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Allylic Substituent Effects in the Peracid Oxidation of Cyclopropenes to Enones

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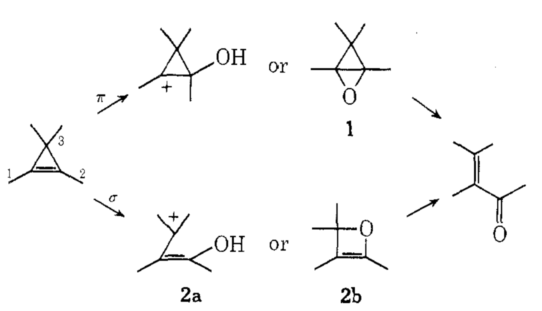
The second-order rate constants ($\times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$) for *m*-chloroperbenzoic acid oxidation in CCl_4 at 0° have been measured for the following 1,2-diphenyl-substituted cyclopropenes: 3-unsubstituted, 3.4; 3-methyl, 1.24; 3,3-dimethyl, 0.40; 3-phenyl, 0.122. These values were compared to those for epoxidation of the following cyclopentenes: unsubstituted, 9.1; 3-methyl, 10.6, 64:36 ratio of cis:trans epoxides; 3-phenyl, 1.93, 25:75 ratio of cis:trans epoxides. These results are discussed in an attempt to determine whether peracid oxidation of cyclopropenes occurs with σ- or π-bond attack.

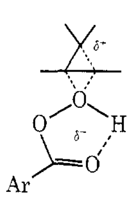
The reaction of electrophilic reagents with strained σ bonds has been extensively studied in recent years. Since these reagents also react with π systems of olefins, the interesting question is raised of σ *vs.* π reactivity.[2] The question becomes operationally acute when an exceptionally strained σ bond is incorporated in a molecule that possesses a π system with possibly normal reactivity.

The cyclopropene system is an especially good example of this class of molecules. Fragmentation of the $C_{1,3}$ or $C_{2,3}$ σ bond of cyclopropenes thermodynamically releases *ca.* 55 kcal/mol of strain.[3] In cyclopropene and related systems, there are numerous literature postulates concerning reactions which occur preferentially with strained σ bonds.[4]

Our work concerns the detailed mechanism by which cyclopropenes are electrophilically oxidized to enones by peracids. At present, product studies provide the major evidence that peracid oxidation of cyclopropenes to enones proceeds *via* oxabicyclobutane intermediates.[5]

The evidence, however, is equally consistent with mechanisms which involve electrophilic cleavage of a cyclopropene σ bond. Such cleavage would preclude intermediates such as oxabicyclobutane **1** in favor of species such as **2a**, **2b**, or other variants formed from electrophilic oxidation of a σ bond. On the other hand, if cleavage of a σ bond is occurring simultaneously with reaction of the π bond to produce a transition state like **2c**, the overall electronic effect of allylic substituents would be expected to mimic that produced by **2a** or **2b**.

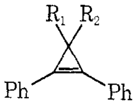




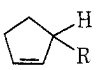
2c

Unfortunately, there is a dearth of kinetic data on the electrophilic oxidation of strained σ bonds with peracids. Oxidation of the strained σ bonds of methylbicyclobutane 1-carboxylate with peracid is reported to be slow and to lead to polymer.[6] It is unclear, however, to what extent the ester functionality retards oxidation. Oxidation of the strained σ bonds of cyclopropenes to form, after $C_{1,3}$ bond rotation, the highly stabilized allylic cation **2a** could conceivably occur in competition with electrophilic addition to the π system. This possibility becomes especially important since we know that the rate of cyclopropene oxidations with peracid is more than a power of ten times slower than epoxidations of analogous cyclopentenes.[7] Whatever the oxidation mechanism, the reactivity of the π double bond is clearly not so great to preclude competitive reaction with the σ bonds of cyclopropenes.

