Organometallic Catalysis: Formation of 1,3-Dioxolanes and Their Analogs Catalyzed by Methylrhenium Trioxide (MTO)

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Received March 20, 1997[⊗]

Methylrhenium trioxide (MTO) catalyzes several cycloaddition reactions. 1,3-Dioxolanes were obtained in good yields from the reactions of epoxides with aldehydes or ketones; the geometric configuration of the epoxide substituents remains unchanged in the product, which was shown to be the consequence of two configuration inversions in sequence. The independently known bis(alkoxy)rhenium complex formed from MTO and the epoxide is an intermediate that could be detected at a low level during the reaction; indeed, its formation limits the rate of the overall reaction. Related cycloaddition reactions are the formation of ketene acetals from diphenylketene and epoxides and of oxazolidines from aromatic imines and epoxides, both MTO-catalyzed.

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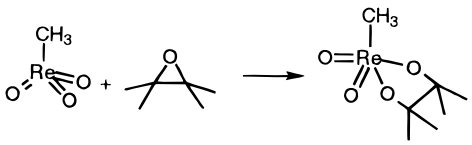
Published on August 5, 1997 on http://pubs.acs.org | doi: 10.1021/om970225r

Introduction

Methylrhenium trioxide (CH_3ReO_3, abbreviated as MTO) is an attractive catalyst for a considerable range of organic transformations. MTO catalyzes numerous oxidations with hydrogen peroxide: the epoxidation of olefins[1−4] and the oxidation of anilines,[5] alkynes,[6] arenes,[7] sulfides,[8,9] phosphines,[10] and cobalt thiolates.[11] Other organic transformations catalyzed by MTO include oxygen transfer,[12] transfer of a carbene fragment from diazo compounds and of a nitrene from organic azides,[13] dehydration and disproportionation of alcohols,[14] metathesis of olefins,[15,16] and aldehyde olefination.[17,18]

Bis(alkoxy)rhenium(VII) complexes are formed in excellent yield from MTO and excess epoxide (eq 1).[19]



(1)

This reaction illustrates the affinity of the electropositive rhenium center for oxygen-donor Lewis bases. Interactions such as this are the key to the catalytic reactions of MTO. They suggested to us that the compound so formed could be a useful intermediate in certain organic transformations.

Practical applications abound for 1,3-dioxolanes (acetals),[20] including synthetic carbohydrate[21] and steroid[22] chemistry. In the pharmaceutical[23] and fragrance[24] industries, 1,3-dioxolanes are used both as intermediates and as end products. Many polymers and copolymers have been reported in the patent literature.[25] The current methods are these: 1,3-dioxolanes can be prepared from acid-catalyzed dehydration reactions between carbonyl compounds and diols, from the reactions of vinyl ethers or 2,2-dimethoxypropane and DMF with diols, from carbonyl compounds and cyclic sulfites, and from interchange reactions as with alcohols.[20] 1,3-Dioxolanes can also be prepared from 1,2-dioxetanes and diazoalkanes, with considerable loss to byproducts.[26] The MTO reaction, as described subsequently, retains the configuration of the epoxide in the dioxolane product and appears to be distinctive in that respect.[20] Despite the slowness of the reactions described here, they may find use because of their stereoselectivity.

Unlike these reactions between oxiranes and carbonyl compounds, ketene acetals and oxazolidines need a longer time to form and give low yields; thus, these procedures may be not useful as preparative methods. Therefore, only a limited investigation was undertaken on two such reactions: ketene acetals prepared from diphenylketene and epoxides and oxazolidines from organic imines and epoxides. These reactions are

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S0276-7333(97)00225-2 CCC: $14.00 © 1997 American Chemical Society

Table 1. Yields of 1,3-Dioxolanes from Epoxides and Carbonyl Compounds

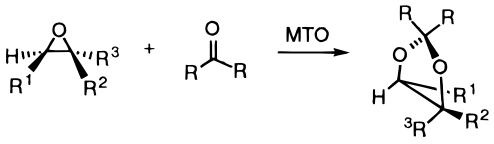
Carbonyl compound ↓ / Epoxide→	Me	Ph	Ph, Ph (4 days)[j]	Ph, Ph
cyclopentanone	87%	81%	89%	87%
3-pentanone	37	trace	42	44
cyclohexanone[a]	>95	86[b]	>96	90
acetaldehyde		88[c]	>96	~100[d]
benzaldehyde	>96[e]	94[f]	91	88[g]
n-butyraldehyde	87[h]	>95[i]		
acetone	82	61		
2-cyclohexenone	16 (5 days)			

