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Kinetics and Mechanism of the Dihydroxylation and Epoxidation of Conjugated Dienes with Hydrogen Peroxide Catalyzed by Methylrhenium Trioxide

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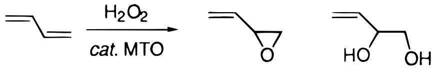
The title reactions occur readily. With acetonitrile chosen as the solvent, 17 of them were studied by kinetic methods. As is true for other MTO-catalyzed reactions, peroxorhenium complexes are the active species. Under the conditions of hydrogen peroxide present in large excess, usually employed here, $CH_3Re(O)(\eta^2\text{-}O_2)_2(OH_2)$ was the major reactive catalyst present. The rate constant between it and the dienes increase or decrease as substituents add or remove electron density from the $C{=}C$ bonds, suggesting a concerted mechanism in which the double bond attacks a peroxide oxygen. Many of the products are diols, some rearranged, except when the stability of carbocation intermediates for epoxide ring opening are so unstable as to prolong their lives. When urea−hydrogen peroxide was used instead, the monoepoxides were obtained.

Introduction

Theoretical interest and the practical importance of the epoxidation of olefins have generated sustained efforts in this area. Any number of catalysts effect epoxidations, those of greatest interest here being high-valent metal oxo compounds that activate hydrogen peroxide.[1−6] A new catalyst, methylrhenium trioxide (CH_3ReO_3, abbreviated as MTO), first found important application in epoxidation reactions based on hydrogen peroxide as the oxidizing agent.[7,8] Since that time, quantitative studies of the MTO-catalyzed reactions have been carried out to define in some detail the steps and intermediates in the epoxidation mechanism[9,10] and other work has sought to improve the selectivity for epoxides.[11]

Conjugated dienes are important because useful compounds are derived from their epoxidation and dihydroxylation reactions. Conceptually, this can be represented as follows, showing the parent 1,3-butadiene as the reactant:



We have investigated 16 analogous compounds and have explored the structural and electronic features of the mechanism that govern the rates and products. Our search of the literature did reveal earlier work on catalytic diene epoxidations[12−16] but no earlier catalytic system in which the kinetics of epoxide (oxirane) formation from dienes and hydrogen peroxide had been studied systematically.

Most of the reactions gave the generally-less-desired diols, a consequence of epoxide ring-opening reactions under the reaction conditions brought about by the water present in 30% hydrogen peroxide. Consequently, we replaced hydrogen peroxide with urea−hydrogen peroxide, $H_2NC(O)NH_2{\cdot}H_2O_2$, abbreviated as UHP. This reagent is insoluble and thus unsuited for kinetics, but it gave the epoxides in good yield.

Experimental Section

Materials. Acetonitrile was used as the solvent for quantitative kinetic studies (HPLC-grade, Fisher). Dienes and methylrhenium trioxide were purchased (Aldrich). Solutions of CH_3ReO_3 in CH_3CN were stored at 5 °C and used within 3 days. Hydrogen peroxide solutions were made by diluting the 30% material with acetonitrile; dilute solutions were discarded after 3 h. High-purity water was obtained by passing laboratory distilled water through a Millipore-Q water purification system.

^1H and ^{13}C NMR spectra were obtained from Varian VXR-300 or Bruker DRX-400 spectrometers. Chemical shifts were referenced to Me_4Si. A GC (Varian 3400)/MS(Finnegan TSQ 700 triple quadruole) spectrometer was used for certain product studies.