As a result, we have studied the C-3 allylic substituent effects on oxidations of cyclopropenes **3a–d**. We judge that a rate-determining π oxidation process should produce small allylic substituent effects similar to that in the true epoxidation of C-3 substituted cyclopentenes, **4a–c**. Contrastingly, electrophilic cleavage of a cyclopropene strained



3a; $R_1 = R_2 = H$
b; $R_1 = H$; $R_2 = Me$
c; $R_1 = R_2 = Me$
d; $R_1 = H$; $R_2 = Ph$



4a; R = H
b; R = Me
c; R = Ph

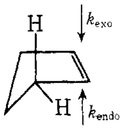
σ bond to yield intermediates such as **2a** or **2b** might proceed with a larger reaction constant, ρ.[8]

Results and Discussion

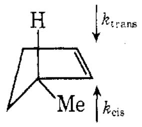
Cyclopropenes **3a**,[9] **3c**,[10] and **3d**[11] are known. Oxidation of **3a** with *m*-chloroperbenzoic acid (MCPBA) in CCl_4 at 0° gave a quantitative yield of 1,2-diphenyl-2-propen-1-one.[12] Similar treatment of **3c** afforded 1,2-diphenyl-3-methyl-2-buten-1-one.[13] The chalcone products from peracid treatment of **3d** have been reported.[5b] The air-sensitive cyclopropene **3b** was prepared by reaction of methylmagnesium iodide with diphenylcyclopropenyl fluoroborate at −78°. Oxidation of **3b** with MCPBA gave a quantitative yield of the known *Z* and *E* isomers of 1,2-diphenyl-2-buten-1-one[14] in a 75:25 ratio.

Cyclopentenes **4a**,[15] **4b**,[16] and **4c**[17] are also known. Reaction of cyclopentene **4a** with MCPBA at 0° in CCl_4 gave the expected epoxide[18] in quantitative yield. The peracid oxidation products from cyclopentene **4b** have been reported[19] and were obtained in a 64:36 (cis:trans[19]) ratio under our conditions. Reaction of MCPBA with cyclopentene **4c** gave a 75:25 (trans:cis) ratio of epoxides. Structure proof of the epoxides from **4c** was provided by $LiAlH_4$ reduction and comparison of the product alcohols with authentic samples (see Experimental Section). The rate constants reported in Table I were found to be second order throughout 40–70% conversion in peracid as well as independent of olefin and peracid concentration.

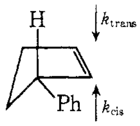
Analysis of the results from the substituted cyclopentenes **4a–c** provides a basis for evaluation of the cyclopropene kinetics. Of importance is an estimation of the polar effect of the 3-methyl and 3-phenyl groups in the absence of steric retardation. The analysis is complicated, however, by the finding[19] that epoxidation of **4b** occurs preferentially cis to the C-3 methyl substituent, but trans to the C-3 phenyl group in **4c**. The results are similar to those of Kauffman,[20] who found that 3-methyl-, 3-ethyl-, and 3-isopropylcyclopentene epoxidize preferentially cis whereas 3-*tert*-butylcyclopentene epoxidizes mainly trans to the substituent. Evidently, a moderate-sized substituent at C-3 maintains a pseudo-equatorial position[19] in which $k_{cis} > k_{trans}$. However, as the substituent size reaches *tert*-butyl or phenyl, the cis face of the π bond becomes so hindered by the pseudo-equatorial substituent that $k_{trans} > k_{cis}$. For the purposes of this study, we are interested in the partial rate factors due to the polar effect of the C-3 substituents which are devoid of the C-3 substituent steric factors. In the case of both **4b** and **4c**, these are the partial rate constant factors for trans epoxidation.



4a



4b



4c

Determination of k_{exo} (k_{trans}) for **4a** cannot be made experimentally, because, in part, the cyclopentene ring in **4a** may be essentially planar. If so, one-half of the observed rate for epoxidation of **4a** is an upper limit for a k_{exo} (k_{trans}) approach to a puckered cyclopentene such as **4b** and **4c**.

A simple linear free energy (LFE) analysis, however, can provide approximate values for the polar effects of the methyl and phenyl substituents in **4b** and **4c**, if certain assumptions are made. In particular, we assume that the steric substituent effects only operate with endo attack, but not with exo approach of peracid; see structures **4b** and **4c**. With this assumption and the partial rate factors for trans attack in **4b** and **4c**, the following two LFE equations can be written.