[a] With cyclododecane epoxide, >96% product. [b] This reaction was also carried out in refluxing chloroform in effort to improve the yield; in 22 h 87% conversion of styrene oxide was obtained but only a 42% yield of the dioxolane, owing to the catalytic polymerization of styrene oxide at this temperature. [c] cis/trans = 1.5. [d] cis/trans = 1.3. [e] cis/trans = 1.4. [f] cis/trans = 1.6. [g] cis/trans = 2.5. [h] cis/trans = 1.5. [i] cis/trans = 2.0. [j] All the reaction times are 2 days unless noted.

related to dioxolane formation and thus shed further light on the mechanism involved.

Results

1,3-Dioxolanes. These compounds are formed from epoxides and carbonyl compounds as represented by eq 2. Five epoxides were used in this study: propylene



(2)

oxide, styrene oxide, cyclododecane epoxide, *trans*-stilbene oxide, and *cis*-stilbene oxide. Without MTO, no reaction occurred between any of these compounds and the aldehydes and ketones used. The catalytic preparations were carried out in chloroform at room temperature; the carbonyl compounds were taken in small excess over the epoxide, and MTO was added at the 1% level.

Table 1 lists the results of these preparations. Most reactions proceeded in good to excellent yields. Lower yields were obtained with 3-pentanone and cyclohexenone, in comparison with e.g. cyclopentanone and cyclohexanone; 2,6-dimethylcyclohexanone did not react at all. The conformations of the epoxide substituents remained the same in the products. A control reaction between propylene oxide and cyclohexanone in chloroform-*d* was monitored by ^{1}H NMR. It proved possible

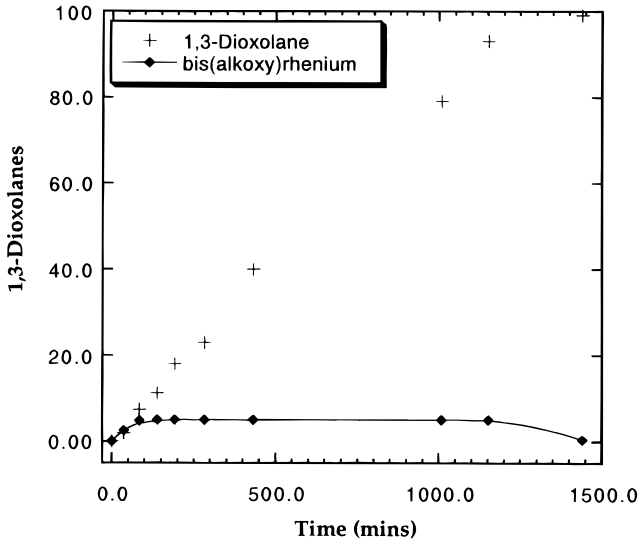


Figure 1. Concentrations from ^{1}H NMR data of the product (1,3-dioxolane) and the bis(alkoxy)rhenium intermediate during the reaction of propylene oxide (0.2 mL, 2.8 mmol) and cyclohexanone (0.32 mL, 3 mmol) in 1.5 mL of deuterated chloroform. The solution contained 0.14 mmol (5%) of MTO.

to follow not only the buildup of the dioxolane product but also the rise and fall of the bis(alkoxy)rhenium complex (eq 1). This intermediate rose in concentration rapidly at the beginning and then quickly leveled off to some 5−7% of the material balance until dioxolane formation was complete, at which point it fell off again. An example of the concentration profiles is shown in Figure 1.

Among the reactions given in Table 1 is that between *trans*-stilbene oxide and several carbonyl compounds. This is noteworthy, in that this is the only epoxide that failed to react with MTO to yield a bis(alkoxy)rhenium complex.[19] At the higher concentrations used for the catalyzed reaction, however, a small concentration of the bis(alkoxy)rhenium complex could be detected by ^{1}H NMR when the two compounds were mixed in chloroform-*d*. The intensities of the peaks were imprecise since the concentration of the intermediate was so low, but they were about in the expected 3:2:10 ratio for the three peaks at δ 2.47 (s), 4.57 (s), and 7.44 (m). The reaction between the carbonyl compounds and this low-level complex draws dioxolane formation to completion *via* the bis(alkoxy)rhenium complex.