Kinetics. Kinetics determinations were carried out in CH_3CN at 25.0 ± 0.2 °C. Quartz cuvettes with different optical paths of 0.01−0.2 cm were used. The kinetics data were obtained by following the loss of diene absorption in the region 230−260 nm using a Shimadzu UV−visible spectrometer. The experiments used 0.004−0.50 M H_2O_2, 0.2−20 mM diene, 0.1−20 mM MTO generally but as high as 100 mM in one very slow reaction, and 0.0176−2.2 M H_2O. Reaction

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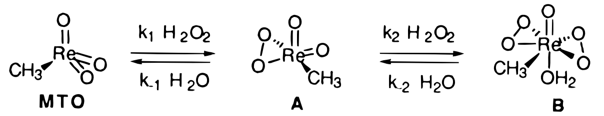
Scheme 1



mixtures were prepared in a spectrophotometric cell with the last reagent added being either H_2O_2 (method I) or the diene (method II) to optimize the kinetic conditions as explained later.

The absorbance–time curves were analyzed by pseudo-first-order or initial rate methods. The pseudo-first-order rate constants (k_ψ) were evaluated by nonlinear least-squares fitting of the absorbance–time profiles to a single exponential equation:

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)\exp(-k_\psi t) \quad (1)$$

For method I, the initial rate method was used. The concentration of the product was calculated from the absorbance at each time. The equation is

$$[\mathrm{diene}]_t = [\mathrm{diene}]_0 \frac{\mathrm{Abs}_t - \mathrm{Abs}_\infty}{\mathrm{Abs}_0 - \mathrm{Abs}_\infty} \quad (2)$$

The concentration–time data were then fit to a power series, $C_t = m_0 + m_1 t + ... + m_n t^n$, with the program KaleidaGraph. Differentiation shows that the value of m_1 is the initial rate. Between 4 and 9 terms were used in the series, the choice being largely immaterial. Initial rates are less precise, but they are particularly useful when a complex kinetics pattern invalidates a simpler treatment.

Products. To identify the products, 0.30 mmol of diene was added to an NMR tube containing 6 μmol of MTO, 1.2 mmol of H_2O_2, and 5.3 mmol of water in 0.6 mL of CD_3CN, which was held at room temperature for 2 h. If a complex mixture was formed, the major products were separated by TLC; in most cases this step was unnecessary. The products were characterized by their ^{1}H and ^{13}C NMR spectra and by GC-MS. Since most of these products are known materials, it suffices to present the results in the Supporting Information.

Results

It has been well documented that two peroxorhenium compounds exist in equilibrium with MTO and hydrogen peroxide.[17] The species are depicted in Scheme 1, where they are designated **A** and **B**. These species have proved responsible for the O-atom transfer reactions of MTO–hydrogen peroxide. The equilibrium constants are markedly dependent on the water concentration. Two sets of values of K/L mol^{-1} will be cited, in 1:1 CH_3CN–H_2O at pH 1,[18] $K_1 = 1.3 \times 10^1$ and $K_2 = 1.36 \times 10^2$; in CH_3CN containing 2.6 M H_2O, $K_1 = 2.1 \times 10^2$ and $K_2 = 6.6 \times 10^2$.[19] As reported in related instances, the products are favored thermodynamically the lower the water content of the solvent, but they are disfavored kinetically. In solvents with less water these equilibria are not rapidly established; indeed, in certain circumstances they become the rate-controlling steps.

In accord with earlier findings, both **A** and **B** react with the substrate. Their respective second-order rate constants are designated k_3 and k_4, eqs 3 and 4.

$$\text{alkene} + \mathbf{A} \rightarrow \text{epoxide} + \text{MTO} \quad (3)$$

$$\text{alkene} + \mathbf{B} \rightarrow \text{epoxide} + \mathbf{A} \quad (4)$$

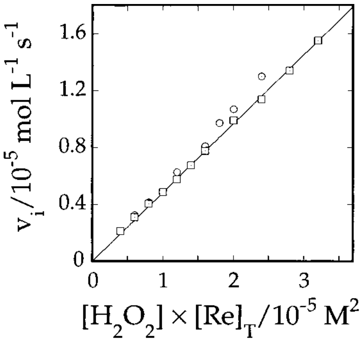


Figure 1. Kinetic data at relatively low concentrations of hydrogen peroxide shown as a plot of the initial rate (v_i) for the oxidation of 2,5-dimethyl-2,4-hexadiene, represented by squares, against the product of two concentrations, $[Re]_T[H_2O_2]$. The slope of the line defines k_1. The coincident data defined by the oxidation of thioanisole are given by the circles.

