1995

Organic transformations catalyzed by methylrhenium trioxide

Zuolin Zhu
Iowa State University

Organic transformations catalyzed by methylrhenium trioxide

Zuolin Zhu

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1995

Organic transformations catalyzed by methylrhenium trioxide

Zuolin Zhu

Major Professor: James H. Espenson

Iowa State University

Several organic transformations were found to be catalyzed by methylrhenium trioxide, CH_3ReO_3 (MTO): decomposition of ethyl diazoacetate (EDA) to 2-butenedioic acid diethyl esters; cycloadditions of EDA with imines (to aziridines), with olefins (to cyclopropanes), and with aldehydes or ketones (to epoxides). In the presence of MTO, the reactions of EDA with alcohols, phenols, thiols or amines yield, respectively, the corresponding α-alkoxy, α-phenoxy, α-thio ethyl acetate or ethyl glycine esters. These reactions occur under mild conditions and give satisfactory to high product yields.

The other reactions catalyzed by MTO are dehydration of alcohols to ethers and olefins; direct amination of aromatic alcohols, and the disproportionation of alcohols to alkanes and carbonyl compounds.

MTO activates H_2O_2 through the formation of two active species (mono-peroxo-Re(VII) **A**, and bisperoxo-Re(VII), **B**). These two peroxo species oxidize alkynes to the corresponding 1,2-dicarbonyl compounds or carboxylic acids, and anilines to nitroso benzenes or *N*-oxides in high yields. Tertiary phosphines are oxidized by molecular oxygen to the corresponding phosphine oxides in the presence of MTO. Similarly, oxygen transfer from sulfoxides, epoxides, *N*-oxides, triphenylarsine oxide and triphenylstibine oxide to triphenylphosphine is also catalyzed by MTO. The reactions of MTO and epoxides yield bis(alkoxy)rhenium(VII) complexes.

TABLE OF CONTENTS

GENERAL INTRODUCTION

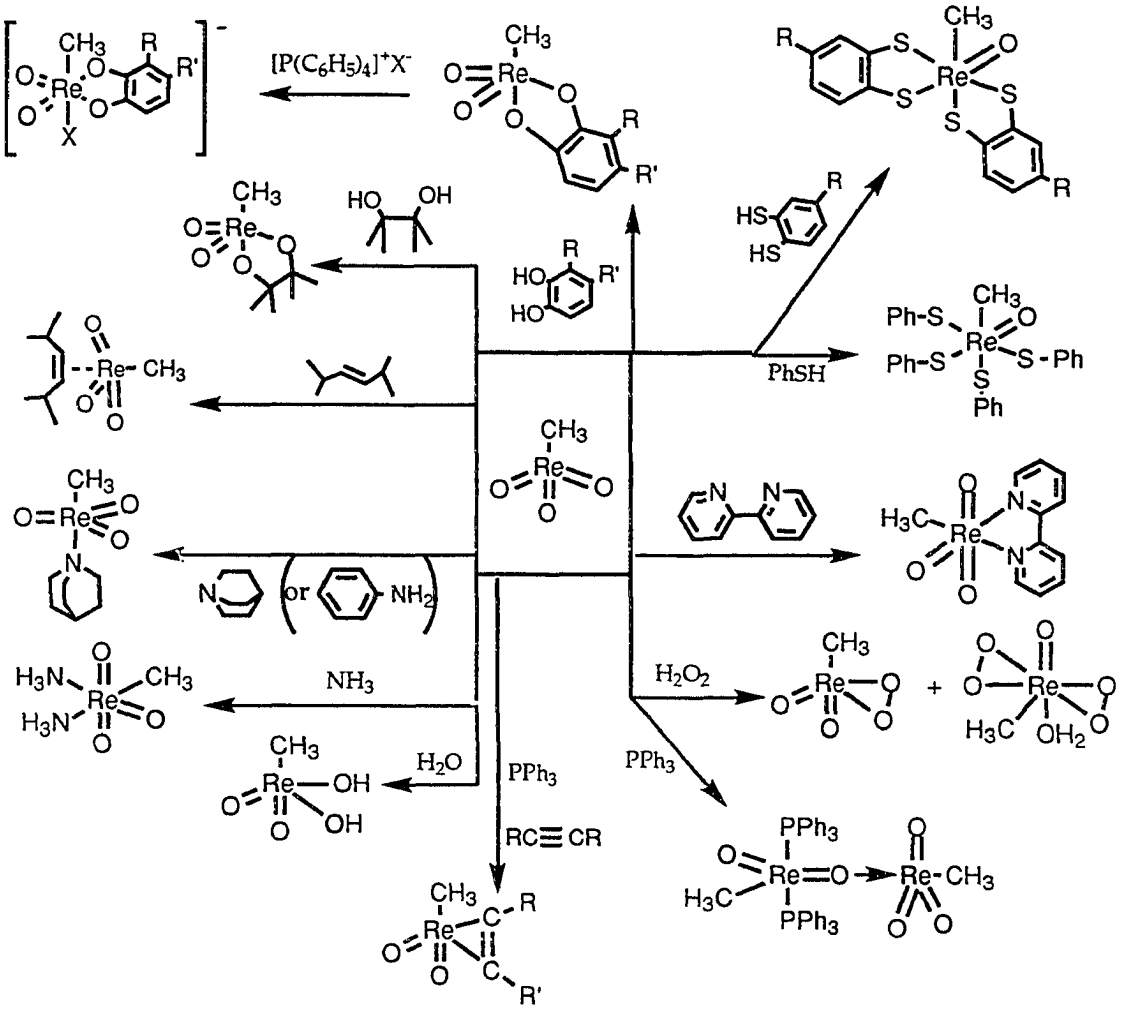
Introduction

Methylrhenium trioxide (MTO), CH_3ReO_3, was first prepared in 1979. An improved route to MTO was devised from dirhenium heptoxide and tetramethyltin in the presence of hexafluoroglutaric anhydride reported by Herrmann in 1992.

MTO forms stable or unstable adducts with electron-rich ligands, such as amines (quinuclidine, 1,4-diazabicyclo[2,2,2]-octane, pyridine, aniline, 2,2'-bipyridine), alkynes, olefins, 1,2-diols, catechols, hydrogen peroxide, water, thiophenols, 1,2-dithiols, triphenylphosphine, 2-aminophenols, 2-aminothiophenols, 8-hydroxyquinoline and halides (Cl^-, Br^-, I^-). After coordination, different further reactions will occur for different reagents. Unstable adducts give secondary reaction products, such as the interaction between MTO and olefins that leads to olefin metathesis, and the interaction between MTO and water that results in oxo-exchange of MTO. There are two kinds of stable adducts. One of them reacts with additional substrates, such as the adducts formed from MTO and hydrogen peroxide. That reaction yields two peroxo complexes which catalytically oxidize almost all oxidizable substrates to their corresponding products (sulfides to sulfoxides, olefin to epoxides, tertiary phosphines to tertiary phosphine oxides, etc.). MTO is an attractive catalyst for these oxidations because hydrogen peroxide is considered to be an environmentally "green" oxidant. Another kind of stable adducts are inert, toward further reactions, such as the adducts formed from MTO and catechols, MTO and 2,2'-bipyridine, etc.

These versatile catalytic and noncatalytic reactions of MTO have triggered a massive area of research waiting exploration. In order to provide a detailed understanding of MTO, and to extend this scheme (**Scheme I**) which is far from complete now, more questions need to be answered about this complex. What kind of compounds can coordinate with MTO, are these kinds of complexes stable or not, what kind of further reactions can occur?

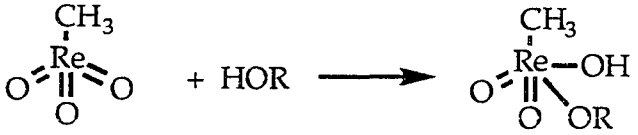
Scheme I



Since the discovery of diazo chemicals in 1858 by Peter Griess, the synthetic uses of organic diazo compounds through thermal and photochemical processes have found important applications in organic chemistry. Due to the complicated thermal or photochemical reactions of diazo chemicals, catalytic methods are need to supplant those processes for efficient cyclopropanation, dipolar addition and insertion.

Methylrhenium trioxide can catalyze the decomposition of diazo chemicals with and without substrates to yield olefins through dimerization; cyclopropanes, aziridines and epoxides by cycloaddition; and α-alkoxy esters, α-thio esters and glycine esters through insertion. Besides diazo compounds, organic azides also have some reactions catalyzed by MTO as described in Chapter I.

