tion and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

References and Notes

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(2) B. Rickborn and R. P. Thummel, *J. Org. Chem.*, **34**, 3583 (1969).

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(5) C. F. Irvin and G. F. Hennion, *J. Am. Chem. Soc.*, **63**, 858 (1941).

(6) (a) W. Oroshnik and R. A. Mallory, *J. Am. Chem. Soc.*, **72**, 4608 (1950); (b) B. Ganem and V. R. Small, Jr., *J. Org. Chem.*, **39**, 3728 (1974), and other unpublished results.

(7) Structure **3** was prepared in two different ways: (a) by chlorination of **4** ($SOCl_2$, CCl_4) and subsequent epoxidation (*m*-chloroperoxybenzoic acid, CH_2Cl_2), or (b) by stereospecific epoxidation[9] of **1** (*m*-chloroperoxybenzoic acid, benzene), then mesylation and displacement by chloride.[10]

(8) Compound **5** was synthesized by chlorination of **1** (Cl_2, CCl_4, 0 °C) then cyclization in base of the resulting dichloroalcohol (sodium isopropoxide, isopropyl alcohol).

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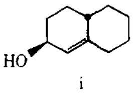
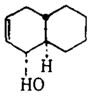
(11) Equatorial cyclohexenols we have examined include Δ^1- and Δ^4-cholesten-3β-ol as well as octalols *i* and *ii*.



i



ii

Although we have not studied hypohalite additions to acyclic alcohols in detail, we have observed that allyl alcohol itself undergoes an explosive 1,2 addition with *t*-BuOCl. No epichlorohydrin is thereby generated.

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Aliphatic Hydroxylation via Oxygen Rebound. Oxygen Transfer Catalyzed by Iron

Sir:

There has been continued intense interest in the mechanism of action of heme-containing hydroxylases and the nature of reactive intermediates in these systems.[1] Two of the more important aspects of enzymic hydroxylation yet to be fully explained are oxygen transfer without equilibration with water and oxidation with net retention of configuration at the functionalized carbon (Scheme I).

Basic to the understanding of such processes is a catalog of the chemistry intrinsic to the higher oxidation state iron complexes (**1**) which have been implicated in these reactions.[2] We report here a single, nonenzymic oxidation, catalyzed by iron, that reveals both of these features.

Table I. Peroxyacid–Ferrous Ion Induced Hydroxylation of Cyclohexanol

	Diol					
Peracid	*cis*-1,2	*trans*-1,2	*cis*-1,3	*trans*-1,3	*cis*-1,4	*trans*-1,4
CF_3CO_3H[a]	32	25	30	7	2	5
MCPBA[a]	37[b]	37	19	2.4	2.2	2.2
CH_3CO_3H[a]	7	16	36	20	4	18

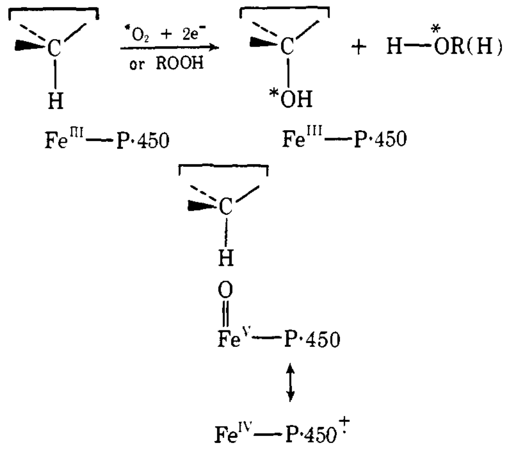
[a] Results for addition of 10 mmol of peracid in 10 ml of CH_3CN to 10 mmol of $Fe(ClO_4)_2 \cdot 6H_2O$ and 10 mmol of cyclohexanol in 60 ml of CH_3CN at 0 °C. Products were analyzed as we have previously described (cf. ref 3). All data are typical of multiple runs. [b] Diol yield 9%; cyclohexanone 40%; recovered cyclohexanol 50%.