Table I
***m*-Chloroperbenzoic Acid Oxidation of Olefins 3 and 4 in CCl_4 at 0°**

Olefin	$10^3\ k_2$, $M^{-1}\ sec^{-1}$ [a]	Rel k_2
Cyclopropene		
3a, $R_1 = R_2 = H$	$3.4 \pm 0.1\ (9)^b$	(1.00)
b, $R_1 = H$; $R_2 = Me$	$1.45 \pm 0.02\ (2)^b$ $1.04 \pm 0.07\ (2)^c$	0.37
c, $R_1 = R_2 = Me$	$0.43 \pm 0.20\ (2)^b$ $0.38 \pm 0.02\ (2)^c$	0.12
d, $R_1 = H$; $R_2 = Ph$	$0.122 \pm 0.002\ (2)^c$	0.04
Cyclopentene		
4a, $R = H$	$9. \pm 0.2\ (3)^c$	(1.00)
b, $R = Me$	$10.6 \pm 0.4\ (2)^c$	1.16^d
c, $R = Ph$	$1.93 \pm 0.10\ (2)^c$	0.21

[a] Errors are standard deviations of independent runs with the indicated degrees of freedom. [b] Run competitively against 1,2-diphenylcyclobutene ($k_2 = 3.32 \pm 0.05 \times 10^{-3}\ M^{-1}\ sec^{-1}$, see ref 7), following the relative loss of both olefins by nmr. [c] Iodometric peracid titration. [d] Olefins **4a** and **4b** were also run competitively against each other, $k_{4b}/k_{4a} = 1.16 \pm 0.10$.

$$\log (k_{Me}/k_H)_{trans} = \rho\sigma_{Me}$$

$$\log (k_{Ph}/k_H)_{trans} = \rho\sigma_{Ph}$$

These two equations can be subtracted to give

$$\log (k_{Me}/k_{Ph})_{trans} = \rho(\sigma_{Me} - \sigma_{Ph})$$

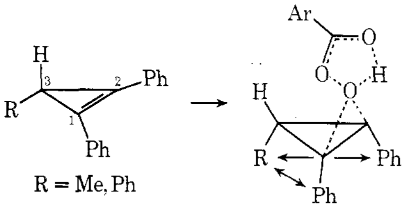
Partial rate factors for k_{Me} and k_{Ph} can be obtained from the data in Table I and the observed per cent trans epoxide from **4b** and **4c**. These values are k_{Me} (trans) = $3.82 \times 10^{-3}\ M^{-1}\ sec^{-1}$ and $k_{Ph} = 1.45 \times 10^{-3}\ M^{-1}\ sec^{-1}$. Substitution of these values into the above equation and using Taft polar substituent constants[21] gives $\rho = -1.34$. Values of k_{Me}/k_H and k_{Ph}/k_H can then be calculated as 1.4 and 0.52, respectively. In other words, the polar effect of a 3-methyl substituent is to increase the rate of epoxidation by 40% whereas a 3-phenyl substituent slows epoxidation by ~48%.

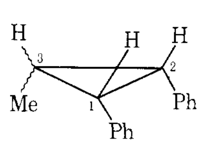
This is the first reported case in which an allylic methyl group accelerates the epoxidation of a *cyclic* olefin. Rickborn and Lwo[22] have shown that complicating steric and conformational effects result in a net lowering (6%) of the reactivity for 3-methylcyclohexene. The moderate accelerating effect of the 3-methyl substituent in cyclopentene **4b**, however, is similar to that observed in acyclic systems (≤20%).

The 3-phenyl substituent of cyclopentene **4c** lowers the partial rate constant for epoxidation by a factor of ~1.9. Once again, this observed polar effect is similar to the relative rate ratio of 2.2 for epoxidation of propene and allylbenzene, respectively, with peracetic acid in acetic acid solution at 25.8°.[24]

The rather small allylic substituent effects in cyclopentenes **4a–c** are contrasted by larger rate reducing effects in cyclopropenes **3a–d**. If the reaction involves π attack, part of the rate reduction may be due to a greater C-3 steric substituent effect in cyclopropenes **3b–d** relative to the cyclopentene series. In hydrogenation,[25] dimide reduction,[26] and in certain Diels–Alder additions[25] of cyclopropenes, 3-methyl or 3-phenyl substituents direct the stereochemical course of the reactions almost exclusively trans (≥90%).