The rate law for product buildup, assuming the steady-state approximation, can be derived. Actually, as in this case and in those for catalytic reactions such as those represented by the Michaelis–Menten mechanism, this is really the situation sometimes referred to as "improved" steady-state kinetics.[20] The resulting rate law needs to be written in terms of $[Re]_T$ rather than [MTO], to allow for varying distributions among the three forms of rhenium with varying concentrations and sometimes with time. With **D** representing diene and **P** product is

$$\frac{d[\mathbf{P}]}{dt} = \frac{k_1k_3[Re]_T[H_2O_2][\mathbf{D}] + \dfrac{k_1k_2k_4[Re]_T[\mathbf{D}][H_2O_2]^2}{k_4[\mathbf{D}] + k_{-2}}}{k_{-1} + k_3[\mathbf{D}] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_4[\mathbf{D}] + k_{-2}}} \quad (5)$$

To simplify the treatment implied by the complete equation, conditions were set to attain one or another limiting form. In the one case, the concentration of the diene was chosen to be higher than that of hydrogen peroxide. The actual concentrations were chosen in combination with the rate constants, to make the second numerator term negligible and the second denominator term dominant. With that, eq 5 simplifies to the form

$$\frac{d[\mathbf{P}]}{dt} = k_1[Re]_T[H_2O_2] \quad (6)$$

The reaction of 2,5-dimethyl-2,4-hexadiene provides an example of this limit. With constant concentrations of hydrogen peroxide (4 mM), water (2.2 M), and diene (6 mM), the concentration of MTO was varied, 4–8 mM. The initial rate of reaction, v_i, was evaluated from each experiment. The plot of v_i against $[Re]_T$ at constant $[H_2O_2]$ was linear, as was the plot of v_i against $[H_2O_2]$ at constant $[Re]_T$. To consolidate the presentation of the kinetic data obtained under these conditions, we display in Figure 1 a plot of v_i against the concentration product $[Re]_T[H_2O_2]$. The data define an excellent straight line, with a slope $k_1 = 0.484 \pm 0.002$ L mol^{-1} s^{-1}. This point agrees well with the value one can interpolate from published data.[19] To check this method of data analysis, similar experiments were performed with PhSMe. The initial rate data for this compound was also determined as a function of the two concentrations. The results are also displayed in Figure 1, where it seen that they are essentially coincident with those for the diene. This aspect of the work was carried no further, however, since kinetic

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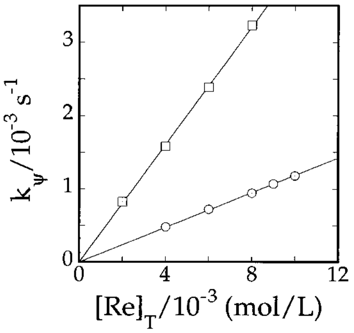


Figure 2. Pseudo-first-order rate constants for the oxidation reactions of 2,4-hexadiene and *cis*-piperylene (*cis*-1,3-pentadiene) (each 4 mM) by hydrogen peroxide (0.50 M) in acetonitrile containing 2.2 M water varying linearly with the total rhenium concentration, in accord with eq 7.

studies carried out under these conditions provide no information other than the already-known rate of interaction of MTO with hydrogen peroxide. Thus other conditions were employed for most of the kinetics experiments.