Table II. Mass Spectra of *cis*- and *trans*-1,2-Cyclohexanediol (**2** and **3**) (Relative Intensities)[f]

m/e	120	119	118	117	116	101	100	99	98
2				8.7	100				160
3				8.7	100				160
a			7.8	100	7.1		9.7	125.6	34.4
b			8.3	100	33.7		12.9	131.4	71.4
c			8.3	6.6	100		4.2		108
d			10.8	6.8	100		9.4		110
e	3.9	41.5	5.3	9.9	100	50.1			122

[a] **2** from MCPBA–Fe $(ClO_4)_2$ oxidation of *trans*-2-deuteriocyclohexanol, D_0/D_1 = 0.07. [b] **3** from *trans*-2-deuteriocyclohexanol, D_0/D_1 = 0.34. [c] **2** from MCPBA–$Fe(ClO_4) \cdot 11H_2{}^{18}O$ (54% enrichment) oxidation of cyclohexanol, $^{18}O/^{16}O$ = 0.083. [d] **3** from MCPBA–$Fe(ClO_4)_2 \cdot 11H_2{}^{18}O$ (54% enrichment), $^{18}O/^{16}O$ = 0.108. [e] **2** and **3** from cyclohexanol–2,2,6,6-cyclohexanol-d_4 (1:1.35), D_3/D_0 = 0.415. [f] All data are typical of multiple runs.

Scheme I



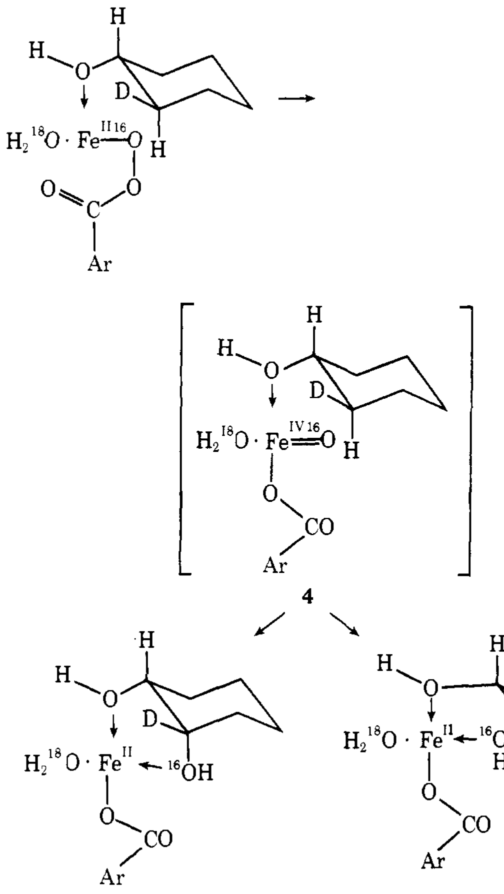
1

Recent developments in our laboratories have provided evidence that modified Fenton's reagent systems (Fe^{2+}–H_2O_2–CH_3CN) produce an iron-bound oxidant, not free hydroxyl radical, that responds to substituent derived directive effects.[3] We have also detailed a photolytic entry to this reactive intermediate which revealed the sensitivity of the observed regioselectivity to changes in conformational equilibria.[4]

We have now examined the hydroxylation of cyclohexanol by ferrous ion–peroxyacid systems with startling and revealing results.[5] Thus, addition of an acetonitrile solution of *m*-chloroperbenzoic acid (MCPBA) to cyclohexanol-ferrous perchlorate in acetonitrile at 0 °C led to the formation of cyclohexanone (40%) and all possible cyclohexanediols (9%).[6]

Critical to the understanding of the mechanism of this hydroxylation and any relationships with biological processes is identification of the source of the new hydroxyl oxygen. We have explored this question by mass spectral examination of the isotopic content of the product diols isolated from an oxidation of cyclohexanol by MCPBA and ferrous perchlorate undecahydrate ($H_2{}^{18}O$, 54% enrichment). Surprisingly, the $^{18}O/^{16}O$ ratios for *cis*- and *trans*-1,2-cyclohexanediol (**2** and **3**) were found to be only 0.08 and 0.1, respectively (Table II).