Although many efforts have been applied to the catalytic direct ether synthesis with transition-metal complexes, there has been no success until the appearance of MTO. Alcohols, one structural analog of water, coordinate with MTO by a similar pathway to water.



This interaction results in formation of ethers, olefins through dehydration of alcohols, or products from alcohol amination or alcohol disproportionation. The first example of the catalytic direct ether preparation using this transition metal complex as catalyst is shown in Chapter II.

The transfer of an oxygen atom is one of the fundamental processes in chemistry, such as olefin formation by epoxide deoxygenation. Oxygen transfer is

still an interesting area of research in organic synthesis and biochemical studies. Deoxygenation of epoxides, *N*-oxides, sulfoxides and triphenylarsine oxide is catalyzed by MTO as described in Chapter III.

Selective oxidation by molecular oxygen is a desirable method for both organic and industrial preparations. The first report of MTO being reactive in catalytic oxidation with molecular oxygen is given in Chapter III.

From the reported studies, it seems to be true that catalytic oxidation with hydrogen peroxide as oxidant occurs for almost all chemicals that have nucleophilic centers. But many compounds remain untouched so far including alkynes and anilines. Investigations of these oxidations are presented in Chapters IV and V.

Chapter VI describes the interaction between MTO and epoxides which offers a synthetic method for bis (alkoxy) rhenium (VII) complexes.

Dissertation organization

The dissertation consists of six chapters. Chapter I corresponds to a manuscript in preparation. Chapters II, IV and VI are three manuscripts submitted. Chapter III is in press in *J. Mol. Catal.*, and Chapter V has been published in *J. Org. Chem.* Each section is self-contained with its own equations, tables, figures and references. Following the last manuscript is the general conclusion. All the work in this dissertation was performed by myself.

CHAPTER I

ORGANIC REACTIONS OF ETHYL DIAZOACETATE AND ORGANIC AZIDES CATALYZED BY METHYLRHENIUM TRIOXIDE

A paper prepared for *Journal of the American Chemical Society*

Zuolin Zhu and James H. Espenson

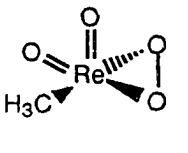
Abstract

Methylrhenium trioxide (CH_3ReO_3 or MTO) catalyzes several classes of reactions of ethyl diazoacetate. Under mild conditions, phenols, alcohols, thiols, amines and imines are converted to α-phenoxy ethyl esters, α-alkoxy ethyl esters, α-thio ethyl esters, *N*-substituted glycine ethyl esters, and aziridines, respectively, in good yield. MTO also catalyzes the conversions of carbonyl compounds and olefins to epoxides or cyclopropanes. Imination of aromatic aldehydes with organic azides in the presence of triphenyl phosphine is also catalyzed by MTO with high yields. The MTO-catalyzed reaction of imines and alkenes forms epoxides. Intermediate carbenoid and nitrenoid species were proposed to explain the results obtained.

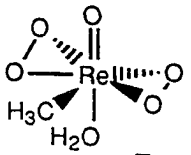
Introduction

Methylrhenium trioxide, during the relatively short period from the original report[1] to the more convenient methods now available,[2-4] already has found wide use in catalysis. The catalytic applications of MTO include the epoxidation[4] and metathesis[5] of olefins, aldehyde olefination,[6] and oxygen transfer.[7] Extensive

reports have now appeared in the area of MTO-catalyzed substrate oxidations with hydrogen peroxide. These include the oxidation of alkenes,[4,8-11] cobalt thiolates,[12] alkyl and aryl sulfides,[13] anilines,[14] alkynes,[15] and phosphines.[16] In many of these instances, the mechanistic features have been explored, implicating either, and usually both, of two rhenium peroxides, $CH_3Re(O)_2(\eta^2\text{–}O_2)$ (**A**) and $CH_3Re(O)(\eta^2\text{–}O_2)_2(H_2O)$, **B**.

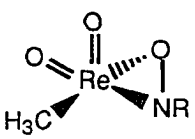


A

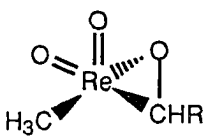


B

Certain catalytic applications of MTO to organic reactions that do not utilize peroxide have now been realized. We were led in this direction from the understanding we had developed about the peroxide mechanism. The isoelectronic principle suggested the plausibility of two other molecules, analogous to **A**. We call them $\mathbf{A_N}$ and $\mathbf{A_C}$:



$\mathbf{A_N}$



$\mathbf{A_C}$

The notation suggests that these intermediates might be nitrene and carbene equivalents ("nitrenoid" or "carbenoid" species), in the sense that **A** itself can be regarded as an "oxene" equivalent. Needless to say, we hoped to learn whether such species might transfer NH, NR, or CHR groups to an appropriate electron-rich acceptor in the same way that **A** transfers an oxygen.

Our initial attempts to form $\mathbf{A_N}$ used hydroxylamines (and, analogously, hydrazines), which are isoelectronic with hydrogen peroxide. Repeated attempts along these lines have not yet succeeded. We then discovered that ethyl diazoacetate and organic azides will transfer "$CHCO_2Et$" and "NR" functional groups in reactions that are catalyzed by MTO, giving satisfactory, and often nearly quantitative, yields of pure product. Methylrhenium trioxide efficiently catalyzes the formation of: (1) alkoxyester, thioester and glycine ester derivatives from alcohols, phenols, thiols and secondary or primary amines; (2) aziridines from organic imines; (3) organic imines from aromatic aldehydes; (4) cyclopropanes from olefins, and (5) epoxides from aldehydes or ketones. The traditional methods for many of these transformations are often time-consuming, requiring significant work-up, sometimes proceeding in lower yields, and, on a large scale, produce by-products and wastes. The MTO reactions, on the other hand, are environmentally preferred.

The catalytic reactions are described here, not the detection or validation of the suggested intermediates. At the present time $\mathbf{A_N}$ and $\mathbf{A_C}$ remain hypothetical constructs that provide a tentative basis for rationalizing the transformations that MTO catalyzes, but they remain unconfirmed.

Results

MTO-catalyzed decomposition of ethyl diazoacetate (EDA). In accord with a previous report,[6] EDA is converted to diethyl maleate (predominantly) and fumarate, and to smaller amount of ethyl glyoxalate azine. Both reactions are catalyzed by MTO, eq 1.1. Complete reaction of EDA (10 mmol) with 10% MTO in dry benzene required 6 hr. at 60 °C, or one week at room temperature.

$$2N_2CHCO_2Et \xrightarrow{cat.\ MTO} EtO_2CCH{=}CHCO_2Et + 2N_2 \qquad (1.1)$$

$$2N_2CHCO_2Et \xrightarrow{cat.\ MTO} EtO_2CCH{=}N{-}N{=}CHCO_2Et + N_2 \qquad (1.2)$$

With MTO, the observed cis:trans ratio of the olefins was 9:1, and in the reactions described in subsequent sections, where the olefins were obtained as byproducts, the cis:trans ratios lay between 7:1 and 9:1. In comparison, the high-temperature (> 200 °C) decomposition of EDA gave a trans:cis ratio of 1.3:1.

The amount of the azine obtained depended on the concentrations of EDA and MTO. The azine was obtained in about 10% yield when the MTO was taken in only 3% of the amount of the EDA. On the other hand, with MTO present at only 0.2% of the EDA, all of the EDA was converted to the azine. The variation in the concentration of the azine found at the end of the decomposition of the EDA is displayed in **Figure 1.1.** The mathematical analysis of this dependence is given in the Discussion section, where the chemical model is presented.

When trace amounts of water were present, ethyl glycolate ($EtCO_2CH_2OH$) formed rapidly; for that reason, all of the reactions reported herein were investigated in dry organic solvents.