If the rate constant for **3a** is divided by 2 to give the rate constant per face of the cyclopropene ring, the relative rate ratios for **3a**:**3b**:**3d** are 1.0:0.74:0.08 for H, Me, and Ph C-3 substituents, respectively. The rate-enhancing polar effect of an allylic methyl group in cyclopentene **4b** is not found in cyclopropene **3b**. Rather, a 26% rate retardation was found. This rate retardation is not at all in line with an epoxidation type of transition state, unless the partial eclipsing of the C-3 methyl with the C-1 and/or C-2 phenyl substituents sufficiently raises the transition state energy for trans attack of peracid. The full effect of such an eclipsing interaction could be estimated if the relative stabilities of the isomeric *cis*-1,2-diphenyl-3-methylcyclopropanes were known. Unfortunately, the data are not available. The full effect can be expected to be moderately large, however, since the $\Delta\Delta H_f$ between *cis*- and *trans*-1,2-dimethylcyclopropane is -1.1 kcal/mol.[27] Similarly, the equilibrium constant for *cis*- and *trans*-1,2-diphenylcyclopropane is ~ 70 at 0°.[28] These values suggest that a moderate rate reduction could occur owing to the pictured developing eclipsing interaction. An early transition state for epoxidation would, of course, produce a diminished effect.





It is much more difficult to estimate the effect of C-3 cyclopropene substituents on the electrophilic oxidation of the $C_{1,3}$ or $C_{2,3}$ σ bond. The best model available in the literature is the electrophilic cleavage of substituted cyclopropanes. To date, however, there is no kinetic or product information on peracid cleavage of cyclopropane rings. Much of the work has involved cleavage by H^+ or Hg^{2+} salts.[8] In general, the effect of a methyl substituent is to increase the rate of electrophilic cleavage. A phenyl substituent, on the other hand, deactivates a cyclopropane ring to attack by H^+, even though cleavage still occurs in the expected fashion to produce products derived from an intermediate benzylic cation.[29] In a Hammett σ–ρ study of arylated cyclopropanes, mercuric acetate also adds to produce an incipient benzylic cation, $\rho = -3.2$ *vs.* σ^+.[30]

As a result, the small rate constant for oxidation of cyclopropene **3d** with an allylic phenyl group is seemingly consistent with either π or σ attack. The slower rate of oxidation for **3b** with one allylic methyl was unexpected, but by hindsight is perhaps most consistent with a π-epoxidation process. The electrophilic cleavage of a cyclopropene σ bond would probably be expected to increase with a C-3 methyl substituent, contrary to what was observed. It is pertinent to note, however, that the relative rates of **3a**:**3b**:**3c** are very closely multiplicative. This trend implies a structural symmetry for the transition state in which the effect of the first allylic methyl (**3b**) on the rate in identical to the effect of the second methyl substituent (**3c**). A σ attack of peracid in the plane of the cyclopropene ring fits this pattern perfectly and cannot be dismissed.

Experimental Section

Olefins. 1,2-Diphenylcyclopropene (**3a**)[9] was prepared by $NaBH_4$ reduction of diphenylcyclopropenyl fluoroborate as reported. 1,2-Diphenyl-3,3-dimethylcyclopropene (**3c**)[10] was prepared by the reaction of benzal chloride and phenylpropyne with methyllithium as reported. Triphenylcyclopropene (**3d**)[11] was prepared by reaction of $LiAlH_4$ with triphenylcyclopropenyl bromide as reported. Cyclopentene (**4a**)[15] was prepared by dehydration of cyclopentanol, and 3-phenylcyclopentene (**4c**) was prepared by the reaction of phenylmagnesium bromide with 3-chlorocyclopentene. All olefins were purified (99%) by recrystallization from methanol or by vpc (0.25 in. × 12 ft 15% Carbowax 20M, 4% KOH column, 40–140°) prior to use.

1,2-Diphenyl-3-methylcyclopropene (3b). A 1-ml portion of a 1 *M* solution of MeMgI in diethyl ether was slowly added to a slurry of 50 mg (0.20 mmol) of diphenylcyclopropenyl fluoroborate in 4.5 ml of diethyl ether under N_2 at $-78°$. The resulting mixture was magnetically stirred and slowly (3 hr) warmed to room temperature. At the end of this time a greenish-brown oily precipitate could be observed.

The mixture was then added to 10 ml of ether and 10 ml of water (0°), and the ethereal layer was separated and dried over anhydrous K_2CO_3. The solvent was removed on a rotory evaporator and the residue was isolated as a colorless oil: ir (CCl_4) 1820 cm^{-1}; nmr (CCl_4) δ 7.70–7.10 (m, 10), 2.12 (q, J = 4.5 Hz, 1), 1.35 (d, J = 4.5 Hz, 3); mass spectrum (70 eV) m/e (rel intensity) 206 (60, molecular ion), 191 (100).

