Influence of Strain on Chemical Reactivity. Relative Reactivity of Torsionally Distorted Double Bonds in MCPBA Epoxidations

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Abstract: The second-order reaction rates were measured for the MCPBA epoxidation in CH_2Cl_2 for a series of cyclic olefins including bridgehead olefins and *trans*-cycloalkenes. As expected, strained bridgehead alkenes and *trans*-cycloalkenes showed faster reaction rates than nonstrained *cis*-cycloalkenes. The MM-2 steric energies of alkenes, alkanes, and their corresponding epoxides were calculated to evaluate the strain energy released in each reaction (ΔSE). Plots of log k_{rel} vs olefin strain did not show a good correlation. However, the plot of log k_{rel} vs ΔSE (which is defined as the steric energy difference between olefin and the corresponding epoxide) showed a good correlation for each set of di- and trisubstituted olefins. This result suggests that ΔSE directly reflects strain energy relief in the transition state. From the slope for the plot log k_{rel} vs ΔSE, it was thought that approximately 42% of strain (ΔSE) was released in the transition state for the MCPBA epoxidation. Also, trialkyl-subtituted alkenes were found to be about 50 times more reactive than dialkyl-substituted alkenes in cases where the strain energy relief (ΔSE) is the same. The reaction rate is also plotted versus ionization potential of the olefin, assuming that the major orbital interaction lies between the LUMO of the peracid and the HOMO of the olefin. Although, in some cases, a rough correlation of the reaction rate with the ionization potential of the olefin exists, the frontier orbital interaction is not viewed as the dominant factor since conjugated alkenes, which have higher HOMO energies than simple olefins, are not more reactive in MCPBA epoxidation.

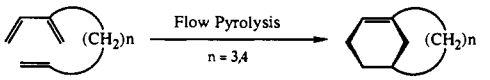
Introduction

The relationship between strain and chemical reactivity has been an important theme throughout chemistry. Strained organic molecules with bond angles and bond distances far beyond normal, strain-free values continue to challenge the ingenuity and creativity of synthetic chemists.[1] Strain often manifests itself by increased chemical reactivity.[2] Strain and reactivity also occupy a pivotal role in biological chemistry. The classical explanation for enzyme activity involved subjecting the substrate molecule to a distortion (stress), the energy for which arose from the binding energy in formation of the enzyme–substrate complex.[3] The distorted enzyme-bound substrate molecule was proposed to be more reactive toward attack by nucleophiles or electrophiles. Although this theory has undergone a number of refinements, the concept of strain and reactivity is still pivotal in biological chemistry.[4]

Despite the importance of strain in organic chemistry, its quantitative relationship to chemical reactivity is only beginning to be understood.[5,6] The present study was designed to quantitatively evaluate the kinetic consequences of torsional distortions in carbon–carbon double bonds. Several isosteric series of strained double bonds have been prepared, and their rates of epoxidation have been measured. The kinetic data have been examined for correlations between reaction rate and structural/thermodynamic properties of reactants and products.

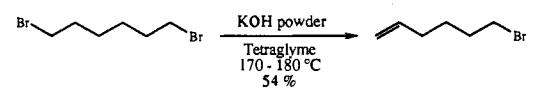
Results

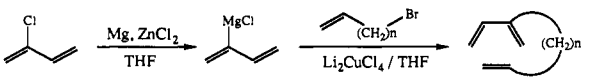
Synthesis. Bridgehead alkenes bicyclo[3.3.1]non-1-ene (**1**) and bicyclo[4.3.1]dec-1(9)-ene (**2**) were synthesized by type 2 intramolecular Diels–Alder reactions from corresponding trienes **3** and **4** using an atmospheric flow pyrolysis method.[7] Trienes **3** and



3 (n = 3)
4 (n = 4)

4 were synthesized from the chloroprene Grignard reagent[8,9] and the corresponding bromoalkenes using a catalytic amount of Li_2CuCl_4. 6-Bromo-1-hexene was made from 1,6-dibromohexane by distillation of 1,6-dibromohexane over KOH/tetraglyme for 3–4 h.[10]

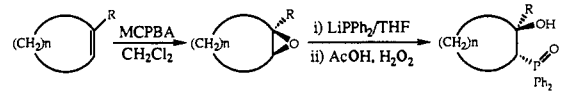




n = 3 53 % 3

n = 4 72 % 4

trans-Cycloalkenes were synthesized by olefin inversion.[11] The reactions involve β-hydroxy phosphine oxides **11**, **12**, and **13**, which were made from the reaction between lithium diphenylphosphide and *cis*-epoxides (**8**, **9**, and **10**) followed by oxidation. Reaction conditions were modified from the literature procedure.[12] The resulting *trans*-cycloalkenes were not contaminated by cis olefins (>99.9% pure by GC). *cis*-Cyclononene (**7**) was synthesized by



n=6, R=H 5 8 11 77%

n=6, R=Me 6 9 12 62%

n=7, R=H 7 10 13 60%

the literature procedure.[13] Dibromocarbene addition with phase-transfer catalyst[14] (benzyltriethylammonium chloride) and

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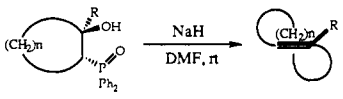
Table I. Bimolecular Rate Constants and Activation Parameters for the Epoxidation of Olefins with MCPBA in CH_2Cl_2; MM-2 Minimized Energies of Olefin and Corresponding Alkane and Epoxide

olefin	k (0 °C)[a] (L/mol·s)	k_{rel} (0 °C)[b]	E_a (kcal/mol)	$\Delta S^{\ddagger}$[c] (eu)	steric energy (kcal/mol) olefin	alkane	epoxide	OS[d]	ΔSE[e]
17	$(2.29 \pm 0.70) \times 10^{-2}$	1	10.9	−28	4.13	6.54	17.27	−2.41	−13.14
5	$(4.62 \pm 0.16) \times 10^{-2}$	4.04	9.9	−30	13.38	19.38	23.70	−6.00	−10.32
7	2.85×10^{-2}	2.48	10.3	−30	17.74	23.36	27.63	−5.62	−9.89
18	$(3.39 \pm 0.25) \times 10^{-2}$	2.96	10.7	−28	25.43	23.08	35.71	2.35	−10.28
16	$(7.26 \pm 0.23) \times 10^{-1}$	6.34×10^{1}	9.4	−27	21.54	23.36	28.38	−2.02	−6.84
14	5.20 ± 0.12	4.54×10^{2}	7.6	−29	23.17	19.38	27.86	3.79	−4.69
19	5.37×10^{-1}	2.34×10^{1}	8.6	−30	7.26	11.54	19.72	−4.28	−12.46
20	$(2.76 \pm 0.13) \times 10^{-1}$	1.21×10^{1}	9.0	−30	3.89	6.88	18.14	−2.99	−14.25
21	$(6.5 \pm 3.8) \times 10^{-1}$	2.9×10^{1}	8.4	−30	7.56	8.53	20.51	−0.97	−12.95
6	$(8.58 \pm 0.37) \times 10^{-1}$	7.50×10^{1}	7.6	−33	13.50	20.26	25.13	−6.76	−11.63
15	$(4.74 \pm 0.91) \times 10^{1}$	4.10×10^{3}	5.6	−32	25.06	20.26	31.90	4.80	−6.84
2	3.02 ± 0.01	2.64×10^{2}	7.6	−30	24.70	24.16	34.34	0.54	−9.64
1	$(1.02 \pm 0.15) \times 10^{2}$	8.90×10^{3}	5.8	−30	29.19	18.24	34.66	10.95	−5.47

[a] Errors are 95% confidence limit. [b] Statistically corrected. [c] Calculated at 0 °C. [d] OS = steric energy of olefin − steric energy of alkane (kcal/mol). [e] ΔSE = steric energy of olefin − steric energy of epoxide (kcal/mol).

1,2-cyclononadiene formation using methyllithium[15] resulted in improved yields over the original procedures.



n=6, R=H	11	14	58%
n=6, R=Me	12	15	54%
n=7, R=H	13	16	89%

Kinetic Studies. Second-order rate constants for the MCPBA epoxidations in CH_2Cl_2 were measured directly by GC. Concentrations of olefins (or epoxides) were obtained by quenching aliquots with a 10% sodium bisulfite solution and analyzing the resulting solutions by GC equipped with FID. The relative intensities of olefin (or epoxide) to the proper internal reference gave the concentrations. Identical concentrations of reactants were used to simplify the kinetics. In this case, the kinetic equation reduces to the following:

$$\text{rate} = k_2[\text{olefin}][\text{MCPBA}]$$

$$1/[\text{olefin}]_t = k_2 t + 1/[\text{olefin}]_0$$

Second-order rate constants (k_2) were obtained from plots of 1/[olefin] vs time (s). Five to ten data points spanning about 3–5 half-lives were used for the calculation. MCPBA of 99% purity[16] was used for the kinetic experiments, and the concentration of MCPBA in CH_2Cl_2 was checked by iodometry.

Extreme care was taken in handling the strained alkenes. Bridgehead alkenes and *trans*-cycloalkenes decomposed faster in CH_2Cl_2 solution than when neat or in nonpolar solvents. Bicyclo[3.3.1]non-1-ene (**1**) was the most reactive olefin. It decomposed to the corresponding epoxide upon contact with air, especially in CH_2Cl_2 solution. The stock solution, therefore, was made just before the kinetic experiment using freshly distilled CH_2Cl_2 under a nitrogen atmosphere. In the kinetic experiments with 1-methyl-*trans*-cyclooctene (**15**), trans-cis isomerization of the olefin was detected after quenching the aliquots with a 10% sodium bisulfite solution. The concentrations of olefin, in this case, were calculated with the total integrations of cis and trans isomers. No cis olefin was found in the reaction mixture before quenching.