Ether formation. A series of phenols and primary, secondary, and tertiary aliphatic alcohols were used in the EDA/MTO catalytic system. This resulted in alkoxy and phenoxy esters, in which a new ether linkage was realized. The net reaction is:

$$ROH + N_2CHCO_2Et \xrightarrow{cat.\ MTO} ROCH_2CO_2Et + N_2 \qquad (1.3)$$

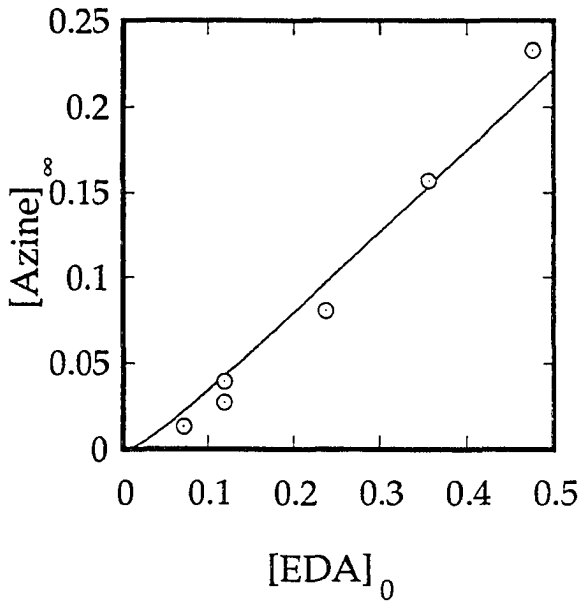


Figure 1.1 The MTO-catalyzed decomposition of ethyl diazoacetate (EDA) yields a mixture of an azine and of diethylmaleate, as shown in Scheme 3. The final concentration of the azine product depends on the initial concentration of EDA; the smooth curve is the least-squares fit to eq A-4, which follows from this reaction scheme.

The reactions were carried out with nearly comparable amounts of EDA and alcohol (50 mmol), and 0.4% (0.2 mmol) of MTO. The substrate alcohols and the yields of products obtained are listed in **Table 1.1.** The phenols and the small molecular weight primary alcohols react nearly quantitatively (≥ 87% isolated yields). Only a trace of the fumarate and maleate esters were obtained then, and none of the azine, even when low levels of MTO were used. The yields dropped with the larger and more branched alcohols, the lowest being a 57% yield from tert-amyl alcohol. The balance of the material was the fumarate and maleate esters.

Table 1.1 Yields[a] of alkoxy and phenoxy esters obtained from the reactions of alcohols (ROH, ArOH) and ethyl diazoacetate in the presence of MTO

R	Yield (%)	Ar	Yield (%)
Methyl	93	C_6H_5	87
Ethyl	90	*p*-Me-C_6H_4	91
n-Propyl	92	*p*-Et-C_6H_4	90
n-Butyl	88	*p*-Bu^t-C_6H_4	90
n-Heptyl	84	*p*-MeO-C_6H_4	92
$PhCH_2CH_2$	87	*p*-Cl-C_6H_4	84
$C_6H_5CH_2$	89		
p-Me-$C_6H_4CH_2$	90		
PhC(Me)H	72		
2-Propyl	63		
tert-Amyl	57		

[a] The yields are referred to EDA, which was limiting (50 mmol) compared to the alcohol (54 mmol).

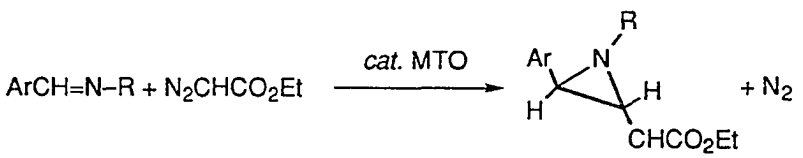
Formation of S–C and N–C single bonds. Analogous to the reactions in the preceding section, thiols and (mostly primary) amines are converted with EDA/MTO into thioesters (eq 1.4) and glycine esters (eq 1.5). Only a trace of the fumarate or maleate esters was observed, and none of the azine, even when MTO was used at the 0.5% level.

$$RSH + N_2CHCO_2Et \xrightarrow{cat.\ MTO} RSCH_2CO_2Et + N_2 \qquad (1.4)$$

$$RNH_2 + N_2CHCO_2Et \xrightarrow{cat.\ MTO} RNHCH_2CO_2Et + N_2 \qquad (1.5)$$

The use of the thiol and amine reagents as solvent resulted in very fast reactions. For the thiols either the MTO was dissolved in EDA and the thiol added promptly to the mixture, or (without difference) the EDA was added to a solution of the MTO in the thiol. These reactions were complete within minutes with isolated yields exceeding 95%; see **Table 1.2**. For the amines, the MTO was dissolved in the amine, and the EDA added last. There reactions were complete in one hour and gave >85% product yield; see **Table 1.3.**

Synthesis of aziridines. Aziridines result from EDA/MTO in reaction with imines, also prepared with MTO catalysis as reported in a subsequent section. Aromatic imines were used as substrates in this study. The C=N double bond of the imines was converted to an aziridine under mild conditions; this cycloaddition reaction (eq 6) was catalyzed by MTO.



(1.6)

Table 1.2 Yields[a] of thioesters obtained from the reactions of thiols and ethyl diazoacetate in the presence of MTO

RSH	Yield (%)	RSH	Yield (%)
EtSH	93	C_6H_5SH	96
n-PrSH	95	*p*-MeO-C_6H_4SH	94
n-$C_6H_{13}SH$	95	*p*-Cl-C_6H_4SH	91
sec-C_4H_9SH	89		

[a] The yields are referred to EDA, which was limiting (50 mmol) compared to the thiol (54 mmol).

Table 1.3 Yields[a] of glycine esters obtained from the reactions of amines and ethyl diazoacetate in the presence of MTO

R	Yield (%)	R	Yield (%)
n-Propyl	87	C_6H_5	89
n-Hexyl	91	*p*-Me-C_6H_4	91
tert-Butyl	82	*p*-Cl-C_6H_4	83
$PhCH_2$	84		
$PhCH_2CH_2$	85	1-Piperidinyl	88
		1-Pyrrolidinyl	90

[a] The yields are referred to EDA, which was limiting (50 mmol) compared to the amine (54 mmol).

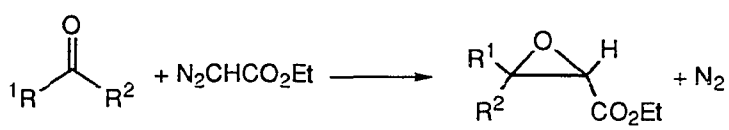
The yields of the aziridines were essentially quantitative (≥ 87%), as specified in **Table 1.4.** As to by-products, only a trace amount of the fumarate and maleate esters could be detected, and none of the azine. Only a single isomer of the aziridine was obtained, as determined by GC-MS. The coupling constant for the ring protons for these products are in the range 2–6 Hz, which verifies that the trans (E) isomer obtained. For example, the product from PhCH=NPh has J_{HH} = 2.2 Hz in $CDCl_3$, which agrees with an earlier report.[17]

Table 1.4 Yields[a] of aziridines obtained from aryl imines (ArCH=NR) and EDA, with MTO as catalyst

	Yield (%)		
Ar	R = *n*-Hexyl	R = *n*-Butyl	R = Phenyl
C_6H_5	93	92	87
p-MeO-C_6H_4	94	94	92
p-NO_2-C_6H_4	92	91	
p-Me-C_6H_4	93	93	
2-Napthyl	96	96	

[a] Isolated yields, after vacuum distillation, relative to EDA, the limiting reagent.

Formation of epoxides. Carbonyl compounds, both aldehydes and ketones, are converted to epoxides by EDA. The net reaction is



(1.7)

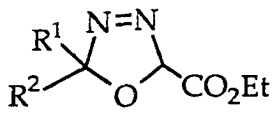
Table 1.5 Yields[a] of epoxides obtained from aldehydes and ketones

R^1	R^2	Yield (%)
C_6H_5	H	79 (52)[b]
n-Propyl	H	75
sec-Bu	Me	64
C_6H_5	Me	57
iso-Propyl	Me	49

[a] Isolated yields, after vacuum distillation, relative to EDA, the limiting reagent.

[b] The lower yield was obtained when the EDA was added all at once.

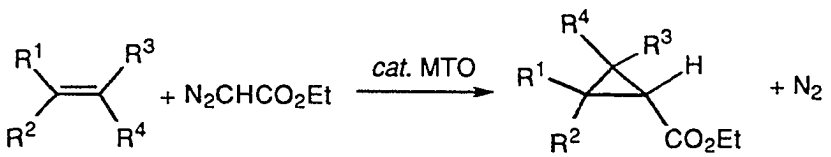
The rates decrease in the order aliphatic aldehydes > aromatic aldehydes > ketones. The aldehyde reactions form largely the isomer of the epoxide in which the two bulkiest groups ($CHCO_2Et$ and, say, R^1) are in a trans disposition. The ketone reactions, on the other hand, yield both geometric isomers in comparable amounts, as described in experimental section. In addition to the epoxides, which are formed in yields of 49–79% (see **Table 1.5**), a minor product was also seen in the GC–MS data. Although this method is not quantitatively reliable, a yield of some 5–15% of that product might be inferred. It has a molecular weight exactly equal to the combined formula weights of EDA and the carbonyl compound. We were unable to isolate this product with vacuum distillation or column chromatography; it decomposed in both cases. This product is Δ^3-1,3,4-oxadiazoline, **1**, an analogy with the 1-pyrazolines formed as a side product along with the cyclopropanes formed from alkenes and EDA (see the next section).