After the oil had stood under air for *ca.* 1 hr, the nmr for cyclopropene **3b** contained small absorptions at δ 1.72 and 1.83 which could be attributed to the presence of 1,2-diphenyl-2-buten-1-one. The mass spectrum of this material showed new peaks at m/e 222 and 238 which are presumably due to incorporation of oxygen into the molecule.

Cyclopropene **3b** which was used in kinetic runs was freshly prepared and purified (silica gel chromatography, elution with hexanes) before use.

Olefins with *m*-Chloroperbenzoic Acid in CCl_4 at 0°. 1,2-Diphenylcyclopropene (**3a**) gave a quantitative yield of 1,2-diphenyl-2-propen-1-one[12] when treated with MCPBA. 1,2-Diphenyl-3-methylcyclopropene (**3b**) gave a quantitative yield of 1,2-diphenyl-2-buten-1-one[14] in a 75:25 (*Z*:*E*) isomeric ratio (by nmr) when treated with less than 1 equiv of MCPBA. 1,2-Diphenyl-3,3-methylcyclopropene (**3c**) gave quantitative yield of 1,2-diphenyl-3-methyl-2-buten-1-one[13] when treated with less than 1 equiv of MCPBA. 1,2,3-Triphenylcyclopropene (**3d**) has been shown[5b] to give an 80:20 (cis:trans) mixture of α-phenylchalcones in quantitative yield when treated with less than 1 equiv of MCPBA. Consistent results were obtained in this study. The spectra of all reaction products were identical with those of authentic samples.

When the cyclopropenes **3a–d** were treated with an excess of MCPBA, oxidation products of the enones mentioned above were observed. In order to eliminate this problem all kinetic runs were performed with the initial olefin concentration greater than the initial peracid concentration.

Cyclopentene (**4a**) gave a quantitative yield of epoxide when treated with MCPBA. 3-Methylcyclopentene (**4b**)[16] gave a quantitative yield of a 64:36 (cis:trans) mixture (by vpc) of epoxides[19] when treated with MCPBA. 3-Phenylcyclopentene (**4c**) gave a quantitative yield of a 75:25 (trans:cis) mixture of epoxides when treated with MCPBA (see below).

In all cases, the oxidation products from the olefins mentioned above were compared with authentic material or had spectral properties which were identical with those reported in the literature.

3-Phenylcyclopentene (4c) with *m*-Chloroperbenzoic Acid in CCl_4 at 0°. A solution of 310 mg (2.10 mmol) of 99+% pure 3-phenylcyclopentene (**4c**) was added to a mixture of 360 mg (2.10 mmol) of *m*-chloroperbenzoic acid in 5 ml of CCl_4 at 0°. The reaction mixture was stored at 0° for 36 hr and the precipitate (presumably *m*-chlorobenzoic acid) was filtered from the solution at that time. The solution was washed with three 3-ml portions of saturated aqueous $NaHCO_3$ and one 3-ml portion of saturated aqueous NaCl, and finally dried over anhydrous K_2CO_3. This solution was concentrated on a rotary evaporator and the products were isolated by vpc (0.25 in. × 12 ft 15% Carbowax 20M, 4% KOH column, 138–140°).

In order of elution, the vpc (thermal detector) trace showed only two closely spaced peaks with an area ratio of 2.98:1.00. These were the trans epoxide and cis epoxide, respectively, of 3-phenylcyclopentene.

trans-3-Phenylcyclopentene epoxide was isolated by vpc and analyzed: ir (CCl_4) transparent 1750–1600 cm^{-1}; nmr (CCl_4) δ 7.20 (broad s, 5), 3.62–3.51 (m, 1), 3.51–3.30 (m, 2), 2.20–1.50 (m, 4).

cis-3-Phenylcyclopentene epoxide was also isolated and analyzed: ir (CCl_4) transparent 1750-1600 cm^{-1}; nmr (CCl_4) δ 7.30 (broad s, 5), 3.51–3.20 (m, 2), 3.20–2.80 (m, 1), 2.30–1.40 (m, 4).

The combined nmr spectra of the cis and trans epoxides give a composite spectrum which is superimposable with the nmr spectrum of the worked-up sample of oxidation products from 3-phenylcyclopentene. For assignments of cis and trans structures to the epoxides see the following experiment.