All of the olefins in the MCPBA epoxidation in CH_2Cl_2 obeyed second-order kinetics, which could be evaluated by the linear correlation of 1/[olefin] vs time. The second-order rates at 0 °C were obtained by the average of more than three runs. Activation parameters were calculated by an Arrhenius plot. The activation parameters may have considerable uncertainty because they were calculated at only two (or three) different temperatures. The reliability of the values, however, can be evaluated by the literature values. For example, the rate constant for epoxidation of norbornene by MCPBA at 25 °C in CH_2Cl_2 was reported to be 0.16 mol^{-1} s^{-1}.[17] This should be compared with 0.177 mol^{-1} s^{-1} at 25 °C with MCPBA/CH_2Cl_2 in the present work. A report of the E_a = 10.4 kcal/mol and $\Delta S^{\ddagger}$ = −32.7 eu in the perbenzoic acid epoxidation of cyclohexene in CH_2Cl_2[18] is also in good agreement with E_a = 10.9 kcal/mol and $\Delta S^{\ddagger}$ = −27.8 eu with MCPBA/CH_2Cl_2 in the present work. Second-order rate constants of MCPBA epoxidations at 0 °C in CH_2Cl_2 and the calculated activation parameters are summarized in Table I.

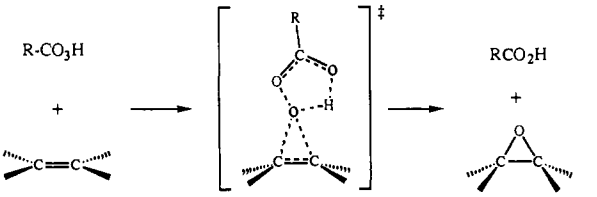
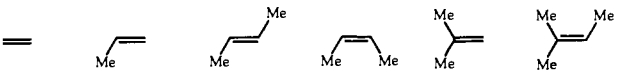


Figure 1. Bartlett's epoxidation mechanism.

Chart I. Relative Rates of Epoxidation with Peracetic Acid at 25.8 °C[20]



0.045	1.0	20	22	22	230

When comparing the reactivity of cyclic olefins, statistical factors should be considered. Symmetric or almost symmetric olefins like cyclohexene and cyclopentene have equal probability for attack on both sides of the double bond. However, bridgehead olefins and *trans*-cycloalkenes have only one possible reaction face. The same situation is found in medium-ring *trans*-cycloalkenes.[19] Norbornene also has a nonequivalent face; only exo epoxide is formed. The relative rates in Table I are statistically corrected values.

Discussion

Epoxidation of olefins with organic peracids is second order overall and first order in olefin and peracid.[20] A large amount of data clearly show that electron-donating groups on the olefin increase the reaction rate and electron-withdrawing groups on the peracid increase the rate.[20] The reaction is quite insensitive to the steric environment. For example, disubstituted olefins show almost the same reaction rate regardless of the substitution pattern (Chart I).

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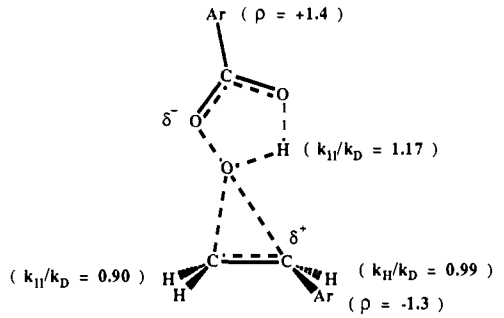

Figure 2. Transition state of peracid epoxidation.[25]

Although several mechanisms have been proposed,[21] Bartlett's cyclic planar concerted mechanism[22] (Figure 1) is generally accepted as being able to account for the experimental observations. Evidence for Bartlett's mechanism is as follows:[23] (1) the reaction is second order; (2) the reaction readily takes place even in nonpolar solvents; (3) the addition is stereospecific; and (4) the reaction is insensitive to steric effects.

A key observation is the insensitivity to steric effects. For example, bulky ortho-substituted perbenzoic acids or perisubstituted pernaphthoic acids failed to distinguish cis- and trans-disubstituted olefins, and only huge C-shaped peracids showed moderate selectivity (k_{cis}/k_{trans} = 3–8 in 2-octene).[24]

A Hammett σ–ρ study and isotope effects provide information about the transition state of peracid epoxidations (Figure 2).[25] These results indicate that partial negative charge develops in the peracid (ρ = +1.4) and a partial positive charge develops in the olefin (ρ = −1.3). A small primary isotope effect in the peracid hydrogen (k_H/k_D = 1.17) shows that O–H bond breaking does not take place to a significant extent in the transition state (or, less likely, the O–H bond is completely broken). Secondary isotope effects in the olefinic hydrogens (k_H/k_D = 0.90 and 0.99) show that the sp² carbons in the olefin are partly rehybridized to sp³. *It is expected that, in strained bridgehead olefins, this rehybridization would result in partial strain relief in the transition state and this strain energy relieving process would increase the reaction rate.*

In relatively unstrained *cis*-cycloalkenes, trisubstituted alkenes react more than 10 times faster than disubstituted alkenes with MCPBA. A similar trend is found in the *trans*-cyclooctene series in which the reaction rate of 1-methyl-*trans*-cyclooctene (**15**) is 10 times faster than *trans*-cyclooctene (**14**). This result reflects the electrophilic nature of peracid reactions with the double bond. As expected, strained olefins such as bridgehead alkenes or *trans*-cycloalkenes show much faster reaction rates than the corresponding *cis*-cycloalkenes. When the disubstituted olefins are compared, the relative reactivities of cyclohexene (**17**), *trans*-cyclononene (**16**), and trans-cyclooctene (**14**) are 1:63:450. In this series, apparently the most strained *trans*-cyclooctene has the highest reaction rate and the order is quite straightforward. When the trisubstituted olefins are compared, the relative reactivities of 1-methylcyclohexene (**2**), bicyclo[4.3.1]dec-1(9)-ene (**2**), 1-methyl-*trans*-cyclooctene (**15**), and bicyclo[3.3.1]non-1-ene (**1**) are 1:22:360:740. This trend is similar to that in the disubstituted series. Bicyclo[3.3.1]non-1-ene (**1**) contains *trans*-cyclooctene and bicyclo[4.3.1]dec-1(9)-ene (**2**) contains *trans*-cyclononene. The *trans*-cyclooctene system is more strained and is expected to react faster. With trisubstituted olefins containing the *trans*-cyclooctene system, the bridgehead olefin bicyclo-[3.3.1]non-1-ene (**1**) is more reactive than 1-methyl-*trans*-cyclooctene (**15**). In this comparison it is obvious that the reaction rate also depends on the strain energy incorporated in the olefin.

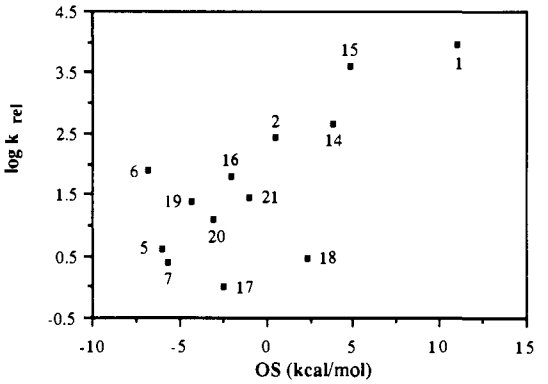

Figure 3. MCPBA epoxidation rate vs olefin strain.

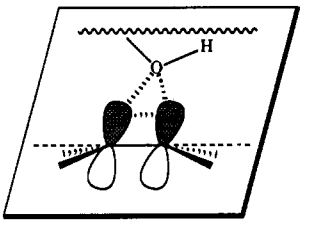

Figure 4. Transition state of peracid epoxidation.

Analysis of the activation parameters gives information about the transition state. The activation energies vary uniformly. That is, as the reaction rate increases, the activation energy goes down. However, the entropy of activation ($\Delta S^{\ddagger}$) shows little variation. Disubstituted olefins have a slightly higher $\Delta S^{\ddagger}$, but all olefins have quite similar values regardless of whether they are strained or not. $\Delta S^{\ddagger}$ values range from −27 to −33 eu. These values are similar to those for concerted reactions such as Diels–Alder cycloadditions (−30 to −40 eu)[26] and 1,3-dipolar cycloadditions (−22 to −39 eu).[27] We may conclude that the transition-state structure is similar for all of the olefins. The trends in the reaction rate, which are enthalpic in origin, must be closely tied to the relief of strain energy in the transition state. The exact relationships between the reaction rate and strain energy can be established by estimating the relief of strain energy in the transition state.

In order to approach this problem, force field calculations (MM-2)[28] were performed; the results are summarized in Table I. MM-2 minimized energies were obtained by calculating all possible structures and selecting the global minima. Steric energy is defined as the thermally averaged energy relative to a hypothetical strainless molecule with the same constitution.[28] Thus, the steric energy represents rough thermodynamic stability. The lowest is in cyclohexene (4.00 kcal/mol) and the highest is in bicyclo[3.3.1]non-1-ene (29.20 kcal/mol). Although the steric energy in force field calculations reflects the strain in a molecule, steric energy itself cannot explain the strain involved in a double bond because the steric energy reflects the energy of the entire molecule and not the double bond itself. For this reason, Schleyer proposed determining the stability of an olefin using the concept of olefin strain (OS), which is defined as the difference between the strain energy (steric energy) of an olefin and that of its parent hydrocarbon (alkane).[29] Thus, OS values show relative thermodynamic stabilities of olefins.