Data that are more informative as to the oxygen-transfer step of the reaction were obtained when the concentration of the diene, 0.20−20 mM, was taken to be much lower than that of hydrogen peroxide, itself at a much higher concentration, 0.50 M. Again, these experiments were done with $[H_2O]$ maintained at 2.2 M (otherwise the activity water would change significantly with varying $[H_2O_2]$) and variable $[Re]_T$, 0.1−20 mM or 100 mM on occasion. At these concentration ranges, the limiting form becomes

$$-\frac{d[\mathbf{D}]}{dt} = \frac{d[\mathbf{P}]}{dt} = k_4[\mathrm{Re}]_T[\mathbf{D}] \qquad (7)$$

Since the catalyst concentration remains constant, the reaction follows pseudo-first-order kinetics. The rate constant so obtained, labeled k_ψ, is expected to be a linear function of $[Re]_T$ but not expected to show other dependences. Figure 2 confirms the linearity of the variation, with data shown for two dienes, 2,4-hexadiene and *cis*-piperylene (*cis*-1,3-pentadiene), each at 4 mM concentration. From the slopes of the lines, the respective values of k_4 are 0.401 ± 0.002 and 0.119 ± 0.005; the standard deviations represent the goodness of the fit to the line, and the true precision considering various sources of random error is perhaps ±5%. The rate constants so determined for 16 conjugated dienes and 1 nonconjugated analog are presented in Table 1.

Products. We used ^1H NMR, ^{13}C NMR, and GC-MS to identify the reaction products. They are also shown in each case in Table 1, along with the reaction yields. As with the kinetics, the products were studied in the case where hydrogen peroxide was used. Most (but, interestingly, not all) of the products were diols; if, however, the products were monitored early in the reaction, largely the epoxides were detected. To no surprise, then, the epoxides are undergoing a ring-opening reaction during the course of the reaction.

In an attempt to minimize diol formation, many of the reactions were carried out with the solid reagent urea−hydrogen peroxide (UHP, $H_2NC(O)NH_2 \cdot H_2O_2$) and without any addition of water to the acetonitrile. In these cases, most of the dienes gave only epoxides, Table 1. The UHP reactions are heterogeneous and, thus, have no applications for kinetics, but they do provide a useful means of obtaining the desired epoxides.

Epoxide Stability to UHP. Certain of the epoxides were tested with UHP and MTO for an extended time. Provided water was absent, the epoxides could be kept for 1 week without evidence of ring opening. On the other hand, when water (2.2 M) was added to the reaction, diol was formed over several hours. When instead perrhenic acid (10 mM), 2-methyl-2-vinyloxirane (0.20 M), and water (2.2 M) were combined, the ring-opening reaction finished in several hours. With 2-methyl-3-vinyloxirane, the reaction time was several days.

Discussion

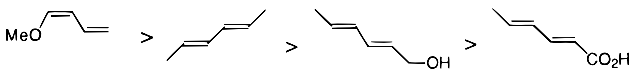
Kinetic Model. The reaction sequence, a combination of Scheme 1 and eqs 3 and 4, represents the essence of the mechanism. As shown, both of the peroxorhenium compounds are active catalysts. Under most of the conditions employed here, however, the contribution of **A** was negligible compared to that of **B**, and the direct reaction between **B** and the alkene, eq 4, was rate-controlling. The occurrence of this reaction gave rise to **A**, not MTO, and so nearly all of the catalytic cycle involves the recycling of **A** to **B** via the step of Scheme 1 with the rate constant k_2.

The subsequent step that gives rise to diols is often faster than epoxide formation but not always. The relative rates of these steps are immaterial in the kinetic analysis, however, since the UV monitoring procedure for the first reaction experiences almost no distortion from the subsequent reaction of the epoxide. As shown in Table 1, some of diol formation is accompanied by rearrangement, owing to the relative stability of carbocation intermediates, as will be explained.

Kinetic Effects of Substituents. Previous data have shown that substituents have a regular effect on the rate, depending on the direction in which they alter the electron density at the double bond: An electron-donating group increases the value of k_4, whereas an electron-attracting group lowers it.[10] First, let us examine the effect of replacing one or more diene protons by methyl groups. From Table 1, we can examine the rate ratios for these substituents. These are the comparisons: hexadienes, entries 1 and 3, k_4 ratio 9.8; pentadienes, entries 2−7, ratios 2.5−5.3; butadienes, entries 6−9, ratios 1.2−1.7. The indicated accelerations are clear.