1

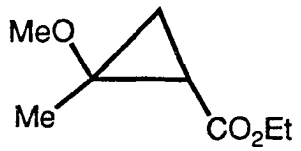
The reaction of aldeydes or ketones with EDA is clearly not the most useful epoxide synthesis that one might devise. More useful epoxide-forming reactions include alkene-hydrogen peroxide reactions catalyzed by MTO.[4,8,18,19] Nonetheless, epoxide formation in these cases provides information as to the breadth of MTO catalytic chemistry and is instructive as to the mechanisms.

Formation of cyclopropanes. Owing to the importance of cyclopropyl rings, we chose to investigate cycloaddition reactions of alkenes with EDA/MTO. The cyclopropanation reactions occur according to this net reaction,

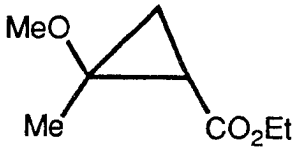


(1.8)

The olefin itself was used as the solvent; reactions occur but very slowly in dry benzene and methylene chloride. Isolated yields of 57–87% of the cyclopropanes were obtained (**Table 1.6**). Again, the reaction forms the cyclopropane product in which the bulkiest groups are disposed trans relative to one another; singly-substituted olefins give solely the trans product. For 1,1-disubstituted olefins, two isomers were obtained as reported in experimental section. For example, 2-methoxy-propene yields the cyclopropanes **C** and **D** in 2:1 ratio.

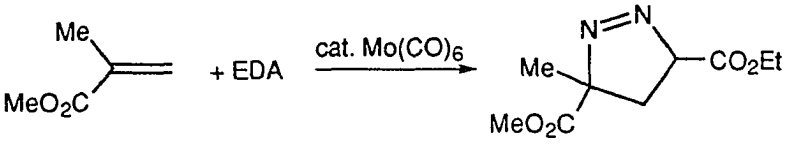


C



D

As was the case with the carbonyl compounds, a minor product was obtained, but we were unable to isolate or identify it. It has a molecular weight equal to the sum of EDA and olefin, and appears to be the 1-pyrazoline on the basis of the MW and the ^{1}H–NMR spectra (see Discussion). 1-Pyrazolines are produced (observed by NMR, but not isolated) from the following reaction:[20]

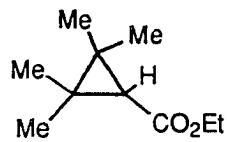
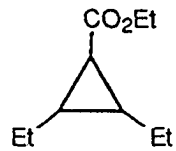
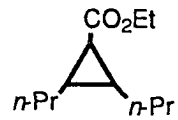
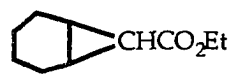
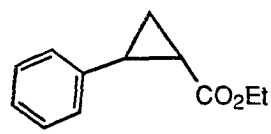
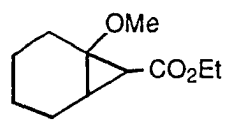


(1.9)

Decomposition of Phenyl azide. Phenyl azide is catalytically decomposed under mild conditions by a trace of MTO in dry benzene (eq 1.10). The product is diphenyl diazene (azobenzene), whose ^{13}C–NMR spectrum in $CDCl_3$ (δ 122.69, 128.80, 130.71, and 152.52 ppm) agrees with the literature.[21]

$$2PhN_3 \xrightarrow{cat.\ MTO} Ph\text{–}N{=}N\text{–}Ph + 2N_2 \qquad (1.10)$$

Table 1.6. Yields[a] of cyclopropanes formed from olefins and ethyl diazoacetate, catalyzed by MTO

Alkene	Product	Yield (%)
2,3-Dimethyl-2-butene		57
cis-3-Hexene		63
trans-4-Octene		59
Cyclohexene		71
Styrene		81
α-Methoxystyrene		87
2-Methoxypropene		69
1-Methoxycyclohexene		74

[a] The yields refer to isolated product based on the EDA used.

Table 1.7. Yields of imines formed from organic azides and aryl aldehydes, catalyzed by MTO, in the presence of triphenylphosphine.

	RN_3; R =		
ArCHO	Ph	*n*-Bu	*n*-Hexyl
C_6H_5CHO	91	91	90
p-MeO-C_6H_4CHO	90	88	91
p-NO_2-C_6H_4CHO	92	87	89
2-NapthylCHO	88	85	86

[a] Yields refer to isolated product, relative to the amount of RN_3, the limiting reagent.

Catalytic formation of imines. The reactions of aromatic aldehydes with alkyl and aryl azides were examined. They produced imines in good yields (**Table 1.7**) when a stoichiometric quantity of triphenylphosphine was added along with a catalytic amount of MTO (eq 1.11). These reaction occur even in the absence of MTO, but more slowly.

$$RN_3 + ArCHO + PPh_3 \xrightarrow{cat.\ MTO} ArCH{=}N{-}R + N_2 + Ph_3PO \qquad (1.11)$$

Aliphatic imines are very water sensitive. We presume that was the reason analogous reactions of aliphatic aldehydes did not succeed.

Discussion

Decomposition of EDA. When catalyzed by MTO, the *cis*-olefin was formed preferentially, like the same reaction catalyzed by rhodium(II) and rhodium(III) complexes.[22] In contrast, reactions with ceric ammonium nitrate,[23] lithium bromide,[24] and copper(II) salts[25] yield predominantly the fumarate.

Comparisons with traditional methods. The procedures reported herein offer certain advantages over those known previously. In particular, the reaction conditions are mild and no wastes are produced. To cite some examples we note:
(1) Ethyl glycine esters are normally prepared by refluxing ethyl bromoacetate and amines.[26]

$$RNH_2 + BrCH_2CO_2Et \xrightarrow[EtOH(reflux)]{NaOAc} RNHCH_2CO_2Et + NaBr + HOAc \qquad (1.12)$$

(2) α-Alkoxy ethyl acetate, on the other hand, can be obtained from sodium alkoxide, α-haloacetic acid, and ethanol.[27] This requires strong base in one step, strong acid in the next:

$$RONa + ClCH_2CO_2H \xrightarrow{EtOH} ROCH_2CO_2H + NaCl \qquad (1.13a)$$

$$ROCH_2CO_2H + EtOH \xrightarrow[(reflux)]{conc.\ H_2SO_4} ROCH_2CO_2Et \qquad (1.13b)$$

(3) α-Thio ethyl acetate can be prepared from α-thio acetic acid, sodium methoxide, and alkyl bromide under reflux:[28]

$$HSCH_2CO_2H \xrightarrow[(2)\ RBr\ /\ reflux]{(1)\ NaOEt} RSCH_2CO_2Et + NaBr + H_2O \qquad (1.14)$$

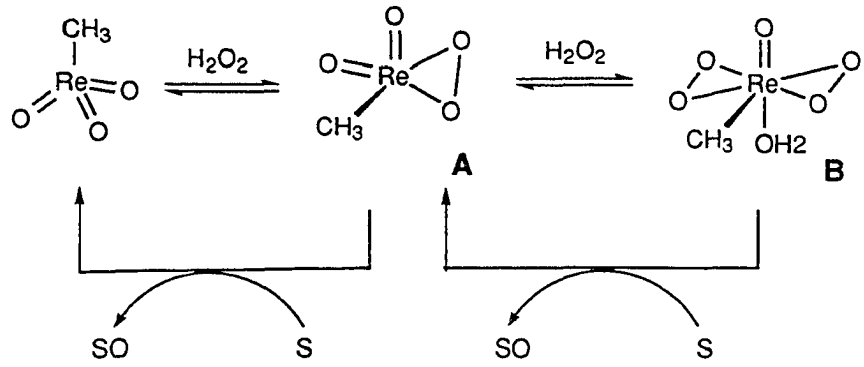
(4) Aziridines are formed from aromatic imines and EDA, catalyzed by metallic copper.[29] These reactions require one day at 80 °C, and give only 15–30% of the aziridine.