The plot of log k_{rel} vs olefin strain is shown in Figure 3. Although olefins having higher OS values have higher rates of reaction, the correlation is very poor, and one observes that there

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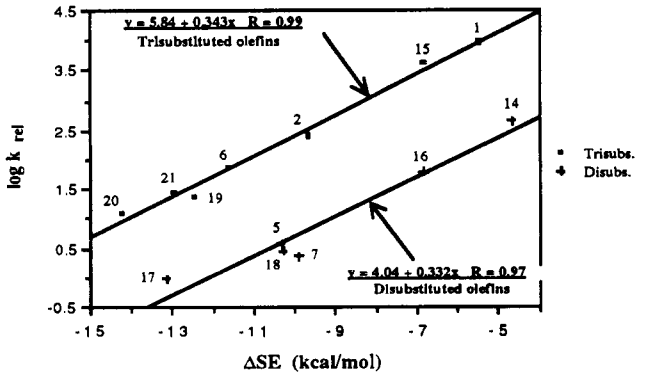

Figure 5. Correlation between epoxidation rate and strain energy relief difference between olefin and epoxide (see Table I).

is no direct relationship between the rate and olefin strain in the MCPBA epoxidation. This is quite clear if we think about the transition-state geometry. As already discussed, the transition state of peracid epoxidation has a fixed geometry with an in-plane relationship between the attacking oxygen and the π-system of the double bond, with the sp^2 carbons in the olefin partly rehybridized to sp^3 (Figure 4). The calculation of olefin strain, however, is performed using the most stable conformer of the olefin and its parent hydrocarbon. In many cases, the ground-state conformation of the parent hydrocarbon is different from the transition state of the epoxidation of the alkene.

In order to establish the strain energy associated with the transition state, the steric energy of the product epoxide was calculated and compared with the steric energy of the olefin. Because the transition state partly resembles the product epoxide, the strain energy relief in the transition state would be a part of the total strain energy relief in the reaction from olefin to epoxide. Moreover, the structure of product epoxide contains important structural information regarding the transition state that olefin strain could not give, namely, the in-plane relationship between the attacking oxygen and the π-system of the double bond (see Figure 4). The epoxide automatically has an in-plane relationship by virtue of the oxirane ring system. Thus, ΔSE, *which is defined here as the difference between the steric energy of the olefin and that of the corresponding epoxide*, is calculated in an effort to find the reactivity vs strain energy relationship (Table I). The validity of this approach can be evaluated from the correlation between log k_{rel} vs ΔSE shown in Figure 5.

In Figure 5, two separate correlations emerge: one for trisubstituted olefins and one for disubstituted olefins. Both correlate separately in the plot of log k_{rel} vs ΔSE. The slopes of the correlation lines are 0.343 (trisubstituted olefins) and 0.332 (disubstituted olefins), respectively, and the difference between intercepts of the two correlation lines is 1.7. Similar slopes between the two correlation lines indicate that the transition states in the MCPBA epoxidation of disubstituted and trisubstituted olefins are very similar. This is so because similar proportions of strain energies are relieved in the transition state. If disubstituted and trisubstituted olefins had different transition-state geometries, the strain energy relief in the two transition states would be different; this would result in different slopes in the correlation between plots of log k_{rel} vs ΔSE. The slope (0.34) of the plot of log k_{rel} vs ΔSE represents the efficiency of strain relief to the reaction rate. Thus, 1 kcal/mol relief of strain energy from an olefin to the corresponding epoxide results in a 2.2-fold increase in reaction rate in the MCPBA epoxidation ($10^{0.34} = 2.2$) or a 0.42 kcal/mol decrease in $\Delta G^{\ddagger}$ ($\Delta\Delta G^{\ddagger} = RT \ln (10^{0.34}) = 0.42$ kcal/mol). Therefore, it can be said that approximately 42% of the ΔSE is released in the transition state for the MCPBA epoxidation. The difference between the intercepts of the two correlation lines (Δ log k = 1.7) shows that an additional alkyl substituent on the double bond increases the reaction rate 50 times ($=10^{1.7}$), assuming the ΔSEs are the same. This 50-fold increase in rate is higher than the observed rate increase of 10–20 in the same series of di- and trisubstituted olefins. The reason for this difference could

Table II. Ionization Potentials for the Olefins

olefin	log k_{rel}	ΔSE′ (kcal/mol)[a]	IP (eV)	ref
cyclohexene (**17**)	0	0	9.12	33
cyclooctene (**5**)	0.606	2.82	8.98	33
norbornene (**18**)	0.471	2.86	8.97	34
trans-cyclooctene (**14**)	2.657	8.45	8.69	35
trans-2-*cis*-4-hexadiene (**22**)	−0.33[b]	3.51	8.25	36
1,4-diphenylbutadiene (**23**)	0.36[b]	4.23	7.55	37
1-methylcyclopentane (**19**)	1.369	1.79	8.6	38
1-methylcyclohexene (**20**)	1.083	0	8.7	39
bicyclo[3.3.1]non-1-ene (**1**)	3.950	8.78	8.35	39

[a] ΔSE relative to cyclohexene and 1-methylcyclohexene for each di- and trisubstituted alkenes. [b] Extrapolated from the data at 25 °C.[17]

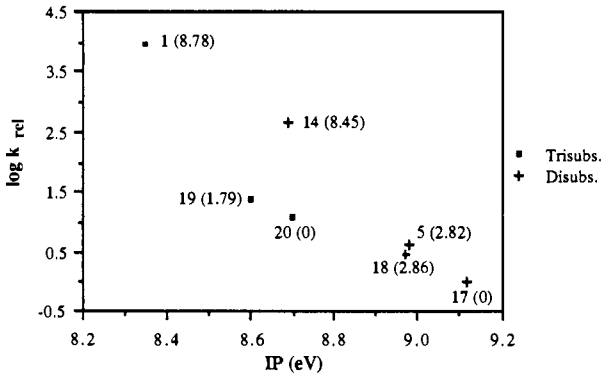

Figure 6. Plot between log k_{rel} and ionization potential. Numbers identify the alkenes of Table II. Numbers in parentheses are ΔSEs.

be that the additional alkyl group in the trisubstituted olefin produces more steric hindrance (back strain) than the disubstituted olefin in the partially rehybridized (sp^3-like) transition state compared to the reactant olefin of sp^2 hybridization. Peracid epoxidation is an electrophilic addition to the double bond. The major frontier orbital interaction is between the HOMO of the olefin and the LUMO of the peracid. Because the LUMO energy is fixed in MCPBA epoxidations, the reactivity may depend on the HOMO energies of the reacting olefins. Using Koopman's theorem,[30] the ionization energy is equal to the orbital energy ($IP_j = -e_j$), and the first ionization band in photoelectron spectrum may be taken as the HOMO energy. In the case of olefins, the lowest ionization energy is the π-orbital; thus, the HOMO energy can be obtained from the first ionization band of the photoelectron spectrum.[31,32] In the olefins used in this work, HOMO energies range from −8.35 eV in bicyclo[3.3.1]non-1-ene to −9.12 eV in cyclohexene. Available ionization potentials of olefins are listed in Table II.

The plot of log k_{rel} vs ionization potential is shown in Figure 6. One observes a rough correlation between log k_{rel} and ionization potential. However, careful examination with regard to the relief of strain energy reveals that the higher reactivities in the strained olefins such as bicyclo[3.3.1]non-1-ene (**1**) and *trans*-cyclooctene (**14**) are accounted for by relief of strain as already shown in Figure 5.

It may be possible that there is a correlation between log k_{rel} and ionization potential if one compensates for the relief of strain. However, it was found that the MCPBA reaction rates of dienes,

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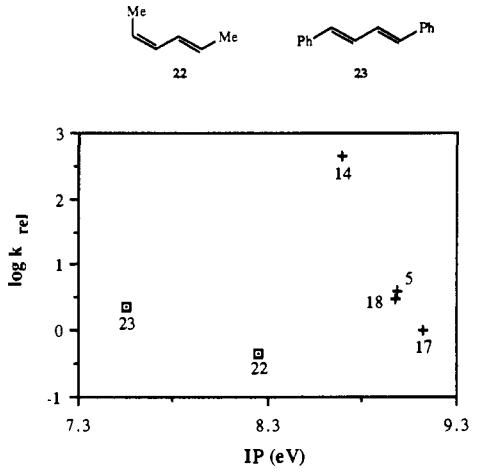

Figure 7. Plot of log k_{rel} vs ionization potential for disubstituted olefins. Numbers identify the alkenes of Table II.

which have higher HOMO energies than monoenes, showed similar reactivities to the alkenes containing the same number of alkyl substituents.[17] The plots of *trans*-2-*cis*-4-hexadiene (**22**) and 1,4-diphenylbutadiene (**23**) in Figure 7 show this situation. Although the ionization potentials change significantly for compounds **22** and **23**, the reaction rate does not. Thus, the reaction rate does not increase significantly as the HOMO energy increases over the IP range 7.5–9.1 eV. We may conclude therefore that the frontier orbital interactions are not dominant in determining the differences in the MCPBA epoxidations of alkyl-substituted olefins.

The higher reactivity of trialkyl-substituted olefins than dialkyl-substituted olefins in Figure 5 could be due to the stabilization of partial positive charge in the transition state by the additional alkyl group rather than to the HOMO energy increase resulting from an additional alkyl group. Thus, it is thought that the first-order Coulombic interaction is more important than the second-order perturbation (frontier orbital interaction) in the peracid epoxidation. From this result, the reactivity in the MCPBA epoxidation depends mainly on the strain relief for the transition state, especially in the highly strained bridgehead olefins and *trans*-cycloalkenes. Steric factors may be different between disubstituted and trisubstituted olefins; however, it would not be significant because the peracid epoxidation is quite insensitive to steric hindrance, and the MM-2 energy of the epoxide already includes this steric factor.