Controls. An experiment concerning the intermediacy of the bis(alkoxy)rhenium complex was conducted with MTO and styrene epoxide in a 1.5:1 ratio in chloroform. After about 1 day, when nearly the maximum concentration of MTO had been converted to its bis(alkoxy) complex according to eq 1, benzaldehyde was then added in the usual amount, ca. 20 times the amount of MTO. Twelve hours later, all of the bis(alkoxy)rhenium complex had been converted to the corresponding 1,3-dioxolane. The presence of air proved immaterial. The final solutions contained MTO at very nearly the same concentration level taken at the outset: catalyst deactivation is not an issue.

The effect of water was also examined. When the reaction was carried out as before, save that water had been added in an amount equivalent to the MTO (and 1% of the epoxide), no reaction was observed. To explore the effect of water further, two 1,3-dioxolanes, obtained

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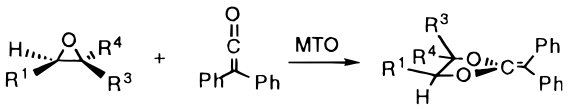
from the reactions of butyraldehyde with styrene oxide and propylene oxide, were dissolved in chloroform. With or without water added at the 10 mM level of the substrate, MTO did not catalyze the reverse reaction. Clearly, water prevents dioxolane formation and it does not hydrolyze the dioxolane, once formed.

^{18}O Tracer Experiments. In the reaction between acetaldehyde and propylene oxide, ^{18}O-labeled MTO, 84% enriched, was used as catalyst. In this reaction, 0.35 mL of propylene oxide (5 mmol) and 0.5 g of MTO (2 mmol) were mixed in 20 mL of chloroform at room temperature, and 0.28 mL of acetaldehyde was then added. The high-resolution mass spectrum of the 1,3-dioxolane was determined after isolation. In addition to a larger amount of product with the parent peak at 102.0608, the MS of this compound also has a peak that was absent with unlabeled MTO. Its mass of 104.0724 compares with 104.1328, the theoretical mass of a product with one oxygen-18. This finding suggests that one, but only one, oxygen of the 1,3-dioxolane is from ^{18}O-labeled MTO; moreover, it supports our conclusion that MTO does mediate the reaction.

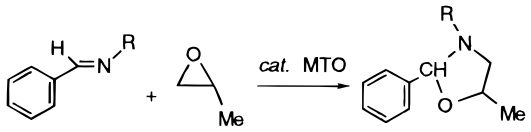
Formation of Ketene Acetals. In the presence of MTO, diphenylketene and epoxides yield diphenylketene acetals in chloroform at room temperature (eq 3). The



(3)

major product of this reaction was a ketene polymer, and so the acetal yields were 22−39%, as summarized in Table 2 for three epoxides.

Oxazolidines. The reaction between organic imines and epoxides is also catalyzed by MTO; in two trials it yielded oxazolidines as the only product (eq 4). The reaction is prohibitively slow, however, even when run in propylene oxide as the solvent. With 10% MTO, the product was formed in ca. 60% yield after 3 weeks. The data are given in Table 3. No other diastereoisomers were observed in these reactions.



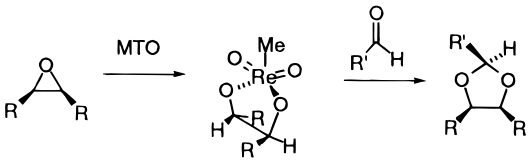
(4)

Discussion

In our previous study of the reaction between MTO and epoxides (eq 1) we did not observe a back-reaction by dissolving isolated bis(alkoxy)rhenium complexes in anhydrous chloroform-*d*.[19] Here, we have shown that bis(alkoxy)rhenium compounds can be detected during the reactions with carbonyl compounds but that they are absent at the end. It is reasonable to surmise, therefore, that the bis(alkoxy)rhenium compound is an intermediate. For that to be the case, it needed to be shown that such compounds, formed independently, yield the dioxolane upon addition of an aldehyde or ketone. This proved to be so.