(5) Certain other routes to epoxides are preferable. For example, $ClCH_2CO_2Et$ and PhCHO are converted by (Na,K)OEt to the epoxide in 49–63% yields;[30] and the same method is valid for aryl aldehydes in general.[31] Carbonyl compounds are converted to epoxides with $LiCH_2CO_2Et$, $LiNPr^i_2$, and I_2.[32] Ethyl diazoacetate reacts with cyclopentanone, catalyzed by boron trifluoride etherate, to yield an epoxide, but the yield is <5%.[33]

Except for the epoxides, the new reactions with EDA/MTO gave higher yields. Strong base or acid is not required, which facilitates the workup. The reaction between amines and EDA is also catalyzed by Lewis acids other than MTO,[34,35] although none of them gave more than a 50% yield.

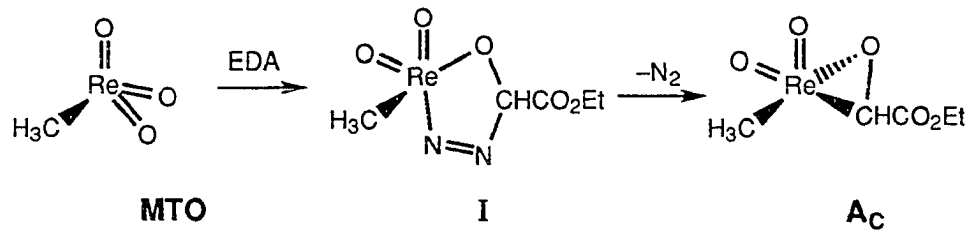
The proposed intermediates. A catalytic mechanism by which MTO activates hydrogen peroxide for the selective oxidation of an appreciable number of substrates has been established.[11-16,19,36-38] In the course of that research, two rhenium peroxides, designated **A** and **B** in **Scheme 1**, have been identified. The reaction is accomplished by oxygen transfer from a peroxidic oxygen in these compounds, to a substrate with a nucleophilic center that also can accept an oxygen atom. The oxygen transfer step recycles the catalytic forms from **A** to MTO and from **B** to **A**.

Scheme 1



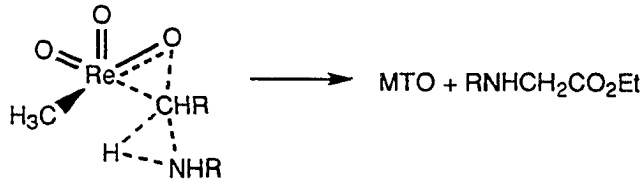
Based on this mechanism and on the analysis of the products obtained in the EDA/MTO systems, we suggest that similar intermediates may intervene as well. In particular, we imagine that there might be species we would call, by analogy $\mathbf{A_C}$ and $\mathbf{B_C}$. Furthermore, another intermediate, **I**, may intervene between MTO and $\mathbf{A_C}$. The suggested structures are shown in **Scheme 2.**

Scheme 2



The suggested mechanism. We propose that the key steps in the EDA/MTO system are these. First is the formation of these intermediates. Those substrates that react to form N–C, S–C, and O–C single bonds (i.e., amines, thiols, and alcohols) can be thought of doing so by nucleophilic attack at the new Re–C bond. It is well

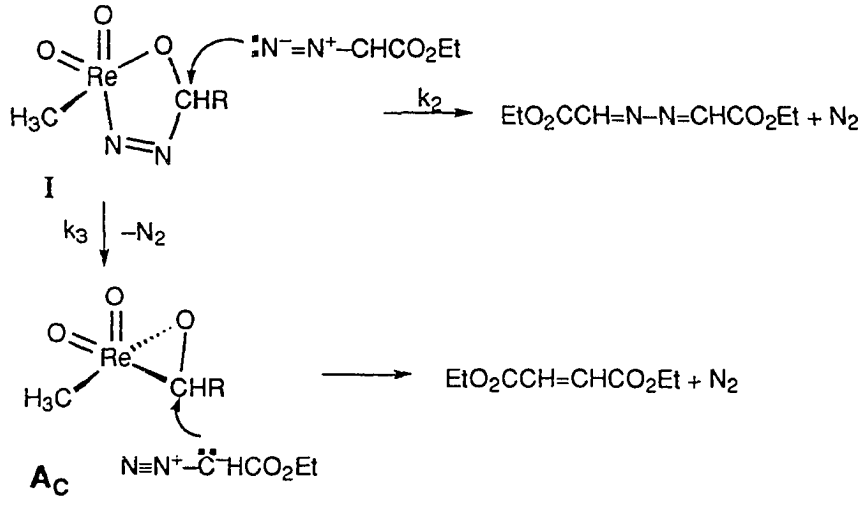
known that atoms become more electrophilic upon coordination to a high oxidation-state metal.[39-41] Indeed, were there no other examples, the conversion of the normally nucleophilic peroxide ion into an electrophilic center upon coordination to MTO would provide a convincing demonstration. The nucleophilic center (the heteroatom) of RNH_2, RSH, and ROH will attack the carbon atom of $\mathbf{A_C}$. This will lead to the products found, as shown, for example, by the amine reaction in eq 1.15.



(1.15)

The products (slowly) obtained when $\mathbf{A_C}$ is allowed to form in the absence of a substrate can be rationalized on a similar basis. Attack of the nucleophilic EDA upon $\mathbf{A_C}$ will afford the ester products. On the other hand, attack of EDA upon I prior to loss of N_2 will afford the azine, as in **Scheme 3.**

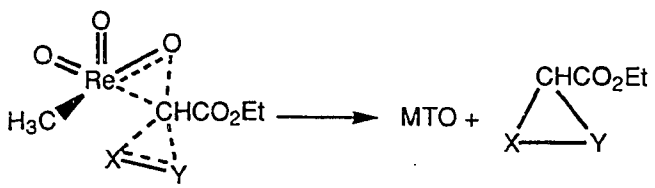
Scheme 3



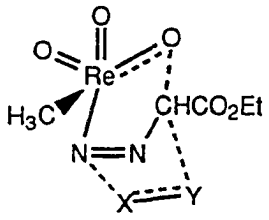
It is the competition between these reactions, which are wasteful of EDA, and the desired reaction such as that in Scheme 2, that accounts for the best yields being obtained when the EDA is not added all at once. We can also use this scheme to account for the varying proportions of azine as compared to maleate (including fumarate) when the concentration of EDA was varied. The expression for the product ratio can be derived from the rate ratio, as given in the Appendix. The fit of the data to the resulting equation is displayed in **Figure 1**. This fit gives the ratio of the rate constants $k_2/k_3 = (64 \pm 28)$ L mol^{-1}.

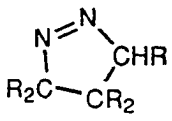
Those substrates that contain C=N and C=C double bonds yield three-membered-ring products; that with the C=O group we presume does the same, except that the phosphine disrupts the structure to excise the oxygen atom from the aldehyde. In general, the reaction appears to proceed as shown in **Scheme 4**.

Scheme 4



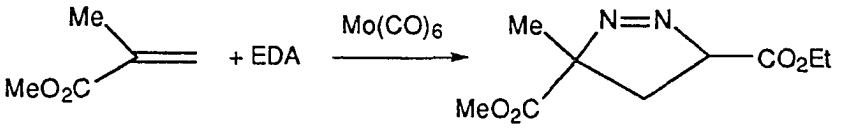
Indeed, even the minor product found in these systems—that with a molecular weight equal to the sum of that for the starting material and EDA—might be similarly reconciled by this proposal. The unidentified material may be formed by a [3+2] addition reaction that involves **I** rather than $\mathbf{A_C}$:





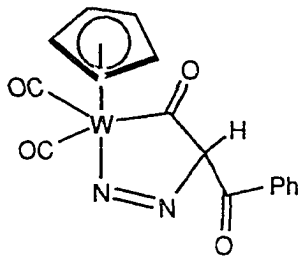
P

This would lead to the 1-pyrazoline, **P**, consistent with the GC-MS and NMR data.[42] 1-Pyrazolines are a known class of compound, and they have been observed from another reaction of EDA, eq 1.17, but were not isolated owing to decomposition.