Conclusion

The second-order reaction rates were measured for the MCPBA epoxidations in CH_2Cl_2 for series of cyclic olefins including bridgehead olefins and *trans*-cycloalkenes. As expected, strained bridgehead alkenes and *trans*-cycloalkenes showed faster reaction rates than nonstrained *cis*-cycloalkenes. The MM-2 steric energies of alkenes, alkanes, and their corresponding epoxides were calculated to estimate the strain energy relief in each transition state. Plots of log k_{rel} vs olefin strain did not show a good correlation. However, the plot of log k_{rel} vs ΔSE (defined as the steric energy difference between olefin and the corresponding epoxide) showed a good correlation for each set of di- and trisubstituted olefins. This result implies that ΔSE directly reflects strain energy relief in the transition state. From the slope for the plot of log k_{rel} vs ΔSE, it was found that approximately 42% of strain (ΔSE) was released in the transition state for the MCPBA epoxidation. Also, trialkyl-substituted alkenes were found to be about 50 times more reactive than dialkyl-substituted alkenes in cases where the strain energy relief (ΔSE) is the same.

The reaction rate is also plotted versus the ionization potential of the olefin, assuming that the major orbital interaction lies between the LUMO of the peracid and the HOMO of the olefin. Although some correlation of the reaction rates with the ionization potentials of the olefins exists, the frontier orbital interaction is not viewed as the dominant factor in modulating reactivity since conjugated alkenes, which have higher HOMO energies than simple olefins, are not more reactive in MCPBA epoxidation.

In summary, the reactivity of olefins, including strained olefins, in the MCPBA epoxidation depends primarily on the strain energy relief in the transition state.

Experimental Section

Proton NMR spectra were obtained with Bruker WM 250 (250 MHz) and General Electric QE-300 (300 MHz) spectrometers. Chemical shifts are reported in δ-units with TMS as an internal reference for ^{1}H NMR. Coupling constants are reported in hertz (Hz) and refer to apparent multiplicities. Carbon NMR spectra were obtained with QE-300 (75.43 MHz) and General Electric GN-500 (125.7 MHz) spectrometers. Low-resolution mass spectra were obtained with a Finnigan Model 4000 GC/MS using a 70-eV electron impact source or 100-eV chemical ionization source. High-resolution mass spectra were obtained with a VG 7070e high-resolution mass spectrometer. Infrared spectra were recorded on an Analect RFX-40 FT-IR spectrophotometer and calibrated with polystyrene. UV–vis spectra were obtained with a Perkin-Elmer Lambda-4 spectrometer, and data were collected and analyzed with a Softways UVSL 4 program. Analytical gas–liquid chromatography was performed on a Hewlett-Packard Model 5790A gas chromatograph equipped with a Hewlett-Packard 3390A integrator. A methyl silicon support capillary column (length = 15–30 ft, i.d. = 0.20 mm) was used with helium as carrier gas and a flame ionization detector. Preparative vapor-phase chromatography was performed on a Varian Aerograph Model 920 gas chromatograph with a thermal conductivity detector. Samples were collected at −78 °C. The collection tubes were maintained air and water free by nitrogen backflow. A standard Pyrex column (3 ft × $^3/_8$ in. i.d.) packed with 10% Supelco SP-2100 on 80/100 Supelcoport was used. Flow pyrolysis was performed with a quartz tube (45 cm × 10 mm i.d.) heated by a cylindrical furnace. The reactants were swept through the tube by a stream of N_2 at atmospheric pressure. The resulting reaction mixture was trapped in a dry ice cooled U-shaped condenser. Molecular mechanics calculations were performed with the Macromodel version 3.0 program on a microvax computer.

Materials. Cyclohexene, cyclooctene, bicyclo[2.2.1]hept-2-ene, 1-methylcyclopentene, 1-methylcyclohexene, ethylidenecyclohexane, and 1,6-dibromohexane were purchased from Aldrich Chemical Co., and chloroprene was a gift from Du Pont. Alkenes were distilled prior to use. CH_2Cl_2 for the kinetic experiments was dried ($CaCl_2$) and distilled. MCPBA of 99% assay was obtained by washing the commercial 80–85% material (Aldrich) with phosphate buffer of pH 7.5 and drying the residue under reduced pressure.[16] Stock solutions of MCPBA were made by dissolving the 99% MCPBA into methylene chloride and filling up the volumetric flask. The concentration of the stock solution was determined iodometrically. Aliquots of 5 mL were removed to an Erlenmeyer flask. Glacial acetic acid (1 mL), KI (0.53 g), and water (5 mL) were added, and the resulting solution was titrated with a 0.1 M $Na_2S_2O_3$ solution which had been standardized against KIO_3 as a primary standard. Stock solutions of alkene were prepared by diluting a weighed sample of alkene in a volumetric flask.

Chloroprene Grignard Reagent.[9] To a 500-mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet tube were added Mg turnings (3.7 g, 150 mg-atom), THF (5 mL), and 1,2-dibromoethane (0.5 mL). After the exothermicity disappeared, $ZnCl_2$ (410 mg, 3 mol %) was added. To this reaction mixture was added a small amount of freshly distilled chloroprene (ca. 1 g), and the solution was stirred vigorously with heating until initiation occurred. Several drops of dibromoethane may be added to assist initiation. After initiation occurred, chloroprene (8.9 g total, 100 mmol) in THF (100 mL) was added dropwise at a rate to maintain gentle reflux. An additional 3 h of reflux ensured complete reaction. The concentration of this Grignard reagent was approximately 1 M as determined by titration with 1 M HCl.

3-Methylidene-1,7-octadiene (3). To a solution of chloroprene Grignard reagent (1.0 M in THF, 40 mL, 40 mmol) was added Li_2CuCl_4[40] in THF (0.1 M, 8 mL, 0.8 mmol) followed by 5-bromo-1-pentene (4.0 g, 27 mmol) in diethyl ether (10 mL) at 0 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was poured into a saturated NH_4Cl solution, extracted with diethyl ether, washed with saturated $NaHCO_3$ and H_2O, dried over anhydrous $MgSO_4$, concentrated, and distilled under vacuum (72–74 °C at 73 mmHg) to yield 1.7 g (53%) of 3-methylidene-1,7-octadiene:[7] ^{1}H NMR ($CDCl_3$) δ 6.37 (dd, J = 17.6, 10.7 Hz, 1 H, =CH), 5.83 (ddt, J = 17, 10, 7 Hz, 1 H, =CH), 5.22 (d, J = 17.5 Hz, 1 H, =CH), 4.94–5.07 (m, 5 H, =CH), 2.22 (t, J = 7.7 Hz, 2 H, allylic H), 2.09 (dt, J = 6–7 Hz, 2 H, allylic H), 1.59 (quintet, J = 7.7 Hz, 2 H,

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CH_2); ^{13}C NMR ($CDCl_3$) δ 146.21, 138.88, 138.65, 115.69, 114.62, 113.12, 33.58, 30.72, 29.35; IR (cm^{-1}, CCl_4) 3082 (m), 3005 (w), 2979 (m), 2935 (s), 2864 (w), 1817 (w), 1795 (w), 1641 (m), 1595 (s), 1462 (w), 1439 (w), 1415 (w), 991 (s); CI-MS (isobutane, relative percent) *m/e* 123 (M + 1, 100), 109 (53), 95 (34), 83 (23), 81 (87); EI-MS (relative percent) *m/e* 122 (M, 1), 107 (14), 94 (31), 93 (32), 91 (14), 81 (17), 80 (25), 79 (84), 77 (21), 68 (100), 67 (12), 65 (16), 55 (27), 54 (27), 53 (69), 52 (13), 51 (19).

Bicyclo[3.3.1]non-1-ene[7] **(1).** 3-Methylidene-1,7-octadiene (**3**) (0.2 g, 1.5 mmol) was swept by a stream of nitrogen gas through the quartz tube which was inserted in a furnace. The resulting thermolysis mixture, which was trapped in a U-shaped glass tube at −78 °C, consisted of unreacted triene and bicyclo[3.3.1]non-1-ene. Maximum yield was obtained when the furnace temperature was 410 °C and the contact time was approximately 30 s. The conversion as determined by GC was 34%. Bicyclo[3.3.1]non-1-ene was isolated by preparative GC (10% Carbowax, column temperature 80–100 °C). This compound has a longer retention time than that of the starting material: ^1H NMR ($CDCl_3$) δ 5.75 (t, J = 6.6 Hz, 1 H, =CH), 2.58 (br, 1 H), 2.37–2.28 (m, 1 H), 2.28–2.12 (m, 2 H), 2.07–1.89 (m, 3 H), 1.89–1.76 (m, 2 H), 1.6–1.35 (m, 2 H), 1.1–0.9 (m, 2 H); ^{13}C NMR ($CDCl_3$, one carbon is accidentally overlapped) δ 147.98 (quarternary), 125.82 (J_{C-H} = 158 Hz), 37.09, 36.75 (bridgehead carbon), 35.06, 32.10, 31.07, 25.78; IR (cm^{-1}, CCl_4) 3016 (w), 2924 (s), 2858 (s), 1620 (w), 1479 (w), 1454 (m), 1444 (w), 1348 (w), 1315 (w), 1230 (w), 1211 (w), 1097 (w), 1022 (w), 911 (w), 952 (w).

Bicyclo[3.3.1]non-1-ene oxide:[7,41,42] ^1H NMR ($CDCl_3$) δ 2.85 (t, J = 6.3 Hz, 1 H, hydrogen at the oxirane ring), 2.42 (m, 1 H), 1.9–2.05 (m, 3 H), 1.8 (m, 1 H), 1.6–1.75 (m, 2 H), 1.4–1.6 (m, 2 H), 1.1–1.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 60.04 (quaternary carbon), 57.25 (J_{C-H} = 176 Hz), 34.51, 33.92, 32.49, 30.69 (bridgehead carbon), 25.91, 23.49, 22.59; IR (cm^{-1}, CCl_4) 2943 (s), 2864 (m), 1462 (m), 1446 (m), 1309 (w), 1163 (w), 1034 (w), 1005 (m); EI-MS (relative percent) *m/e* 138 (M, 0.9), 137 (10), 110 (100), 109 (41), 97 (18), 96 (20), 95 (47), 94 (13), 93 (11), 91 (11), 84 (12), 82 (18), 81 (47), 80 (15), 79 (90), 77 (17), 69 (20), 68 (55), 67 (93), 66 (15), 65 (12), 55 (73), 54 (32), 53 (42), 51 (13).