To express this effect in graphic terms, we display in Figure 3 a plot of log k_4 against the number of methyl substituents on the nine compounds shown as entries 1−9. In the construction of this plot, the rate constant of the symmetric diene, entry 1, was divided by 2 to provide a statistical correction. A straight line was drawn through the values, which span 2 orders of magnitude in rate, with a correlation coefficient 0.992. The linearity of the correlation is not the issue, however. This graph is simply to show how consistent the effects of electron-donating methyl groups are. This shows how the electron-rich dienes are more rapidly epoxidized by MTO/H_2O_2. It would be of considerable interest to compare quantitatively the extent of correlation with diene epoxidation rate constants with other catalysts. As remarked earlier, systematic studies are lacking in the literature.

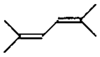
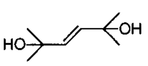
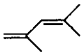
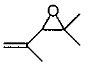
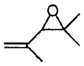
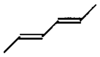
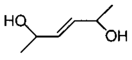
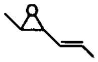
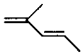
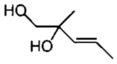
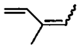
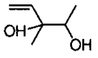
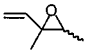
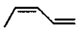
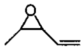
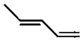
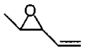
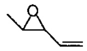
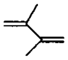
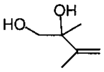
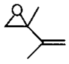
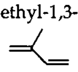
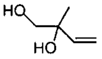
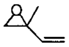
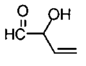
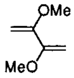
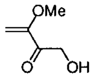
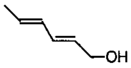
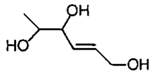
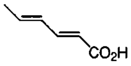
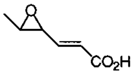
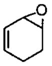
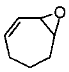
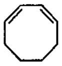
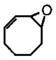
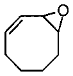
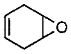
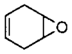
Further examples of the effect of electron-donating and electron-attracting substituents can be seen in this series of compounds, the k_4 values for which are shown:



1.47 0.401 0.297 0.0041 L mol^{-1} s^{-1}

It is interesting to explore the reason behind the diminution of the reactivity of the cyclic conjugated 1,3-dienes with C_6,

Table 1. Rate Constants and Products for the MTO-Catalyzed Oxidation of (Mostly) Conjugated Dienes by Hydrogen Peroxide

Entry	Diene	k_4 /L mol^{-1} s^{-1}	Product w/ H_2O_2	% Yield[a]	Product with UHP[b]	% Yield[a]
1	2,5-Dimethyl-2,4-hexadiene 	3.92		82		
2	2,4-Dimethyl-1,3-pentadiene 	0.562		45		58
3	2,4-Hexadiene (80% trans-trans) 	0.401		62		79
4	trans-2-Methyl-1,3-pentadiene 	0.324		61		
5	3-Methyl-1,3-pentadiene (cis:trans = 1:1.4) 	0.294		77	 (cis : trans = 1 : 1.4)	91
6	cis-Piperylene (1,3-Pentadiene) 	0.120		72		84
7	trans-Piperylene (1,3-Pentadiene) 	0.105		65		70
8	2,3-Dimethyl-1,3-butadiene 	0.0867		69		86
9	Isoprene (2-methyl-1,3-butadiene) 	0.0714		74		88
10	1-Methoxy-1,3-butadiene (cis & trans) 	1.47	 + MeOH	67		
11	2,3-Dimethoxy-1,3-butadiene 	1.36	 + MeOH	85		
12	trans,trans-2,4-Hexadien-1-ol 	0.297		64		
13	trans, trans-2,4-Hexadienoic acid 	0.00410		94		
14	1,3-Cyclohexadiene 	1.00	mixture of diols			86
15	1,3-Cycloheptadiene 	0.387	mixture of diols			93
16	cis,cis-1,3-Cyclooctadiene 	0.189		80		96
17	1,4-Cyclohexadiene 	0.102		75		85

