectrum M^+ 128.

Competitive Norbornene vs. Cyclohexene Reaction Rate Determination. A stock solution was prepared by mixing 28 ml of *tert*-butyl alcohol and 52 ml of H_2O; the resultant mixture was adjusted to pH 10 with 10% NaOH. Into one 35-ml, single-neck, round-bottom flask was pipetted 20 ml of the stock solution; the flask was stoppered, and the solution was stirred in a constant-temperature bath (7.5°) for 1 hr. Next, 3.4 μl (0.0336 mmol) of cyclohexene were injected into the solution with a microsyringe. Into a 100-ml volumetric flask was weighed 0.00948 g (0.1008 mmol) of norbornene and 30 ml of stock solution was added. Ten milliliters of the norbornene solution and 10 ml of the original stock solution were pipetted into a second 35-ml, single-neck, round-bottom flask to give 0.0336 mmol of norbornene in the reaction solution. The norbornene solution was stoppered and placed into the constant-temperature bath. Into a 10-ml pear-shaped flask was pipetted 10 ml of the stock solution for the initial XeO_3 concentration and XeO_3 disproportionation rate determinations. This flask was stoppered and placed into the constant-temperature bath. After temperature equilibration, 2 ml of 0.1 *N* (0.0334 mmol) XeO_3 was pipetted into each 35-ml flask; into the 10-ml flask was pipetted 1 ml of 0.1 *N* (0.0167 mmol) XeO_3. Aliquot removal and analysis were accomplished as previously described.

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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-