6-Bromo-1-hexene. 1,6-Dibromohexane (5.0 g, 20.5 mmol) and finely powdered KOH (5.6 g, 100 mmol) were placed in a 15-mL round-bottomed flask equipped with vacuum distillation setup. The flask was heated (160–190 °C) at 80 mmHg with stirring. The elimination product was distilled out and condensed in a dry ice cooled receiver. The distillate was diluted with pentane, washed with H_2O, dried over $MgSO_4$, concentrated, and distilled under vacuum (80–82 °C, 63 mmHg) to yield 1.8 g (54%) of 6-bromo-1-hexene: ^1H NMR ($CDCl_3$) δ 5.79 (ddt, J = 17.1, 10.3, 6.7 Hz, 1 H, =CH), 4.95–5.06 (m, 2 H, =CH), 3.41 (t, J = 6.7 Hz, 2 H, $BrCH_2$), 2.09 (br q, J = 7.2 Hz, 2 H, allylic hydrogens), 1.88 (quintet, J = 7.2 Hz, 2 H, CH_2), 1.54 (quintet, J = 7.2 Hz, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 138.1, 115.0, 33.7, 32.8, 32.1, 27.3; IR (cm^{-1}, CCl_4) 3080 (w), 3003 (w), 2979 (w), 2962 (w), 2937 (s), 2859 (m), 1641 (m), 1456 (m), 1439 (m), 1286 (s), 1252 (m), 1242 (s), 993 (m).

3-Methylidene-1,8-nonadiene (4). The triene **4** was prepared by the same technique as that used in the synthesis of 3-methylidene-1,7-octadiene with 6-bromo-1-hexene (4.0 g, 24 mmol), chloroprene Grignard reagent (36 mL, 1 M in THF, 36 mmol), and Li_2CuCl_4 (7 mL, 0.1 M in THF, 0.7 mmol) to yield 2.43 g (72%) of the triene **4**:[7] bp 85–88 °C (60 mmHg); ^1H NMR ($CDCl_3$) δ 6.37 (dd, J = 10.8, 17.6 Hz, 1 H), 5.82 (m, 1 H), 5.22 (d, J = 17.6 Hz, 1 H), 5.09–4.92 (m, 5 H), 2.22 (t, J = 7.1 Hz, 2 H), 2.08 (q, J = 6.66 Hz, 2 H), 1.58–1.36 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 146.36, 138.93, 138.88, 115.54, 114.30, 113.03, 33.62, 31.16, 27.59; IR (cm^{-1}, CCl_4) 3082 (m), 3005 (w), 2978 (m), 2935 (s), 2860 (m), 1816 (w), 1722 (w), 1641 (m), 1595 (s), 1462 (w), 1439 (w), 1415 (w), 991 (s).

Bicyclo[4.3.1]dec-1(9)-ene[7] **(2).** Bicyclo[4.3.1]dec-1(9)-ene was obtained from 3-methylidene-1,8-nonadiene (**4**) by flow pyrolysis and purified by preparative GC as in the synthesis of bicyclo[3.3.1]non-1-ene. Maximum yield was obtained at 470 °C with ca. 30 s contact time (80% yield by GC): ^1H NMR ($CDCl_3$) δ 5.60 (br t, J = 5.7 Hz, 1 H, =CH), 2.3 (br m, 1 H), 2.23 (br, 1 H), 1.7–2.1 (m, 7 H), 1.2–1.6 (m, 5 H), 0.78 (ddt, J = 12.0, 6.0, 3.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 141.20 (quarternary carbon), 125.52 (J_{C-H} = 159 Hz), 39.30, 34.26, 31.54, 29.58, 29.14, 26.44, 23.51, 21.66; IR (cm^{-1}, CCl_4) 3032 (w), 2997 (w), 2929 (s), 2852 (s), 1649 (w), 1469 (w), 1448 (w), 1360 (w), 1340 (w), 1211 (w), 1184 (w), 1093 (w), 1012 (w), 991 (w); CI-MS (isobutane, relative percent) *m/e* 137 (M + 1, 28), 79 (100); EI-MS (relative percent) *m/e* 136 (27), 121 (24), 108 (11), 107 (18), 95 (40), 94 (56), 93 (52), 91 (23), 81 (25), 80 (49), 79 (100), 78 (18), 77 (28), 68 (45), 67 (77), 66 (11), 65 (15), 55 (17), 54 (15), 53 (28), 51 (13).

Bicyclo[4.3.1]dec-1(9)-ene oxide: ^1H NMR ($CDCl_3$) δ 2.91 (t, J = 5.5 Hz, 1 H, hydrogen at the oxirane ring), 2.25–2.12 (m, 2 H), 2.12–2.02 (m, 1 H), 1.97 (dd, 1 H, J = 13.9, 2 Hz), 1.9–1.75 (m, 2 H), 1.65–1.42 (m, 5 H), 1.4–1.27 (m, 2 H), 1.27–1.12 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 59.47 (J_{C-H} = 182 Hz), 58.11 (quaternary carbon), 37.60, 34.10, 32.78, 27.30, 25.27, 24.50, 23.26, 21.90; IR (cm^{-1}, CCl_4) 2981 (w), 2939 (s), 2925 (s), 2862 (m), 1460 (m), 1446 (m), 1200 (w), 1155 (w), 964 (w), 953 (m); CI-MS (isobutane, relative percent) *m/e* 153 (M + 1, 100), 135 (12); EI-MS (relative percent) *m/e* 152 (M, 3), 124 (9), 123 (37), 110 (8), 109 (14), 98 (13), 95 (17), 93 (11), 83 (10), 82 (11), 81 (52), 80 (10), 79 (29), 77 (12), 69 (11), 68 (21), 67 (89), 66 (12), 65 (12), 59 (10), 58 (100), 54 (29), 53 (40), 51 (12); HR-MS (CI) calcd for $C_{10}H_{17}O$ (M + 1) 153.1279, found 153.1277.

***cis*-Cyclooctene Oxide (8).** To a solution of MCPBA (9.79 g of 80–85% MCPBA) in CH_2Cl_2 (100 mL) was added *cis*-cyclooctene (5.00 g, 45.4 mmol). The resulting solution was then stirred for 5 h at room temperature. The reaction mixture was washed with saturated sodium carbonate solution (three times) and water (three times). The organic layer was dried ($MgSO_4$) and evaporated to yield 5.61 g (98%, >99% by GC) of cyclooctene oxide: ^1H NMR ($CDCl_3$) δ 2.9 (m, 2 H, hydrogens at oxirane ring), 2.15 (m, 2 H), 1.2–1.7 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 55.50 (J_{C-H} = 172 Hz), 26.46, 26.20, 25.50; IR (cm^{-1}, CCl_4) 2976 (m), 2931 (s), 2856 (m), 1471 (m), 1463 (m), 1448 (m), 1184 (w), 1016 (w), 924 (m); CI-MS (isobutane, relative percent) *m/e* 127 (M + 1, 58), 109 (100); HR-MS (EI) calcd for $C_8H_{14}O$ 126.1044, found 126.1020.

Lithium Diphenylphosphide.[43] Chlorodiphenylphosphine (Aldrich, 6.24 g, 28.3 mmol) in dry THF (12 mL) was added dropwise to lithium wire (0.432 g, 62.3 mg atom) in dry THF (30 mL) with vigorous stirring, and the reaction mixture was stirred overnight to give dark red lithium diphenylphosphide solution.

(*trans*-2-Hydroxycyclooctyl)diphenylphosphine Oxide (11). To the lithium diphenylphosphide solution was added cyclooctene oxide (3.24 g, 25.7 mmol) in dry THF (12 mL). The solution was allowed to stand for 2 days at room temperature, at which time the dark red color had faded to a pale yellow. Acetic acid (1.87 g, 31.2 mmol) and 3% H_2O_2 (38 mL, 34.0 mmol) were then added dropwise in turn at 0 °C. After stirring for 1 h at room temperature, the resulting reaction mixture was extracted with CH_2Cl_2, washed with water (three times), dried ($MgSO_4$), and evaporated under vacuum. The crude product was crystallized from benzene to give 6.5 g (77%) of compound **11** (mp 149–150 °C): ^1H NMR ($CDCl_3$) δ 7.82–7.7 (m, 4 H), 7.6–7.45 (m, 4 H), 5–4 (br, 1 H, OH), 4.13 (m, 1 H, CHO), 2.78 (broad quintet, 1 H, CHP), 2.0–1.15 (m, 12 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 132.58 (J_{C-P} = 8.37 Hz, carbons ortho to phosphine in phenyl ring), 132.16 (J_{C-P} = 2.79 Hz, carbon para to phosphine in phenyl ring), 132.09 (J_{C-P} = 2.05 Hz, carbon para to phosphine in phenyl ring), 132.0 (J_{C-P} = 100 Hz, quaternary carbon in phenyl ring), 131.13 (J_{C-P} = 9.22 Hz, carbons ortho to phosphine in phenyl ring), 129.20 (J_{C-P} = 93.98 Hz, quaternary carbon in phenyl ring), 128.78 (J_{C-P} = 11.65 Hz, carbons meta to phosphine in phenyl ring), 128.41 (J_{C-P} = 11.32 Hz, carbons meta to phosphine in phenyl ring), 70.37 (J_{C-P} = 3.36 Hz, COH), 42.41 (J_{C-P} = 68.17 Hz, CP), 30.68 (J_{C-P} = 12.14 Hz), 28.83 (J_{C-P} = 10.05 Hz), 26.86, 24.82, 24.48, 21.08; IR (cm^{-1}, KBr) 3276 (s), 3048 (w), 2925 (s), 1479 (w), 1456 (w), 1438 (m), 1324 (w), 1309 (w), 1176 (s), 1117 (m), 1103 (w), 1062 (w), 752 (w), 736 (w), 717 (s), 698 (m), 551 (s), 536 (s); CI-MS (isobutane, relative percent) *m/e* 329 (M + 1, 100), 330 (21), 328 (9), 203 (10): EI-MS (relative percent) *m/e* 285 (23), 257 (8), 244 (11), 229 (44), 215 (12), 203 (17), 202 (100), 201 (51), 155 (19), 151 (12), 125 (27), 104 (15), 78 (20), 77 (58), 67 (11), 51 (12); HR-MS (EI) calcd for $C_{20}H_{25}O_2P$ 328.1591, found 328.1605.