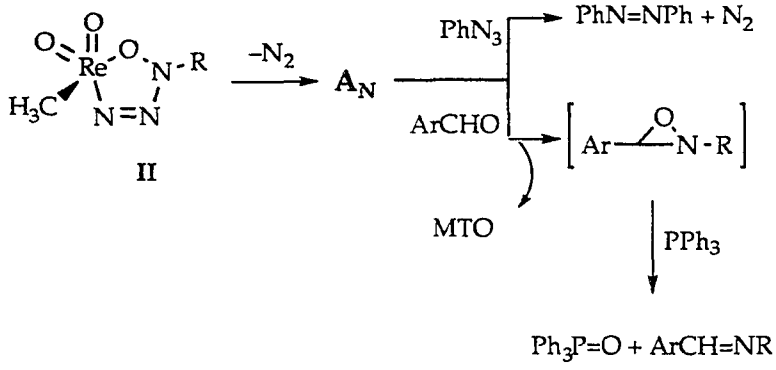
(1.17)

The first intermediate, **I**, represents the product of a [3+2] cycloaddition reaction of EDA to a rhenium–oxygen double bond. The second intermediate, $\mathbf{A_C}$, is formed by the elimination of molecular nitrogen. Neither has been isolated to this point. A tungsten analog, **W**, of the first intermediate has been reported.[43]



W

The reactions of the organic azides may also be explained in terms of the proposed intermediate $\mathbf{A_N}$. Species I would presumably be formed from MTO by the analogous process, and would be subject to nucleophilic attack, leading to the products observed, eq 1.18.



(1.18)

Experimental section

Materials. Butyl, hexyl[44] and phenyl[45] azides were prepared according to the literature. [***CAUTION***: Although we encountered no difficulties, the potentially explosive nature of organic azides should be kept in mind.] The methylrhenium trioxide was synthesized from dirhenium heptoxide and tetramethyl tin in the presence of perfluoroglutaric anhydride.[2-4] Methylene chloride was first purified[46] and stored under argon in an amber bottle over molecular sieves. Anhydrous benzene, ethyl diazoacetate, and all of the substrates were purchased commercially. Their purity was checked by GC-MS.

General procedures:

(1) α-Alkoxy ethyl esters. The alcohol (50 mmol) and MTO (50 mg, 0.2 mmol) were dissolved in 100 mL dry benzene (usually) or methylene chloride in a three-necked round bottom flask filled with a water-cooled condenser. The

temperature was maintained below 60 °C (benzene) or at reflux (methylene chloride). Ethyl diazoacetate (50 mmol) was added dropwise. After two days, during which time the reaction was monitored by GC-MS, the product was recovered by vacuum distillation. The products were identified by comparison to literature data.[21,27,47,48] For these and other previously-known materials, the spectroscopic parameters and other analytical data are given in the Supporting information; only for the new compounds will the data be given here.

(2) *N*-Substituted glycine ethyl esters. The first method was the same as in (1). Alternatively, MTO (0.2 mmol) was dissolved in the amine (54 mmol) under dry argon in a three-necked round-bottom flask fitted with a water-cooled condenser and heated to 60 °C. The ethyl diazoacetate (50 mmol) was added dropwise; with this method the reactions were complete within one hour, it being much faster here where no solvent diluent was used. The products were identified (Supporting information), in comparison with literature data.[21,26,34,47,49,50]

(3) α-Thio ethyl esters. The first method under (1) was used, except that the reaction was allowed to proceed for three days before isolation of the product by vacuum distillation. Alternatively, the MTO (0.2 mmol) was dissolved in the thiol (54 mmol) under dry argon in a three-necked round-bottom flask. The EDA (50 mmol) was added dropwise with vigorous stirring; this highly exothermic (***caution!***) reaction was complete within a few minutes. This procedure can equally well be carried out in the reverse order: the thiol may be added dropwise into a solution of MTO in EDA. The products were identified by comparison with data in the literature;[21,28,47,51,52] see the Supporting information.

(4) Aziridines. The imine (35 mmol, prepared as in (7)) and MTO (250 mg, 1 mmol) were dissolved in 100 mL dry benzene in a three-necked round bottom flask fitted with a water-cooled condenser, flushed with dry argon or nitrogen for ca. 10 min., and maintained at ca. 60 °C. Ethyl diazoacetate (30 mmol) was added dropwise with stirring. After the addition was complete, stirring was continued another 4–6 hr., during which time the reaction was monitored by GC-MS. Finally, the mixture was cooled to room temperature and the solvent removed under vacuum. The aziridines were isolated by vacuum distillation, and purified on a silica gel column from which they were eluted with benzene.

The products were identified by spectroscopic and analytical data:[29,53-55]

From PhCH=N-Bu^n, ^{1}H–NMR ($CDCl_3$), δ ppm 0.93-1.36 (m, 8H), 1.70 (m, 2H), 3.36 (d, 1H), 3.61 (t, 2H), 3.88 (d, 1H), 4.14 (q, 2H), 7.41-7.70 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 13.89, 14.08, 20.44, 33.01, 45.94, 47.45, 61.02, 61.34, 127.98, 128.35, 130.40, 139.12, and 167.62. Anal. Calcd for $C_{15}H_{21}NO_2$ (247.338): C, 72.84; H, 8.56; N, 5.66. Found: C, 72.61; H, 8.50; N, 5.71.

PhCH=N-Ph, ^{1}H–NMR ($CDCl_3$), δ ppm 1.09 (t, 3H), 3.27 (d, 1H), 3.82 (d, 1H), 4.09 (q, 2H), 7.19-7.82 (m, 10H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.10, 45.82, 46.31, 61.13, 120.85, 125.91, 126.98, 128.53, 129.14, 129.30, 136.71, 152.09, and 167.53. Anal. Calcd for $C_{17}H_{17}NO_2$ (267.33): C, 76.35; H, 6.40; N, 5.23. Found: C, 76.54; H, 6.30; N, 5.09.

PhCH=N-Hexyl^n, ^{1}H–NMR ($CDCl_3$), δ ppm 0.87 (t, 3H), 1.13-1.68 (m, 11H), 3.41 (d, 1H), 3.59 (t, 2H), 3.84 (d, 1H), 4.17 (q, 2H), 7.31-7.81 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.07, 14.14, 22.61, 27.02, 30.69, 31.66, 46.02, 47.51, 61.21, 61.77, 126.89, 128.15, 130.25, 136.33, and 167.65. Anal. Calcd for $C_{17}H_{25}NO_2$ (275.391): C, 74.14; H, 9.15; N, 5.09. Found: C, 74.12; H, 9.20; N, 5.04.

***p*-Me-C_6H_4CH=N-Bu^n,** ^{1}H–NMR ($CDCl_3$), δ ppm 0.95-1.36 (m, 8H), 1.71 (m, 2H), 2.31 (s, 3H), 3.25 (d, 1H), 3.62 (t, 2H), 3.81 (d, 1H), 4.09 (q, 2H), 6.91-7.30 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 13.92, 14.19, 20.41, 21.45, 33.01, 45.64, 46.10, 60.71, 61.14, 127.35 , 127.95, 129.11, 138.76, and 167.58. Anal. Calcd for $C_{16}H_{23}NO_2$ (261.36): C, 73.52; H, 8.87; N, 5.34. Found: C, 71.23; H, 8.42; N, 5.21.

***p*-Me-C_6H_4CH=N-Hexyl^n,** ^{1}H–NMR ($CDCl_3$), δ ppm 0.87-1.68 (m, 14H), 2.31 (s, 3H), 3.21 (d, 1H), 3.60 (t, 2H), 3.77 (d, 1H), 4.07 (q, 2H), 6.80-7.21 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.07, 14.11, 21.46, 22.61, 27.02, 30.70, 31.65, 45.67, 46.05, 61.11, 61.73, 126.77, 127.95, 129.09, 138.65, and 167.54. Anal. Calcd for $C_{18}H_{27}NO_2$ (289.417): C, 74.70; H, 9.40; N, 4.84. Found: C, 74.48; H, 10.33; N, 4.81.

***p*-MeO-C_6H_4CH=N-Bu^n,** ^{1}H–NMR ($CDCl_3$), δ ppm 0.91-1.70 (m, 10H), 3.14 (d, 1H), 3.58 (t, 2H), 3.76 (d, 1H), 3.82 (s, 3H), 4.31 (q, 2H), 6.80-7.70 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 13.81, 14.12, 20.41, 32.08, 45.57, 46.22, 55.51, 61.04, 61.55, 113.85, 116.85, 129.13, 129.45, 167.14. Anal. Calcd for $C_{16}H_{23}NO_3$ (277.364): C,69.29; H, 8.36; N, 5.05. Found: C, 69.02; H, 8.11; N, 5.06.