Scheme II



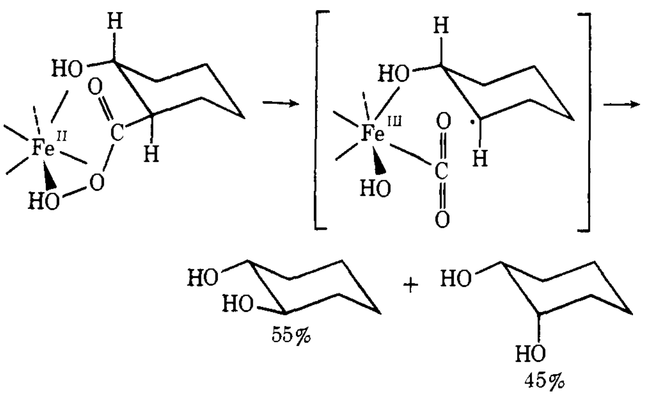
If the hydroxyl oxygen were derived randomly from water in the milieu, including that produced from the peroxyacid (i.e., by attack of solvent on an intermediate carbonium ion), an $^{18}O/^{16}O$ ratio of 0.98 would have been expected Accordingly, the peroxy oxygen is incorporated 90% of the time *without equilibration with water!*

The observed equal distribution of cis and trans 1,2-diols, in marked contrast to the stereoselectivity of C-3 oxidation, has also been found to be revealing when examined in more detail. Hydroxylation of *trans*-2-deuteriocyclohexanol (>98% *d*-**1** from the reaction of cyclohexene oxide with lithium triethylborodeuteride) with Fe^{2+}-MCPBA again provided *cis*- and *trans*-1,2-cyclohexanediol. Analysis of the mass spectra of the products (Table II) showed predominant *retention* of deuterium in the cis isomer (D_0/D_1 = 0.07) while the trans isomer showed significant *loss* of the label (D_0/D_1 = 0.34).

Examination of the deuterium content of the products from a competitive oxidation of cyclohexanol and 2,2,6,6-cyclohexanol-d_4 led to a substantial isotope effect (k_H/k_D = 3.2). An inescapable conclusion from these data is that cis hydrogen abstraction leads preferentially to cis diol formation while trans hydrogen abstraction affords trans diol.[7] Thus, what appears superficially to be a nonselective process is in fact two stereospecific processes with nonequilibration of any carbon intermediates.[8]

The specific incorporation of peroxy oxygen and the observed retention at C-2 put severe limitations on the range of considerable mechanisms for this process but are completely consistent with our proposed mechanism of the intermediacy of a metal oxo species (**4**),[3] formally a ferryl ion, which is subsequently responsible for hydroxylation[9] (Scheme II). Thus, the oxygen trajectory rebounds from iron to carbon with abstraction of the only three hydrogens chemically available to the iron-oxo complex (**4**).

Scheme III



More problematical is the mode of retention of this stereochemical information. We have demonstrated elsewhere the intermediacy of discrete carbon radicals and carbonium ions in the related Fe^{II}/H_2O_2 mediated hydroxylation of cyclohexanol.[3] If such a stepwise process is also involved when MCPBA is the oxidant, hydrogen abstraction, electron transfer, and nucleophilic capture of the incipient carbonium ion must be rapid with respect to molecular rotation and ligand exchange on iron[10] which would equilibrate both the deuterium and oxygen labels. The recent observation of reductive decarboxylation of peroxyacids under conditions very similar to those employed here[11] provide strong support for this view. Thus, treatment of *cis*-2-hydroxyperoxycyclohexanecarboxylic acid with ferrous perchlorate in acetonitrile provided a 55:45 mixture of *cis*- and *trans* 1,2-cyclohexanediol, respectively. Conversely, *trans*-2-hydroxyperoxycyclohexanecarboxylic acid gave a 45:55 cis/trans ratio. The degree of retention observed here is significantly less than that observed in the C-2 hydroxylation with ferrous ion-MCPBA. A compelling interpretation of these results is that C-2 hydrogen abstraction by an iron oxo species requires close approach of the iron to the intermediate carbon radical, allowing rapid, subsequent electron transfer and ligand delivery. In contrast, separation of the radical center and $Fe^{III}OH$ by the elements of CO_2 is sufficient to allow the observed loss of stereochemistry (Scheme III).[12]

Acknowledgments. Financial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and The University of Michigan are gratefully acknowledged.