***trans*-Cyclooctene (14).** To NaH (87.8 mg, 3.66 mmol) in dry DMF (10 mL) (mechanically stirred) was slowly added (*trans*-2-hydroxycyclooctyl)diphenylphosphine oxide (**11**) (1.00 g, 3.05 mmol) in dry DMF (8 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. Pentane was then added, and the organic layer was washed with NH_4Cl solution and water (three times), dried ($MgSO_4$), and evaporated under vacuum to give *trans*-cyclooctene (194 mg, 58%, >99% by GC, contaminated by less than 1% of the cis isomer): ^1H NMR ($CDCl_3$) δ 5.50 (m, 2 H, CH=), 2.36 (m, 2 H, allylic), 2.02–1.88 (m, 4 H), 1.82 (m, 2 H), 1.42 (m, 2 H), 0.79 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 133.88 (J_{C-H} = 154 Hz), 35.73, 35.59, 29.13; IR (cm^{-1}, CCl_4) 3010 (w), 2927 (s), 2852 (m), 1648 (w), 1448 (m), 1201 (w), 985 (m), 935 (w); UV (nm, EtOH) 201.9.

***trans*-Cyclooctene oxide**: ^1H NMR ($CDCl_3$) δ 2.72 (br d, 2 H, J = 12.1 Hz), 2.27 (br d, 2 H, J = 12.0 Hz), 2.1–2.03 (m, 2 H), 2.03–1.0 (m, 2 H), 1.6–1.4 (m, 2 H), 1.15–0.98 (m, 4 H); ^{13}C NMR ($CDCl_3$, one carbon overlap) δ 59.56 (J_{C-H} = 173 Hz), 32.47, 28.44; IR (cm^{-1}, neat)

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2974 (m), 2933 (s), 2862 (s), 1479 (m), 1460 (m), 1358 (w), 1213 (w), 1018 (w), 953 (w), 939 (w), 894 (m), 823 (w), 814 (w), 806 (w), 794 (w), 779 (w), 727 (w), 719 (w); CI-MS (isobutane, relative percent) *m/e* 127 (M + 1, 42), 109 (100); EI-MS (relative percent) *m/e* 126 (M, 0.4), 109 (14), 98 (4), 97 (6), 83 (9), 81 (6), 73 (9), 67 (22), 60 (7), 59 (100), 57 (7), 55 (22); HR-MS (CI) calcd for $C_8H_{15}O$ (M + 1) 127.1124, found 127.1120.

1-Methylcyclooctene (6).[42] A solution of cyclooctanone (10.1 g, 80 mmol) in dry ether (100 mL) was added dropwise to methylmagnesium iodide, prepared from methyl iodide (22.7 g, 160 mmol) in ether (50 mL) and Mg turnings (3.9 g, 160 mmol) in ether (20 mL), over a period of 1 h, followed by further reflux for 3 h. The reaction mixture was treated with saturated NH_4Cl. The combined ether extract was washed with saturated sodium bicarbonate and water, dried ($MgSO_4$), and evaporated. The crude 1-methylcyclooctanol was distilled with one drop of H_2SO_4 under atmospheric pressure to give 1-methylcyclooctene and water. The distillate was dried and redistilled to give 8.18 g (82%) of *cis*-1-methylcyclooctene: bp 154–156 °C (760 mmHg); ^1H NMR ($CDCl_3$) δ 5.34 (t with allylic splittings, 1 H, J = 8.1 Hz, CH=), 2.13 (m, 2 H, allylic), 2.05 (br, 2 H, allylic), 1.68 (s with allylic coupling, 3 H, CH_3), 1.55–1.45 (br, 8 H); ^{13}C NMR ($CDCl_3$) δ 136.94 (quaternary), 124.09 (J_{C-H} = 151 Hz), 30.34, 30.19, 28.00, 26.64, 26.51, 26.20, 23.46 (CH_3); IR (cm^{-1}, neat) 3039 (w), 2927 (s), 2852 (s), 1668 (w), 1468 (s), 1446 (s), 1375 (m), 1356 (w), 1279 (w), 1232 (w), 1157 (w), 1090 (w), 1039 (w), 899 (m), 831 (m), 820 (m), 742 (w).

***cis*-1-Methylcyclooctene Oxide (9).** From 1-methylcyclooctene (6.0 g, 48.3 mmol) in CH_2Cl_2 (40 mL) and MCPBA (10.5 g of 80–85% MCPBA) in CH_2Cl_2 (120 mL) was obtained 6.72 g (99%) of *cis*-1-methylcyclooctene oxide: ^1H NMR ($CDCl_3$) δ 2.68 (dd, J = 10.1, 4.3 Hz, 1 H, CHO), 2.15 (m, 1 H), 1.9 (m, 1 H), 1.65–1.2 (br m, 10 H), 1.31 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, one carbon overlap) δ 63.22, 60.01, 31.16, 27.71, 26.51, 25.93, 25.15, 21.38.

(*trans*-2-Hydroxy-2-methylcycloocty1)diphenylphosphine Oxide (12). To a lithium diphenylphosphide solution, prepared from lithium wire (0.69 g, 100 mg-atom) and chlorodiphenylphosphine (10 g, 45.3 mmol), was added 1-methylcyclooctene oxide (6.0 g, 42.8 mmol) in dry THF (20 mL). The solution was allowed to stand for 5 days at room temperature, at which time the dark red color had faded to a pale yellow. Acetic acid (2.92 g, 48.6 mmol) and 3% H_2O_2 (54 mL, 48 mmol) were then added dropwise in turn at 0 °C. After stirring for 1 h at room temperature, the resulting reaction mixture was extracted with CH_2Cl_2, washed with water (three times), dried ($MgSO_4$), and evaporated under vacuum. The crude product was crystallized from benzene to give 9.03 g (62%) of compound **12**: mp 190–192 °C; ^1H NMR ($CDCl_3$) δ 7.88 (m, 2 H), 7.75 (m, 2 H), 7.6–7.4 (m, 6 H), 5.5–5 (br, 1 H, OH), 3.9 (dd and small coupling, J = 18, 8 Hz, CHP), 2.0–1.2 (m, 12 H), 1.27 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 133.86 (J_{C-P} = 95.66 Hz, quaternary carbon in phenyl ring), 132.71 (J_{C-P} = 8.41 Hz, carbon ortho to phosphine in phenyl ring), 131.88 (J_{C-P} = 1.46 Hz, carbon para to phosphine in phenyl ring), 131.77 (J_{C-P} = 2.56 Hz, carbon para to phosphine in phenyl ring), 131.23 (J_{C-P} = 88.20 Hz, quaternary carbon in phenyl ring), 130.95 (J_{C-P} = 9.69 Hz, carbon ortho to phosphine in phenyl ring), 128.64 (J_{C-P} = 11.98 Hz, carbons meta to phosphine in phenyl ring), 128.28 (J_{C-P} = 11.03 Hz, carbons meta to phosphine in phenyl ring), 75.43 (J_{C-P} = 4.23 Hz, COH), 44.22 (J_{C-P} = 66.69 Hz, CP), 40.96 (J_{C-P} = 11.95 Hz, CH_3), 28.52, 27.47 (J_{C-P} = 3.84 Hz), 27.52 (J_{C-P} = 11.04 Hz), 25.28, 25.32, 21.86; IR (cm^{-1}, KBr) 3406 (m), 3076 (w), 3055 (w), 2971 (w), 2922 (m), 2854 (w), 1475 (w), 1454 (w), 1436 (m), 1332 (w), 1155 (s), 1111 (m), 1093 (w), 1072 (w), 725 (m), 712 (s), 698 (m), 571 (s), 540 (m), 534 (m); CI-MS (isobutane, relative percent) *m/e* 343 (MH^+, 100), 344 (23), 342 (12), 325 (28), 203 (24); EI-MS (relative percent) *m/e* 342 (M^+, 0.2), 285 (33), 271 (24), 258 (30), 243 (31), 229 (46), 202 (100), 201 (75), 155 (19), 151 (14), 141 (12), 125 (25), 104 (14), 77 (38); HR-MS (EI) calcd for $C_{21}H_{27}O_2P$ 342.1747, found 342.1723.

1-Methyl-*trans*-cyclooctene (15). To a solution of NaH (33.6 mg, 1.40 mmol, 56.1 mg of 60% NaH) in dry DMF (2 mL) (mechanically stirred) was slowly added (*trans*-2-hydroxy-2-methylcycloocty1)diphenylphosphine oxide (400 mg, 1.17 mmol) in dry DMF (18 mL) at 0 °C. The solution was stirred for 2 h at room temperature. Pentane was then added, and the organic layer was washed with NH_4Cl solution and water (three times), dried ($MgSO_4$), and evaporated under vacuum to give 78.8 mg (54%) of 1-methyl-*trans*-cyclooctene:[43] ^1H NMR ($CDCl_3$) δ 5.37 (dd and allylic coupling, 1 H, J = 12.3, 2.7 Hz, CH=), 2.35–1.55 (m, 10 H), 1.74 (br s, 3 H, CH_3), 1.43 (m, 1 H), 0.90 (m, 1 H), 0.64 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 137.65 (quaternary), 127.17 (J_{C-H} = 150 Hz), 41.68, 36.75, 33.47, 30.97, 30.24, 27.89, 18.19 (CH_3); IR (cm^{-1}, CCl_4) 2925 (s), 2852 (m), 1658 (w), 1448 (m), 1375 (w), 1203 (w); CI-MS (isobutane, relative percent) *m/e* 125 (M + 1, 100), 123 (11), 111 (30), 97 (22), 96 (32), 83 (22), 81 (23); EI-MS (relative percent) *m/e* 124 (M, 6), 96 (23), 95 (9), 82 (18), 81 (59), 79 (15), 69 (21), 68 (55), 67 (100), 56 (39), 55 (73), 54 (48), 53 (51), 51 (15).