[a] Based on ^{1}H NMR peak integrations; [b] UHP = $NH_2CONH_2{\cdot}H_2O_2$

C_7, and C_8 rings. The ground-state conformations of these compounds have been thoroughly studied.[21] The degree of conjugation decreases with ring size owing to the conformational preferences of the carbocyclic ring. The parameters for these compounds are given in Table 2, along with values for the nonconjugated compounds 1,4-cyclohexadiene and cyclohexene.

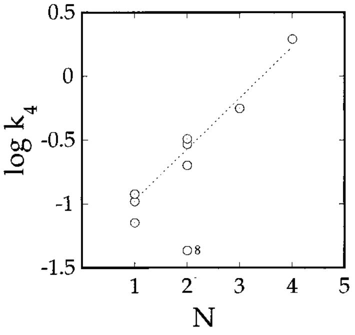
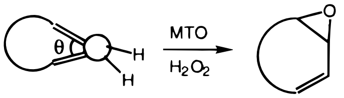
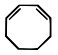
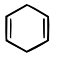
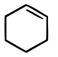


Figure 3. Correlation of the rate constants (log k_4) for the epoxidation of conjugated dienes and **B** with the number of methyl groups on the diene. Entry 8 from Table 1 is noted, in that it fails in this correlation.

Table 2. MTO-Catalyzed Epoxidations of Cyclic Dienes in Comparison with Monoenes



Diene, Mono-ene	θ	k_4 /L mol^{-1} s^{-1}
	10°	1.00
	22°	0.387
	55°	0.189
		0.102
		$2k_4$ =0.22

Very clearly, effective conjugation, such as exists in 1,3-cyclohexadiene, exerts a rate-enhancing effect. Compare the much larger rate constant for this compound ($k_4/2$ = 0.50 L mol^{-1} s^{-1}) with those for two nonconjugated counterparts, 1,4-cyclohexadiene ($k_4/2$ = 0.051 L mol^{-1}s^{-1}) and cyclohexene (k_4 = 0.108 L mol^{-1}s^{-1}).[10]

On the other hand, ring size appears to play an important role, with a decrease in rate along the series $C_6 > C_7 > C_8$. This effect can actually be traced to a decline in conjugation. Note that the dihedral angle is wider for 1,3-cycloheptadiene and wider yet for 1,3-cyclooctadiene; this widening of the dihedral angle lessens the extent of conjugation. The respective rate constants, $k_4/2$ = 0.19 and 0.095 L mol^{-1} s^{-1}, are clearly much smaller than for compounds (e.g., 1,3-cyclohexadiene and 2,4-hexadiene) whose structures allow nearly the full extent of conjugation.

A further correlation was attempted between the rate constant, statistically corrected by a factor of 2 for the symmetric dienes, and the energy of the $\pi \rightarrow \pi^*$ transition as determined from the UV spectrum.[22] Figure 4 displays a plot of log k_4 against energy for all the hydrocarbons, oxygenated compounds being omitted. There is a reasonable correlation, although one entry lies are well off the approximate line defined by the others. The deviant point represents entry 8 in Table 1, the same compound furthest off the line in Figure 3 as well. (We can offer no rationale for it.) This correlation tells us that the chemistry of the epoxidation process is that of an electron-rich double bond nucleophilically attacking the coordinated peroxo ligand in that it correlated with the excitation energy for an electron in that very bond.