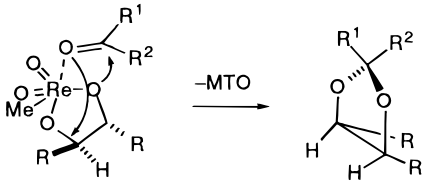
Moreover, approximate rate data showed that the products were formed more slowly than the oxirane was converted to the intermediate. This finding can be seen in Figure 1, in which the concentration of the intermediate reached the level of the initial concentration of MTO and then remained constant during ca. 80% of the total reaction time. Of the two steps, therefore, the first is rate-controlling.

We also found that the stereochemical configuration of the epoxide was maintained in the dioxolane. An independent study[27] of the reactions between MTO and both diol or epoxide showed that the 1,3-dioxolane formation occurs in two steps, each proceeding with inversion of configuration:



(5)

From these results we infer that the carbonyl compound ^{1}R^{2}RC═O, with ^{2}R being the larger group, attacks the bis(alkoxy)rhenium intermediate as depicted in eq 6.

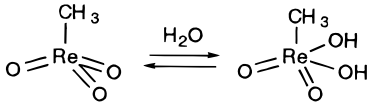


(6)

This picture accounts for cis/trans ratios >1 and for the retention of the steric configuration of the epoxide as a consequence of sequential inversions. In this model, the loose coordination of the carbonyl oxygen to the electropositive rhenium center brings the molecule into the reaction range, allowing two nucleophilic attacks by oxygen on carbon. Since the concentration of the complex formed from MTO and *trans*-stilbene oxide is very low, the reactions of *trans*-stilbene oxide with carbonyl compounds are slower than those of *cis*-stilbene oxide.

Indeed, the formation of both ketene acetals and oxazolidines can be explained by the same pathway. Were there no coordination between the bis(alkoxy)-rhenium complex and the carbonyl compounds, sterically encumbered compounds such as 2,6-dimethylcyclohexanone and 3-pentanone should react as well as the others. Electronic effects are also evident, in that cyclohexenone reacted poorly.

In the presence of water, the competition for MTO between water and the epoxide favors water (eq 7) over the epoxide (eq 1). In this model water is expected to



(7)

inhibit the reaction as it becomes higher in concentra-

(27) The same configuration of substituents on the diol was found in the product of the reaction between (1*R*,2*R*,3*S*,5*R*)-(−)-pinanediol and MTO, showing that the diol configuration was maintained. Reasonably, therefore, the same is true for the other diols. We found that the ^{1}H NMR spectrum of *meso*-2,3-butanediol and MTO product in $CDCl_3$ is the same as that of the material obtained from *trans*-2,3-epoxybutane and MTO (δ 5.23 ppm, m, 2H; 2.44 ppm, s, 3H, CH_3−Re; 1.30 ppm, d, 6H, 2Me). The product from (2*S*,3*S*)-(+)-2,3-butanediol and MTO has the same ^{1}H NMR in $CDCl_3$ as that obtained from *cis*-2,3-epoxybutane and MTO (δ 4.69 ppm, m, 2H; 2.44 ppm, s, 3H, CH_3−Re; 1.35 ppm, d, 2Me).

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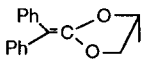
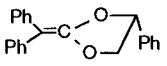
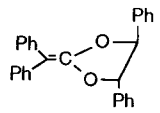
Table 2. Formation of Ketene Acetals