Table III. Summary of Kinetic Data for MCPBA Epoxidations

alkene	$[alkene]_0$ (mol/L, $\times 10^3$)	$[MCPBA]_0$ (mol/L, $\times 10^3$)	temp (°C)	k (mol^{-1} s^{-1})
cyclohexene	7.76	7.76	0	0.0223
	19.9	19.9	0	0.0234
	6.16	6.16	25.0	0.110
	12.0	12.0	25.0	0.137
cyclooctene	11.7	11.7	0	0.0455
	11.9	11.9	0	0.0466
	11.9	11.9	0	0.0466
	11.9	11.9	25.0	0.211
	11.9	11.9	25.0	0.219
cyclononene	12.0	12.0	0	0.0285
	12.0	12.0	25.0	0.140
norbornene	11.5	11.5	0	0.0327
	11.5	11.5	0	0.0346
	3.88	3.88	0	0.0343
	3.88	3.88	25.0	0.177
trans-cyclononene	3.22	3.22	0	0.737
	3.22	3.22	0	0.715
	3.22	3.22	0	0.740
	3.22	3.22	0	0.713
	1.24	1.24	25.0	3.08
trans-cyclooctene	1.43	1.43	0	5.14
	1.42	1.42	0	5.26
	1.42	1.42	0	5.28
	1.42	1.42	0	5.13
	1.02	1.02	25.0	18.1
	1.02	1.02	25.0	16.6
	1.02	1.02	25.0	16.1
1-methylcyclo-pentene	6.04	6.04	0	0.537
	2.29	2.29	22.9	1.83
1-methylcyclo-hexene	3.71	3.71	0	0.272
	3.76	3.76	0	0.274
	3.76	3.76	0	0.269
	3.76	3.76	0	0.289
	3.76	3.76	25.0	1.07
	3.76	3.76	25.0	1.13
	3.76	3.76	25.0	1.11
ethylidenecyclo-hexane	7.62	7.62	0	0.682
	6.10	6.10	0	0.622
	2.00	2.00	21.3	2.01
1-methylcyclo-octene	3.61	3.61	0	0.856
	3.61	3.61	0	0.847
	3.61	3.61	0	0.871
	2.83	2.83	25.0	2.76
1-methyl-*trans*-cyclooctene	0.631	0.631	0	52.6
	0.631	0.631	0	50.2
	0.607	0.631	0	47.6
	0.627	0.627	0	39.4
	0.391	0.391	20.0	95.2
bicyclo[4.3.1]-dec-1(9)-ene	2.98	2.98	0	3.03
	2.98	2.98	0	3.02
	2.22	2.22	0	3.02
	2.22	2.22	23.4	9.15
bicyclo[3.3.1]-non-1-ene	0.513	0.513	0	94.0
	0.513	0.513	0	97.2
	0.503	0.503	0	117
	0.458	0.458	0	88.3
	0.231	0.231	0	113
	0.386	0.386	10	138
	0.194	0.194	10	138
	0.245	0.245	25	252
	0.219	0.219	25	245
	0.207	0.207	25	280

1-Methyl-*trans*-cyclooctene oxide:[43] ^1H NMR ($CDCl_3$) δ 2.98 (dd, 1 H, J = 11.8, 2.3 Hz), 2.12 (m, 2 H), 2.05–1.80 (m, 4 H), 1.7–1.3 (m, 3 H), 1.36 (s, 3 H, CH_3), 1.25–1.0 (m, 3 H); ^{13}C NMR ($CDCl_3$, one carbon overlap) δ 64.61 (J_{C-H} = 172 Hz), 59.74 (quaternary), 38.45, 28.52, 28.40, 27.84, 26.47, 18.46 (CH_3); IR (cm^{-1}, CCl_4) 2970 (m), 2935 (s), 2864 (m), 1458 (m), 1432 (w), 1385 (w), 1265 (w), 1216 (w), 1157 (w), 1080 (w).

9,9-Dibromobicyclo[6.1.0]nonane. Cyclooctene (22.0 g, 200 mmol), bromoform (101.1 g, 400 mmol), CH_2Cl_2 (40 mL), EtOH (2 mL), benzyltriethylammonium chloride (500 mg), and 50% NaOH (160 g, 2.0 mol) were stirred vigorously. The reaction was exothermic, and the

temperature of the solution was maintained at 40–50 °C for 2 h and stirred for an additional 2 h at room temperature. The resulting solution was diluted with water and extracted with CH_2Cl_2 (three times). The combined organic layer was neutralized with dilute HCl and washed with water, dried ($MgSO_4$), evaporated, and distilled under vacuum to give 49.0 g (87%) of 9,9-dibromobicyclo[6.1.0]nonane:[13] bp 74–76 °C (0.15 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.06 (m, 2 H), 1.7–1.3 (m, 10 H), 1.15 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.12, 33.25 (J_{C-H} = 161 Hz), 27.88, 26.35, 25.40; IR (film) 2989 (w), 2960 (m), 2927 (s), 2854 (s), 1466 (m), 1446 (m), 1361 (w), 1232 (w), 1163 (m), 1145 (w), 1061 (w), 1030 (w), 931 (w), 858 (w), 816 (w), 762 (m), 740 (w), 710 (m); CI-MS (isobutane, relative percent) *m/e* 284 (M + 4, 0.56), 282 (M + 2, 1.42), 280 (M, 0.69), 123 (22), 122 (13), 121 (100), 81 (11).

1,2-Cyclononadiene. To a solution of 9,9-dibromobicyclo[6.1.0]nonane (20.0 g, 70.9 mmol) in ether (11 mL) maintained at −30 to −40 °C with an acetone–dry ice bath was added methyllithium (56.7 mL of 1.5 M solution from Aldrich, 85.1 mmol) dropwise, and the resulting solution was stirred for 1 h at −30 to −40 °C. Excess methyllithium was then decomposed by adding water, and the solution was extracted with ether. The combined ether extract was washed with water until neutral, dried, and evaporated under vacuum to give 8.53 g (98.5%, >99% by GC) of 1,2-cyclononadiene:[15] ^{1}H NMR ($CDCl_3$) δ 5.25 (dt, J = 8.6, 4.3 Hz, 2 H, CH=), 2.2 (m, 2 H), 1.85–1.45 (m, 8 H), 1.37 (m, 2 H); IR (cm^{-1}, CCl_4) 2995 (s), 2940 (m), 2865 (s), 1960 (s), 1458 (s); UV (nm, EtOH) 197.3.

***cis*-Cyclononene (7).** 1,2-Cyclononadiene (8.11 g, 66.4 mmol) and 10% palladium on carbon (174 mg) in methanol (170 mL) were hydrogenated in an atmospheric hydrogenator. The reaction was monitored by checking the rate of H_2 addition, and the theoretical amount of H_2 was absorbed within 2 h. The resulting solution was filtered, extracted (pentane), dried ($MgSO_4$), evaporated, and distilled under vacuum to give 6.97 g (85%) of *cis*-cyclononane:[13] bp 84–86 °C (45 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.52 (m, 2 H, CH=), 2.13 (br, 4 H), 1.49 (br, 10 H); ^{13}C NMR ($CDCl_3$) δ 130.20, 26.06, 25.82, 25.37, 25.33; IR (cm^{-1}, neat) 3006 (m), 2927 (s), 2862 (s), 1651 (w), 1473 (m), 1446 (m), 1348 (w), 1271 (w), 1011 (w), 845 (w), 796 (w), 787 (w), 758 (w), 729 (m), 717 (m), 698 (w); CI-MS (isobutane, relative percent) *m/e* 125 (M + 1, 100), 124 (60), 123 (61), 111 (74), 97 (78), 81 (55); EI-MS (relative percent) *m/e* 124 (M, 14), 96 (24), 95 (19), 82 (26), 81 (57), 79 (9), 69 (8), 68 (36), 67 (100), 66 (11), 55 (64), 54 (93), 53 (20).

***cis*-Cyclononene Oxide (10).** From *cis*-cyclononene (5.75 g, 46.3 mmol) in CH_2Cl_2 (40 mL) and MCPBA (10.0 g of 80–85% MCPBA) in CH_2Cl_2 (120 mL) was obtained 6.49 g (99%) of *cis*-cyclononene oxide by flash column chromatography (SiO_2, pentane): ^{1}H NMR ($CDCl_3$) δ 2.90 (dt, J = 10.3, 2.2 Hz, 2 H, oxirane ring), 2.15–2.06 (m, 2 H), 1.7–1.25 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 57.66 (J_{C-H} = 169 Hz), 24.49, 23.97, 23.09, 21.99; IR (cm^{-1}, neat) 2931 (s), 2867 (m), 1479 (m), 1446 (w), 1217 (w), 1011 (w), 974 (w), 958 (w), 949 (w), 891 (w), 829 (w), 793 (w), 777 (w), 766 (w), 735 (w); CI-MS (isobutane, relative percent) *m/e* 141 (MH^+, 100), 139 (16), 123 (68), 81 (14); HR-MS (CI) calcd for $C_9H_{17}O$ (M + 1) 141.1279, found 141.1263.