***p*-MeO-C_6H_4CH=N-Hexyl^n,** ^{1}H–NMR ($CDCl_3$), δ ppm 0.89-1.69 (m, 14H), 3.15 (d, 1H), 3.54 (t, 2H), 3.76 (d, 1H), 3.82 (s, 3H), 4.32 (q, 2H), 6.81-7.73 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.06, 14.09, 22.61, 27.04, 30.98, 31.66, 45.61, 46.27, 55.54, 61.08, 61.74, 113.99, 114.38, 129.36, 129.57, 167.21. Anal. Calcd for $C_{18}H_{27}NO_3$ (305.42): C, 70.79; H, 8.91; N, 4.59. Found: C, 71.16; H, 9.04; N, 4.60.

***p*-MeO-C_6H_4CH=Ph,** ^{1}H–NMR ($CDCl_3$), δ ppm 1.11 (t, 3H), 3.26 (d, 1H), 3.79 (d, 1H), 3.81 (s, 3H), 4.10 (q, 2H), 6.80-7.69 (m, 9H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.07, 45.72, 46.31, 55.53, 61.08, 114.12, 114.47, 120.85, 125.94, 129.21, 129.54, 129.75, 152.11, 167.47. Anal. Calcd for $C_{18}H_{19}NO_3$ (297.357): C, 72.70; H, 6.44; N, 4.71. Found: C, 71.95; H, 6.50; N, 4.66.

***p*-NO_2-C_6H_4CH=N-Bu^n**, ^{1}H–NMR ($CDCl_3$), δ ppm 0.91-1.67 (m, 10H), 3.34 (d, 1H), 3.63 (t, 2H), 3.91 (d, 1H), 4.11 (q, 2H), 7.80-8.33 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 13.84, 14.17, 20.45, 32.79, 46.27, 48.49, 61.24, 61.71, 123.89, 128.11, 129.17, 141.28, 167.71. Anal. Calcd for $C_{15}H_{20}N_2O_4$ (292.336): C,61.63; H, 6.90; N, 9.58. Found: C, 61.51; H, 6.83; N, 9.56.

***p*-NO_2–C_6H_4CH=N-Hexyl^n**, ^{1}H–NMR ($CDCl_3$), δ ppm 0.87-1.70 (m, 14H), 3.33 (d, 1H), 3.66 (t, 2H), 3.87 (d, 1H), 4.09 (q, 2H), 7.80-8.41 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.04, 14.13, 22.57, 27.02, 30.68, 31.61, 46.22, 48.33, 61.19, 62.04, 123.85, 126.78, 128.65, 141.38, 167.67. Anal. Calcd for $C_{17}H_{24}N_2O_4$ (320.39): C, 63.73; H, 7.55; N, 8.74. Found: C, 63.31; H, 7.73; N, 8.70.

2-Naphthyl-CH=N-Bu^n, ^{1}H–NMR ($CDCl_3$), δ ppm 0.94-1.73 (m, 10H), 3.29 (d, 1H), 3.66 (t, 2H), 3.85 (d, 1H), 4.11 (q, 2H), 7.40-8.03 (m, 7H); ^{13}C–NMR ($CDCl_3$), δ ppm 13.92, 14.13, 20.50, 33.06, 45.9, 46.3, 61.19, 61.60, 125.82, 126.98, 127.83, 128.40, 128.54, 128.69, 129.58, 133.12, 134.01, 136.57, 167.73. Anal. Calcd for $C_{19}H_{23}NO_2$ (297.40): C, 76.73; H, 7.79; N, 4.71. Found: C, 76.84; H, 7.62; N, 4.81.

2-Naphthyl-CH=N-Hexyl^n, ^{1}H–NMR ($CDCl_3$), δ ppm 0.87-1.67 (m, 14H), 3.31 (d, 1H), 3.61 (t, 2H), 3.94 (d, 1H), 4.22 (q, 2H), 7.41-8.02 (m, 7H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.07, 14.15, 22.62, 27.07, 30.95, 31.68, 45.75, 46.43, 61.23, 61.95, 123.87, 126.73, 126.97, 127.83, 128.49, 128.57, 129.58, 133.14, 134.05, 134.49, 167.77. Anal. Calcd for $C_{21}H_{27}NO_2$ (325.451): C, 77.50; H, 8.36; N, 4.30. Found: C, 77.39; H, 8.32; N, 4.31.

(5) Epoxides. MTO (50 mg, 0.2 mmol) was dissolved in 20 mL of the aldehyde or ketone. The flask was sealed with a rubber stopper, and the solution brought to 50–60 °C. Ethyl diazoacetate (5 mL, 48 mmol) was added dropwise while the pressure was relieved occasionally. After three days, during which time

the reaction was monitored with GC-MS, the product was isolated by vacuum distillation. The products were identified spectroscopically (see the Supporting information) in comparison with data from the literature.[56-61]

(6) Cyclopropanes. The method was the same as that used for the epoxides, and the products (see the Supporting information) were similarly identified.[62-65] Some of these substrates (e.g., styrene), but not all (e.g., α-methylstyrene), lead to small yields of compounds believed from MS and NMR data (Supporting information) to be 1-pyrazolines. Styrene, for example, forms two isomers in a total yield of 14% (trans:cis ~3.8:1); these products decrease on standing (2% after 3 days), as more cyclopropane is formed.

(7) Imines. The aryl aldehyde (30 mmol), triphenylphosphine (31 mmol) and MTO (1 mmol) were dissolved in 100 mL dry benzene. The solution was flushed with dry argon or nitrogen for ca. 10 min. at room temperature, then the organic azide (30 mmol) was added dropwise with stirring. After an additional 2 hr. stirring, the solvent was removed by rotary evaporation. The imines were obtained by vacuum distillation or by recrystallization from ethanol. The ^{1}H– and ^{13}C–NMR data for these products is given in **Table 1.8.**

Table 1.8. NMR data[a] for imines formed from the reactions of aldehydes, organic azides, and triphenylphosphine in the presence of MTO

Imine	^{1}H–NMR	^{13}C–NMR
2-Naphthyl-CH=N-Bu	0.95 (t, 3H), 7.50(m)	13.92, 20.49, 33.06
	1.40 (m, 2H), 7.85 (m)	61.59, 123.87, 126.38
	1.73 (m, 2H), 7.97 (m)	126.98, 127.83, 128.40
	3.65 (t, 2H), 8.41 (s, 1H)	128.54, 129.58, 133.12
		134.01, 134.59, 160.80
2-Naphthyl-CH=N-Ph	7.28 (m), 7.44 (m)	120.91, 123.91, 125.98
	7.57 (m), 7.93 (m)	126.61, 127.53, 127.93
	8.20 (m), 8.63 (s)	128.67, 128.77, 129.17
		131.23, 133.09, 133.94
		135.02, 152.09, 160.36
2-Naphthyl-CH=N-hexyl	0.87 (m), 1.33 (m)	14.07, 22.62, 27.07
	1.67 (m), 3.60 (t)	30.95, 31.68, 61.94
	7.48 (m), 7.85 (m)	123.88, 126.37, 126.97
	7.95 (m), 8.30 (s)	127.83, 128.40, 128.54
		129.60, 133.11, 134.01
		134.58, 160.77
Ph-CH=N-Bu	0.93 (t), 1.36 (m)	13.88, 20.43, 32.98
	1.69 (m), 3.62 (t)	61.45, 127.96, 128.52
	7.41 (m), 7.71 (m)	130.38, 136.34, 160.67
	8.25 (s)	

Table 1.8
(continued)

Ph-CH=N-hexyl	0.87 (t), 1.34 (m)	14.06, 22.60, 27.01
	1.68 (m), 3.60 (t)	30.87 31.65, 61.80
	7.39 (m), 7.71 (m)	127.98, 128.53, 130.40
	8.25 (s)	136.33, 160.70
Ph-CH=N-Ph	7.15 (m), 7.30 (m)	120.85, 125.91, 128.76
	7.41 (m), 7.84 (m)	128.79, 129.14. 131.36
	8.38 (s)	136.31, 152.09, 160.40
4-MeO-C_6H_4CH=N-Bu	1.71 (m), 3.59 (t)	61.54, 113.95, 114.30
	3.81 (s), 6.89 (m)	129.32, 129.50, 159.99
	7.64 (m), 8.18 (s)	
4-MeO-C_6H_4CH=N-hexyl	0.89 (t), 1.35 (m)	14.06, 22.62, 27.04
	1.68 (m), 3.54 (t)	30.99, 31.67, 55.55
	3.82 (s), 6.89 (m)	61.73, 113.93, 114.30
	7.64 (m), 8.18 (s)	129.33, 129.50,159.98
4-MeO-C_6H_4CH=N-Ph	3.82 (s), 6.88 (m)	55.56, 113.96, 114.30
	7.16 (m), 7.30 (m)	120.85, 125.95, 128.76
	7.41 (m), 7.64 (m)	129.15, 129.34, 129.51
	8.21 (s)	159.89