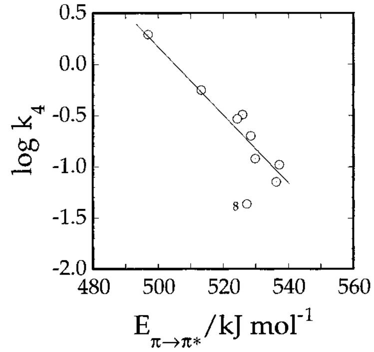
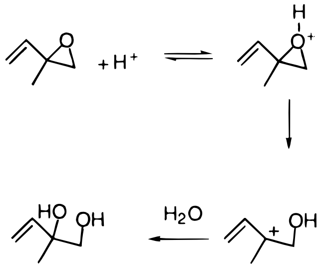
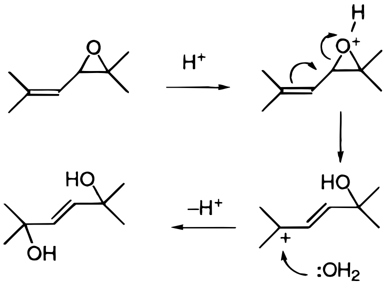


Figure 4. Correlation of the rate constants (log k_4) for the epoxidation of conjugated dienes and **B** with the energy of the $\pi \rightarrow \pi^*$ UV transition for the conjugated diene. Entry 8 from Table 1 is noted, in that it fails in this correlation.

Scheme 2



Scheme 3



Epoxide Disappearance. Many of the reactions produce exclusively or primarily *vic*-diols. The ring-opening reactions that produce this result are well known.[23] Scheme 2 shows the pertinent steps, the most prominent feature being the intervention of a carbocation intermediate. The relative stabilities of the carbocations govern the rate of ring opening. For example, the ring-opening rate of 2-methyl-2-vinyloxirane is much higher than that of 2-methyl-3-vinyloxirane owing the higher stability of the tertiary carbocation intermediate in the rate-controlling step of ring opening. In this way, we can account for the major product being the epoxide from 3-methyl-1,3-pentadiene, whereas the diol is formed from isoprene (2-methyl-1,3-butadiene), this pair being related in just the way described.

The enthalpy of formation of the two epoxides obtainable from *trans*-2-methyl-1,3-pentadiene were calculated by use of the CAChe program.[24] The value of $\Delta H°_f$ for 2-methyl-2-propenyloxirane, −35.4 kJ mol^{-1}, is about 21% lower than that for 2-isopropenyl-3-methyloxirane, −28.3 kJ mol^{-1}. This

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(21) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1983**, *107*, 2000.

(22) We are grateful to Professor R. J. Angelici for the idea of trying this correlation.

(23) Long, F. A.; Pritchard, J. G. *J. Am. Chem. Soc.* **1956**, *78*, 2663.

(24) Stewart, J. J. *J. Comput. Chem.* **1989**, *10*, 221.

driving force may provide an additional reason for the formation of the former compound.

Rearrangements Leading to 1,4-diols. Note that two reactions, entries 1 and 3, give rise not to geminal diols but to diols in which the two OH groups are in relative 1 and 4 positions. This change arises because secondary and tertiary carbocations are more stable than the initially-formed primary ones. This is shown in Scheme 3 for the epoxide derived from 2,5-dimethyl-2,4-hexadiene.

We conclude, therefore, that the MTO-catalyzed epoxidations are controlled in rate by the electron density at the double bond and by the extent of conjugation of the double bonds, most noticeably so when they coexist in a cyclic system. The primarily-produced epoxide is that at the most electron-rich of the double bonds, when there is a difference. Epoxides are obtained when UHP is used instead of hydrogen peroxide, since the activity of water is low, and also when the epoxide undergoes slow a ring-opening reaction, as when the carbocation intermediate is unstable. It seems clear that UHP provides a cleaner route when the epoxides are desired, without sacrifice of reactivity, both being complete in 2−3 h under the conditions described.

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Supporting Information Available: Text giving ^{1}H and ^{13}C NMR and mass spectral data for the products (4 pages). Ordering information is given on any current masthead page.

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