(*trans*-2-Hydroxycyclononyl)diphenylphosphine Oxide (13). To a lithium diphenylphosphide solution, prepared from lithium wire (0.69 g, 100 mg-atom) and chlorodiphenylphosphine (10 g, 45.3 mmol), was added *cis*-cyclononene oxide (6.0 g, 42.8 mmol) in dry THF (20 mL). The solution was allowed to stand for 5 days at room temperature, at which time the dark red color had faded to a pale yellow. After treatment with acetic acid (2.92 g, 48.6 mmol) and 3% H_2O_2 (54 mL, 48 mmol), regular work-up and recrystallization from benzene gave 8.72 g (60%) of compound **13**: mp 194–196 °C; ^{1}H NMR ($CDCl_3$) δ 7.84–7.72 (m, 4 H), 7.6–7.45 (m, 4 H), 4.9 (br, 1 H, OH), 4.19 (m, 1 H, CHO), 2.73 (m, 1 H, CHP), 1.9–1.25 (m, 14 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 132.46 (J_{C-P} = 96.97 Hz, quaternary carbon in phenyl ring), 132.32 (J_{C-P} = 8.22 Hz, carbons ortho to phosphine in phenyl ring), 131.97 (carbon para to phosphine in phenyl ring), 131.95 (carbon para to phosphine in phenyl ring), 131.24 (J_{C-P} = 9.25 Hz, carbons ortho to phosphine in phenyl ring), 129.84 (J_{C-P} = 94.73 Hz, quaternary carbon in phenyl ring), 128.56 (J_{C-P} = 11.63 Hz, carbons meta to phosphine in phenyl ring), 128.45 (J_{C-P} = 10.91 Hz, carbons meta to phosphine in phenyl ring), 71.33 (J_{C-P} = 3.63 Hz, COH), 40.06 (J_{C-P} = 68.20 Hz, CP), 29.10 (J_{C-P} = 11.09 Hz), 26.73 (J_{C-P} = 7.18 Hz), 25.91, 22.50, 22.44, 21.05, 17.71; IR (cm^{-1}, KBr) 3302 (s), 3246 (s), 3076 (w), 3053 (w), 2989 (w), 2924 (s), 2850 (m), 1481 (m), 1473 (m), 1438 (s), 1350 (w), 1321 (w), 1308 (w), 1176 (s), 1159 (m), 1116 (s), 1103 (m), 1070 (s), 1054 (w), 1027 (w), 1014 (w), 999 (w), 752 (m), 746 (m), 717 (s), 700 (s), 544 (s), 538 (s), 515 (m); CI-MS (isobutane, relative percent) *m/e* 343 (M + 1, 100), 344 (22), 342 (10), 203 (15); EI-MS (relative percent) *m/e* 244 (7), 230 (6), 229 (43), 216 (10), 215 (9), 203 (16), 202 (100), 201 (40), 155 (12), 125 (14), 104 (7), 78 (7), 77 (22), 55 (5); HR-MS (EI) calcd for $C_{21}H_{27}O_2P$ 342.1747, found 342.1725.

***trans*-Cyclononene (16).** To a solution of NaH (84.1 mg, 3.50 mmol, 140 mg of 60% NaH) in dry DMF (6 mL) (mechanically stirred) was slowly added (*trans*-2-hydroxycyclononyl)diphenylphosphine oxide (1.00 g, 2.92 mmol) in dry DMF (36 mL) at 0 °C, and the mixture was stirred for 1.5 h at room temperature. Regular work-up as for *trans*-cyclooctene gave 0.322 g (89%) of *trans*-cyclononene: ^{1}H NMR ($CDCl_3$) δ 5.34 (m, 2 H, =CH), 2.23 (m, 2 H, allylic), 1.79 (m, 2 H, allylic), 1.73–1.5 (m, 4 H), 1.4–1.3 (m, 2 H), 1.3–1.13 (m, 2 H), 0.98 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 130.77, 32.87, 32.45, 27.35, 22.56; IR (cm^{-1}, CCl_4) 3018 (w), 2929 (s), 2856 (m), 1658 (w), 1448 (m), 983 (m); CI-MS (isobutane, relative percent) *m/e* 125 (MH^+, 100), 111 (67), 97 (50), 83 (28), 81 (25), 71 (19); EI-MS (relative percent) *m/e* 124 (13), 96 (16), 95 (17), 82 (22), 81 (51), 68 (34), 67 (100), 66 (11), 55 (63); HR-MS (CI) calcd for C_9H_{17} (M + 1) 125.1330, found 125.1316.

***trans*-Cyclononene oxide**: ^{1}H NMR ($CDCl_3$) δ 2.7 (m, 2 H), 2.2 (m, 2 H), 1.95 (m, 2 H), 1.65 (m, 2 H), 1.5 (m, 2 H), 1.4–1.2 (m, 4 H), 1.9 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 60.34 (J_{C-H} = 173 Hz), 31.34, 30.67, 23.39, 23.37; IR (cm^{-1}, neat) 2974 (s), 2933 (s), 2862 (s), 1479 (m), 1458 (s), 1358 (w), 1209 (w), 1082 (w), 1018 (w), 953 (m), 939 (m), 916 (w), 895 (s), 823 (w), 814 (w), 806 (m), 794 (w), 781 (w), 727 (w); CI-MS (isobutane, relative percent) *m/e* 141 (MH^+, 75), 123 (100), 81 (50); EI-MS (relative percent) *m/e* 111 (2), 97 (8), 93 (3), 83 (6), 82 (4), 81 (9), 80 (3), 79 (4), 70 (5), 69 (11), 68 (12), 67 (38), 57 (18), 56 (19), 55 (100), 54 (29), 53 (11); HR-MS (CI) calcd for $C_9H_{17}O$ (M + 1) 141.1297, found 141.1291.

Method of Epoxidation Kinetics. In a typical run, an exact amount of MCPBA solution was added to a round-bottomed flask (10–25 mL) containing a stir bar. To this was added an exact amount of CH_2Cl_2. The flask was stirred and maintained at 0 °C or proper temperatures in a isothermal bath. An appropriate amount of alkene stock solution containing one or two drops of internal standard was also maintained in the bath. About 30 min later, alkene solution was added and the timer started. Aliquots were removed periodically and quenched immediately with a precooled 10% metabisulfite solution, and the elapsed time was recorded. After a while, the organic layer of the quenched solution was separated and dried with anhydrous Na_2SO_4. The resulting solution was analyzed by VPC at least in triplicate. The concentration of alkene was calculated using the relative integrations of alkene and reference signal. Internal standards were chosen so as to have an easily analyzable retention time and to not interfere with the epoxidation reaction itself. The internal standards used are as follows: toluene for cyclohexene and norbornene; cyclooctane for 1-methylcyclopentane, 1-methylcyclohexene, and ethylidenecyclohexane; *n*-decane for *cis*- and *trans*-cyclooctene, 1-methyl-*cis*-cyclooctene, and bicyclo[4.3.1]dec-1(9)-ene; decaline for bicyclo[3.3.1]non-1-ene and 1-methyl-*trans*-cyclooctene. Care should be taken for the reactive olefins, especially for bicyclo[3.3.1]non-1-ene. Bicyclo[3.3.1]non-1-ene easily decomposed to the corresponding epoxide with air contact, especially in CH_2Cl_2 solution. Thus, the kinetic experiments were performed in a nitrogen atmosphere and the CH_2Cl_2 used was distilled under nitrogen before the kinetic experiment. Purification and kinetic experiments were performed within a day to keep the purity of bicyclo[3.3.1]non-1-ene. Second-order rate constants were calculated by plotting $1/[\text{alkene}]_t$ vs time (s). Rate constants were measured at two or three different temperatures for each alkene. The energy and entropy of activation (E_a and ΔS^*) were calculated by the Arrhenius plot (ln k vs $1/T$) at 0 °C. Resulting products were checked and identified by GC and NMR spectra, which had been prepared by the large-scale epoxidation of alkene and MCPBA. Concentrations and rate constants of individual results are summarized in Table III.

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Registry No. 1, 17530-61-9; **1** alkane, 280-65-9; **1** epoxide, 26775-68-8; **2**, 139313-66-9; **2** alkane, 282-53-1; **2** epoxide, 139313-67-0; **4**, 68695-14-7; **5**, 931-88-4; **5** alkane, 292-64-8; **5** epoxide, 4925-71-7; **6**, 933-11-9; **6** alkane, 1502-38-1; **6** epoxide, 52954-47-9; **7**, 3618-11-9; **7** alkane, 293-55-0; **7** epoxide, 139346-65-9; **8**, 4925-71-7; **11**, 38202-37-8; **12**, 139313-68-1; **13**, 139313-69-2; **14**, 931-89-5; **15**, 38229-26-4; **16**, 3958-38-1; **17**, 110-83-8; **17** alkane, 110-82-7; **17** epoxide, 286-20-4; **18**, 498-66-8; **18** alkane, 279-23-2; **18** epoxide, 3146-39-2; **19**, 693-89-0; **19** alkane, 96-37-7; **19** epoxide, 16240-42-9; **20**, 591-49-1; **20** alkane, 108-87-2; **20** epoxide, 1713-33-3; MCPBA, 937-14-4; $H_2C{=}CH(CH_2)_3Br$, 1119-51-3; $Br(CH_2)_6Br$, 629-03-8; $H_2C{=}CH(CH_2)_4Br$, 2695-47-8; chloroprene grignard, 32657-89-9; chloroprene, 126-99-8; 3-methylidene-1,7-octadiene, 68695-13-6; *cis*-cyclooctane, 931-87-3; lithium diphenylphosphate, 4541-02-0; chlorodiphenylphosphine, 1079-66-9; cyclooctanone, 502-49-8; 1-methylcyclooctanol, 59123-41-0; 1,2-cyclononadiene, 1123-11-1; 9,9-dibromobicyclo[6.1.0]nonane, 1196-95-8.