Epoxide	Product (Analysis)	% Yield (mp/°C)	^{1}H–NMR	^{13}C–NMR
	 Anal. Found: C, 80.88; H, 6.48 $C_{17}H_{16}O_2$ requires: C, 80.93; H, 6.39	39 (5-7)	1.37(d, 3H, J 5.1 Hz), 3.58 (dd, 1H, 5.4Hz, 7.2 Hz), 3.98 (dd, 1H, 5.7Hz, 7.2 Hz), 4.11 (m, 1H), 7.17-7.44 (m, 10H)	18.55, 70.61, 72.24, 111.84, 127.40, 128.53 129.33, 132.23, 136.72
	 Anal. Found: C, 83.95; H, 5.81 $C_{22}H_{18}O_2$ requires: C, 84.05; H, 5.77	28 (88-90)	3.89 (dd, 1H, 5.1Hz, 7.8 Hz), 4.31 (dd, 1H, 5.7Hz, 7.8 Hz), 5.07 (m, 1H), 7.14-7.88 (m, 15H)	72.25, 79.37 113.60, 126.37 126.69, 127.36, 128.43, 128.53 129.31, 132.27 136.70, 139.02
	 Anal. Found: C, 86.08; H, 5.73 $C_{28}H_{22}O_2$ requires: C, 86.13; H, 5.68	22 (119-122)	5.61 (s, 2H), 7.11-7.71 (m, 20H)	85.23, 114.68 126.33, 127.40, 128.49, 128.57 129.40, 132.26, 136.14 136.69, 138.26
		<5(from GCMS); not isolated [a]		

[a] A peak in GC–MS has *m/z* equal to the sum of epoxide FW and ketene FW; it may be the acetal.

tion, consistent with experiment. We thus infer that the hydrolyzed form of MTO shown in eq 7 is not active in these reactions. This conclusion is supported by the fact that eq 7 and its analogs provide the pathway for the rapid exchange of oxygen atoms between MTO and water,[28a] for the initial step in the reaction between MTO and H_2O_2,[29] and for condensation and other reactions of alcohols catalyzed by MTO.[14]

Experimental Section

General Considerations. The epoxides, ketones, aldehydes, and solvents are commercially available. They were purified by standard methods.[30] MTO was either prepared from dirhenium heptaoxide and tetramethyltin[28b] or purchased. Organic imines (Schiff bases) were available from a previous study.[13] Diphenylketene was prepared from azibenzil[31] and was used as freshly distilled. The cis isomers were assigned according to the literature or by comparison with typical ^{1}H NMR data.[38]

^{18}O-Labeled MTO. ^{18}O-labeled MTO was prepared using $H_2{}^{18}O$ in reaction 6, conducted under argon: MTO was dissolved in anhydrous acetonitrile, then >4 times the mole ratio of $H_2{}^{18}O$ was added. The solvents were removed under vacuum after 30 min. Then ^{18}O-labeled MTO was sublimed under vacuum at about 40 °C.

High-resolution MS was performed on a Kratos MS 50 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained

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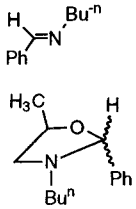
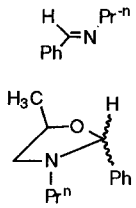
Table 3. Formation of Oxazolidines with Propylene Oxide

Imine (Product) Analysis	% Yield (mp/°C)[c]	^{1}H–NMR	^{13}C–NMR
 Anal. Found: C, 76.59; H, 9.69 N, 6.33 $C_{14}H_{21}NO$ requires: C, 76.67; H, 9.65 N, 6.38	60 [a] (140-143)	**cis**: 0.81 (t, 7.5Hz, 3H), 1.30-2.18 (m, 4H), 1.12 (d, 6.3Hz, 3H), 2.48 (t, 6.9Hz, 2H), 2.70 (dd,1H, 7.2, 9.3 Hz), 2.96 (dd,1H, 4.5, 9.3 Hz), 4.42 (m,1H), 4.76 (s,1H), 7.30-7.85 (m, 5H), **trans**: 0.84(t, 7.5Hz, 3H), 1.28-1.70 (m, 4H), 1.33 (d, 6.6Hz, 3H), 2.39 (t, 6.9Hz, 2H), 3.51 (dd, 1H, 5.4, 8.7 Hz), 3.82 (dd, 1H, 4.2, 8.7 Hz), 4.31 (m, 1H), 4.77 (s, 1H), 7.31-7.84 (m, 5H)	**cis**: 19.72, 20.46, 21.57, 30.74, 51.35, 59.86, 73.18 96.98, 128.06, 128.85, 129.59, 134.29 **trans**: 20.26, 20.28, 20.57, 30.88, 51.58, 58.12, 72.50, 97.94, 128.10, 128.61, 129.98, 133.37.
 Anal. Found: C, 75.94; H, 9.39 N, 6.78 $C_{13}H_{19}NO$ requires: C, 76.06; H, 9.33 N, 6.82	61 [b] (138-141)	**cis**: 0.83 (t, 7.8Hz, 3H), 1.14 (d, 6.3Hz, 3H), 1.45 (m, 2H), 2.18 (t, 6.9Hz, 2H), 2.72 (dd, 1H, 5.1, 9.0Hz), 2.97 (dd, 1H, 4.2, 9.0 Hz), 4.41(m, 1H), 4.76 (s, 1H), 7.31-7.82 (m, 5H) **trans**: 0.84(t, 3H), 1.36 (d, 3H), 1.44 (m, 2H), 2.18 (t, 2H), 3.50 (dd, 1H, J 5.7, 9.9 Hz), 3.78 (dd,1H, J 4.5, 9.9 Hz), 4.31 (m, 1H), 4.78(s, 1H), 7.30-7.81(m, 5H)	**cis**: 17.89, 21.54, 21.85, 53.84, 59.86, 73.18, 97.91, 128.07, 128.24 128.61, 134.31 **trans**: 19.71, 21.42, 21.96, 53.62, 58.12, 72.51, 96.95, 128.12, 128.53 128.86, 134.24