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(3) (a) J. T. Groves and M. Van Der Puy, *J. Am. Chem. Soc.*, **96**, 5274 (1974); (b) J. T. Groves and M. Van Der Puy, *ibid.*, submitted.

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(5) Alkane hydroxylation by CF_3CO_3H in strongly acidic media in the absence of metal ions has been reported (cf. U. Frommer and V. Ullrich, *Z. Naturforsch. B*, **28**, 322 (1971)) and retention of configuration in these reactions has been noted without detail (cf. ref 1d, p 7).

(6) (a) *m*-Chlorobenzoic acid and a small amount (<2%) of chlorobenzene were also isolated from the reaction mixture. Previous studies have demonstrated the quantitative viability of the work-up and assay, ref 3. (b) Similar results were obtained with trifluoroperacetic acid but interestingly peracetic acid showed little regioselectivity. (c) Control experiments showed that *no reaction* took place even after 1 h at room temperature in the absence of Fe(II). Thermal decomposition of MCPBA in acetonitrile (80 °C, 12 h) in the presence of cyclohexanol afforded only trace amounts (<2%) of cyclohexanediols with a near-statistical distri-

bution of isomers. In the presence of Fe(II) the decomposition of MCPBA is instantaneous even at −20 °C in the absence of cyclohexanol. Accordingly, the initial formation of a reactive intermediate upon reaction of MCPBA with Fe(II) is required.

(7) Quantitative analysis of the data lead to the conclusion that cis diol formation proceeds with 89% retention while trans diol is formed with 98% retention (Table II).

(8) Hydroxylation with retention of configuration and with a substantial isotope effect has been observed for chromate[8a] and ozone[8b] oxidations of alkanes suggesting mechanistic similarities to the process reported here: (a) K. B. Wiberg and G. Foster, *J. Am. Chem. Soc.*, **83**, 423 (1961); (b) G. A. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.*, **No. 77**, 15 (1967).

(9) Processes involving hydrogen abstraction by locally generated, free hydroxyl or carboalkoxy radicals and recombination in the solvent cage must also be considered as possible explanations for the observed regioselectivity and stereospecificity (cf. ref 3b), but it is not apparent how such a recombination process could occur without concomitant involvement of the metal.

(10) Exchange rates for aqueous Fe(III) are ca. 10^3; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, p 152.

(11) J. T. Groves and M. Van Der Puy, *J. Am. Chem. Soc.*, **97**, 7118 (1975).

(12) The carbon dioxide produced upon peracid reductive decarboxylation may be regarded as a barrier to electron transfer from the carbon radical to Fe(III). Thus, loss of stereochemistry by intracomplex rotations occurs in the time required for the neutral molecule to diffuse from the molecular cavity. Various aspects of this process are under further study.

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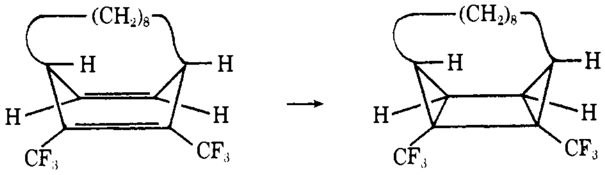
Metathesis. Diene and Cyclobutane Interconversions[1]

Sir:

The remarkable olefin disproportionation reaction commonly referred to as olefin metathesis has received extensive attention in recent years.[2] In particular, the mechanism of these astounding interconversions has been the topic of intensive discussion.[2] The intervention of a "concerted" switching of carbons through a "quasicyclobutane" transition state,[3] the intermediacy of a metallocyclopentane,[4] and the generation of metallocyclobutanes[5] have all been proposed as parts of various mechanistic explanations. A key point in practically every mechanistic discussion has been the failure of olefins and cyclobutanes to interconvert under metathesis conditions. It has been noted that "cyclobutanes are not products of the reaction, and olefins are not converted into cyclobutanes under the disproportionation reaction conditions," [3] and "no cyclobutane has been found to evolve from the reaction." [5] In general, most recent publications[5] have invoked the intermediacy of metallocyclobutanes as a rationale for the data obtained. To some extent, it was indicated that other mechanisms, such as those involving a "quasicyclobutane" transition state, were no longer acceptable. We now wish to report that, in certain cases, cyclobutanes can be converted quantitatively into olefins[6] and more importantly that *in one case two nonconjugated olefinic groups can be converted into a cyclobutane in close to quantitative yield by a commonly accepted metathesis catalyst.*