***trans*-3-Phenylcyclopentene Epoxide with LiAlH$_4$.**[17] A mixture of 40 mg (0.25 mmol) of 3-phenylcyclopentene epoxides (*ca.* 80:20, trans:cis by vpc) was added to *ca.* 30 mg (0.8 mmol) of $LiAlH_4$ in 3 ml of anhydrous ether at room temperature and under nitrogen. The mixture was magnetically stirred at room temperature for 12 hr and then added to 1 ml of saturated aqueous NaOH. The ethereal solution was filtered from the solid precipitate, which was then dissolved in 2 ml of 15% aqueous HCl and extracted with ether, and the ethereal solutions were combined.

The ethereal solution was then washed with 5 ml of saturated aqueous NaCl and dried over anhydrous Na_2SO_4. After concentration on a rotary evaporator, the residual 40 mg (98%) was shown by vpc (0.25 in. × 5 ft 5% Carbowax 20M column, 160°) to contain (area per cent in order of elution) *ca.* 5–10% starting epoxide mixture, 23% *cis*-2-phenylcyclopentanol, 62% *trans*-2-phenylcyclopentanol, and two small peaks (5% each) of presumably *cis*- and *trans*-3-phenylcyclopentanol. These products have been previously reported[17] but the relative yields were not given.

cis-2-Phenylcyclopentanol was isolated and analyzed: nmr (CCl_4) δ 7.23 (s, 5), 4.15–4.05 (m, 1), 3.05–2.70 (m, 1), 2.10–1.60 (m, 6), 0.86 (s, 1) [lit.[31] partial nmr (solvent not specified) δ 4.0 (1), 2.75 (1)].

trans-2-Phenylcyclopentanol was also isolated and analyzed: nmr (CCl_4) δ 7.15 (s, 5), 4.05–3.85 (m, 1) 3.00–2.70 (m, 1), 2.20–1.40 (m, 7) [lit.[31] partial nmr (solvent not specified) 3.90 (1), 2.75 (1)].

A sample of 2-phenylcyclopentanone was treated with a slight molar excess of $LiAlH_4$ as described to give a 60:40 (vpc thermal detector area ratio) mixture of *trans*- and *cis*-2-phenylcyclopentanol (lit.[17] 59:41 mixture of trans:cis by nmr). The nmr spectra and vpc retention times (coinjection) of the vpc-purified *trans*- and *cis*-2-phenylcyclopentanol from this procedure are identical with those obtained from the reaction of $LiAlH_4$ with 3-phenylcyclopentene epoxide (80:20, trans:cis).

Kinetics.[32] Reaction solutions containing known amounts of olefin and 99% *m*-chloroperbenzoic acid (Aldrich material was purified by extraction with a phosphate buffer)[33] were prepared in CCl_4 (Mallinkrodt Spectrar grade) at 0° with magnetic stirring. In all cases the olefin concentration was greater than the peracid concentration.

A short time (1–2 min) later, a 1.0-ml aliquot was withdrawn and quenched in 0.5 ml of HOAc and 1.0 ml of 10% aqueous KI. During the quenching of this sample (time zero), a stopwatch was started. The liberated iodine was titrated with standardized (KIO_3) thiosulfate stock solution. Subsequent aliquots were withdrawn and analyzed at recorded times.

The difference in the prepared and time zero peracid concentrations was used to correct the prepared olefin concentration to its time zero concentration.

All reactions were analyzed to 40–70% loss of peracid. The data were then analyzed with the normal second-order kinetics equation. The method showed good agreement for all rate constants regardless of the reactant concentration used. Use of the first-order kinetics equation gave straight lines whose slopes varied with varying reactant concentration.[34]

Acknowledgment. We thank the National Science Foundation and the Merck Chemical Company Foundation for financial support.

Registry No.—**3a**, 24168-52-3; **3b**, 51425-87-7; **3c**, 50555-61-8; **3d**, 16510-49-9; **4a**, 142-29-0; **4b**, 1120-62-3; **4c**, 37689-22-8; *m*-chloroperbenzoic acid, 937-14-4; 3-phenylcyclopentene epoxide, 20383-31-7; *cis*-2-phenylcyclopentanol, 2362-73-4; *trans*-2-phenylcyclopentanol, 42086-64-6.

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