[a] cis/trans = 2.0. [b] cis/trans = 1.5. [c] Melting point of the cis isomer.

at 300 MHz in $CDCl_3$ solution unless otherwise noted; chemical shifts (δ) are relative to either internal TMS (^{1}H NMR) or the solvent resonance (^{13}C NMR). MS data are in units of m/z. GC–MS was performed on a Magnum GC–MS with temperature programming: 60 °C, 2 min; 10 °C/min to 260 °C; 260 °C for 20 min. IR spectra were recorded neat using 3M disposable IR cards (Type 61). Melting points of all products which were recrystallized from chloroform were recorded with a Fisher digital melting point analyzer, Model 355. Separations by HPLC were performed with a Waters 501 HPLC system equipped with an Econosil C18 column. The yields reported are isolated yields unless otherwise noted.

General Procedure for the Preparation of 1,3-Dioxolanes. The epoxide (50 mmol), carbonyl compound (55 mmol), and MTO (0.5 mmol) were dissolved in 40 mL of chloroform and allowed to stand at room temperature for 2–5 days. The reactions were monitored by GC–MS. The product was isolated by vacuum distillation after the epoxide had been consumed, although in many cases the product precipitated from the solution and could be isolated nearly quantitatively by filtration. The products were identified by their mass spectra and ^{1}H and ^{13}C NMR spectra in comparison with values in the literature.[32–34]

The effect of water on both forward and reverse reactions was investigated in chloroform. The general procedure was used as given but with 0.5 mmol of water (i.e., equal to MTO) added in the reaction between 55 mmol of cyclohexanone and 50 mmol of styrene oxide. After 3 days, no 1,3-dioxolane was

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detected by GC−MS. Meanwhile 10 mmol of the 1,3-dioxolanes from butyraldehyde with styrene oxide and propylene oxide along with 0.5 mmol of MTO were dissolved in 10 mL of chloroform without and with 10 mmol of water.

Ketene Acetals. The epoxide (2 mL) and MTO (5 mol % of the ketene) were dissolved in 10 mL of chloroform and allowed to stand for 1 day at room temperature. A chloroform solution of diphenylketene was added dropwise over 3 days. The products were eluted from a silica gel column with ethyl acetate−hexane (1:5). The products were identified by their MS, elemental analyses, and NMR spectra compared with known ketene acetals.[35,36]

Oxazolidines. MTO (10%) was added to the imine (1 mL) dissolved in 10 mL of propylene oxide. After 3 weeks about 60% of the imine had been converted to products as determined by GC−MS; at that time almost no decomposition of the "Me−Re" complex was observed by ^{1}H NMR. Propylene oxide under reduced pressure at room temperature and hexane were then added to the residue to precipitate colorless crystals. The two isomers were separated by preparative HPLC with acetonitrile (3 mL/min) and methanol (1 mL/min). They were identified by MS, elemental analysis, and NMR spectra.[34,37]

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are grateful to Professor B. Sharpless for suggesting experiments relating to the stereochemical course of these reactions.

Supporting Information Available: A table giving the spectroscopic data for the dioxolane products (6 pages). Ordering information is given on any current masthead page.

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