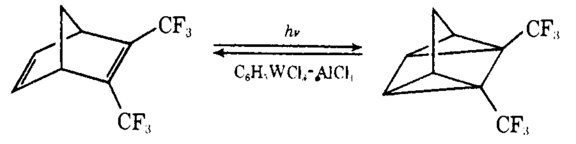
Although there is little difference in the free energy of a cyclobutane as compared to the free energy of two isolated double bonds, the comparable difference between a cyclobutane and a metal-complexed diene system is less well established. In principle, a cyclobutane ring should not be capable of any significant degree of stabilization through complexation with a metathesis catalyst. Thus, in order for a cyclobutyl system to be isolated from a metathesis reaction, a cyclobutane derivative in which the cyclobutyl moiety is more stable than the corresponding metal-complexed diene is required. In considering these principles, we decided that such a system might be available in the inside-outside bicyclic structures that have been of recent interest in our laboratories.[7] We have previously established[7] that 11,12-bis(trifluoromethyl)-(i,o)-bicyclo[8.2.2]tetradeca-11,13-diene (**1**) was readily converted into 1,12-bis(trifluoromethyl)-(i,o)-tetracyclo[$10.2.0.0^{2,14}.0^{11,13}$]tetradecane (**2**) on irradiation. Furthermore, **2** showed excellent thermal stability and was not converted back to **1** on treatment with various transition metal complexes, which were known to convert derivatives of tetracyclo[$3.2.0.0^{2,7}.0^{4,6}$]heptane into derivatives of bicyclo[2.2.1]hepta-2,5-diene.[6] These observations indicated to us that **2** might be considerably more stable than **1**. If **2** were much more stable than **1**, it should serve as an excellent substrate for testing whether cyclobutanes can be isolated from dienes in the presence of metathesis catalysts.



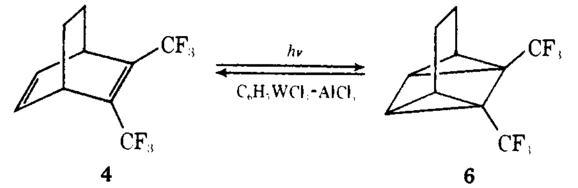
1 **2**

In order to test this concept, a sample of **1** was treated with approximately 0.1 equiv of the 1:1 complex[5,8,9] derived from phenyltungsten trichloride and aluminum trichloride in an argon atmosphere. After stirring for 5 min, the reaction was quenched by bubbling air through the solution.[10,11] Vapor phase chromatographic analysis of the resultant solution indicated that it contained only **1** and **2** in the ratio of 2:98. Analysis vs. an internal standard indicated that the conversion of **1** into **2** had occurred in quantitative yield. Isolation of this isomerization product indicated that it was identical in all respects (VPC retention times, ir, NMR) to a sample of **2** prepared via the irradiation of **1**.[12]

In order to establish that our observations were not due to the presence of the trifluoromethyl groups on **1**, we exposed 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (**3**) and 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (**4**) to the metathesis catalyst described above. These dienes appeared to be unreactive under the reaction conditions. However, when their photoproducts **5** and **6** were exposed to the catalyst system, they were rapidly converted into the dienes **3** and **4**, respectively.



3 **5**



4 **6**

In addition to constituting the first example of a metal complex promoted conversion of a diene into a highly strained polycyclic ring system, the catalytic transformation of **1** into **2** firmly establishes that cyclobutanes can be generated from dienes in the presence of metathesis catalysts. The conversion of **5** and **6** into **3** and **4**, respectively, demonstrates that unless the molecule is suitably designed, the normal course of events would lead to the transformation of a highly strained cyclobutyl moiety into a diene system. The implications of these observations relative to the mechanis-