Table 1.8
(continued)

4-NO_2-C_6H_4CH=N-Bu	0.91 (t), 1.36 (m)	13.84, 20.45, 32.78
	1.66 (m), 3.62 (m)	61.65, 123.83, 128.30
	7.82 (m), 8.21 (m)	128.63, 141.82, 158.33
	8.29 (s)	
4-NO_2-C_6H_4CH=N-Hexyl	1.70 (m), 3.65 (t)	30.68, 31.60, 62.01
	7.88 (m), 8.25 (m)	123.85, 128.31, 128.65
	8.33 (s)	141.83, 158.33
4-NO_2-C_6H_4CH=N-Ph	6.67 (m), 7.16 (m)	115.09, 118.54, 120.97
	7.99 (m), 8.25 (m)	124.01, 127.08, 129.28
	8.45 (s)	129.34, 146.37, 157.39

[a] In $CDCl_3$, chemical shifts referenced to $SiMe_4$.

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. We are grateful to Professor D. K. Hoffman with the derivation given in the Appendix.

SUPPORTING INFORMATION

Contents:

Table S–1.1. NMR parameters in $CDCl_3$ for α-alkoxy ethyl esters obtained from the alcohols listed

---

Methanol. ^{1}H–NMR ($CDCl_3$), δ ppm 1.29 (t, 3H), 3.46 (s, 3H), 4.04 (s, 2H), 4.24 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.21, 59.24, 60.77, 69.95, 170.26.

Ethanol. ^{1}H–NMR ($CDCl_3$), δ ppm 1.26 (m, 6H), 3.56 (q, 2H), 4.08 (s, 2H), 4.21 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.01, 15.27, 60.87, 67.24, 68.03 and 170.26.

1-Propanol. ^{1}H–NMR ($CDCl_3$), δ ppm 0.92 (t, 3H), 1.28 (t, 3H), 1.56 (m, 2H), 3.50 (t, 2H), 4.09 (s, 2H), 4.22 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 10.47, 14.21, 24.32, 60.85, 68.33, 74.12 and 170.68.

***sec*-Propanol.** ^{1}H–NMR ($CDCl_3$), δ ppm 1.24 (m, 9H), 3.62 (m, 1H), 4.05 (s, 2H), 4.21 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.22 , 22.37, 60.80, 68.21, and 170.66.

***tert*-Amyl alcohol.** ^{1}H–NMR ($CDCl_3$), δ ppm 0.90 (t, 3H), 1.18 (s, 6H), 1.28 (t, 3H), 1.52 (q, 2H), 4.05 (s, 2H), 4.21 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 8.75, 14.23, 27.87, 35.40, 60.82, 68.41, 79.68 and 170.45.

1-Butanol. ^{1}H–NMR ($CDCl_3$), δ ppm 0.93 (t, 3H), 1.28 (m, 7H), 3.53 (t, 2H), 4.06 (s, 2H), 4.23 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 13.89, 14.22, 19.02, 34.87, 60.85, 68.35, 71.73 and 170.78.

1-Heptanol. ^{1}H–NMR ($CDCl_3$), δ ppm 0.86 (m, 3H), 1.26 (m, 11H), 1.55 (m, 2H), 3.50 (t, 2H), 4.04 (s, 2H), 4.21 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.09, 14.23, 22.62, 25.96, 29.12, 29.56, 31.81, 60.79, 68.37, 72.02 and 170.65.

Table S-1.1
(continued)

Phenol. ^{1}H–NMR ($CDCl_3$), δ ppm 1.29 (t, 3H), 4.26 (q, 2H), 4.62 (s, 2H), 6.90-7.31 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.17, 61.35, 65.43, 114.66, 121.72, 129.55, 157.82 , and 168.97.

***p*-Me-Phenol.** ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 2.27 (s, 3H), 4.26 (q, 2H), 4.57 (s, 2H), 6.82-7.14 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.16, 20.47, 61.34 , 65.80, 114.67, 129.97, 131.21, 155.87, and 169.10.

***p*-Et-Phenol.** ^{1}H–NMR ($CDCl_3$), δ ppm 1.20 (m, 6H), 2.54 (q, 3H), 4.26 (q, 2H), 4.58 (s, 2H), 6.82-7.12 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.16, 15.83, 28.01, 61.34, 65.79, 114.68, 130.11, 136.92, 157.83, and 169.22.

***p-tert*-Bu-Phenol.** ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (m, 12H), 4.27 (q, 2H), 4.58 (s, 2H), 6.82-7.33 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.16, 31.67, 34.22, 61.35, 65.81, 113.91, 127.33, 143.62, 155.33, and 169.21.

***p*-Cl-Phenol.** ^{1}H–NMR ($CDCl_3$), δ ppm 1.29 (t, 3H), 4.26 (q, 2H), 4.64 (s, 2H), 6.83-7.26 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.16, 61.35, 65.40, 115.82, 126.88, 129.97, 156.52, and 169.19.

***p*-MeO-Phenol.** ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 3.76 (s, 3H), 4.26 (q, 2H), 4.51 (s, 2H), 6.86 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.16, 55.92, 61.33, 65.91, 113.96, 116.72, 149.53, 156.32, and 169.13.

Table S-1.1
(continued)

Benzylalcohol ^{1}H–NMR ($CDCl_3$), δ ppm 1.29 (t, 3H), 4.09 (s 2H), 4.24 (q, 2H), 4.64 (s, 2H), 7.33 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.22, 60.90, 67.24, 73.36, 128.03, 128.10, 128.51, 137.12, and 170.39.

Phenethyl alcohol ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 2.95 (t, 2H), 3.55 (t, 2H), 4.06 (s 2H), 4.20 (q, 2H), 7.18 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.20, 38.02, 60.85, 68.42, 72.83, 126.45, 128.51, 128.96, 138.24, and 170.65.

***p*-Me-Benzylalcohol** ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (m, 6H), 3.66 (s, 2H), 4.03 (s 2H), 4.21 (q, 2H), 7.12 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.22, 21.02, 60.88, 68.42, 73.42, 127.11, 128.91, 137.24, 138.12, and 170.95.

***sec*-Phenethyl alcohol** ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (m, 6H), 3.66 (q, 1H), 4.09 (s 2H), 4.26 (q, 2H), 7.21 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.15, 24.68, 60.76, 65.83, 78.53, 127.86, 128.33, 128.58, 133.14, and 170.59.

Table S–1.2. NMR parameters in $CDCl_3$ for N-substituted glycine ethyl esters obtained from the amines listed

---

***n*-Propylamine,** ^{1}H–NMR ($CDCl_3$), δ ppm 0.91 (t, 3H), 1.28 (t, 3H), 1.52 (m, 2H), 1.81 (s, 1H), 2.56 (t, 2H), 3.38 (s, 2H), 4.16 (q, 2H); ^{13}CNMR ($CDCl_3$), δ ppm 11.78, 14.20, 27.77, 49.65, 51.02, 60.56, and 172.54.

***n*-Hexylamine,** ^{1}H–NMR ($CDCl_3$), δ ppm 0.88 (t, 3H), 1.28 (m, 11H), 1.76 (s, 1H), 2.57 (t, 2H), 3.39 (s, 2H), 4.16 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.01, 14.20, 22.57, 26.88, 30.00, 31.70, 49.65, 51.01, 60.56, and 172.57.

1-Piperidine, ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 1.44 (m, 2H), 1.62 (m, 4H), 2.49 (t, 4H), 3.18 (s, 2H), 4.17 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.22, 24.01, 25.95, 54.30, 54.31, 60.21, and 170.64.

1-Pyrrolidine, ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 1.83 (m, 4H), 2.64 (m, 4H), 3.33 (s, 2H), 4.18 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.21, 23.88, 53.92, 57.04, 60.28, and 170.89.

Aniline, ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 2.03 (s, 1H), 3.88 (s, 2H), 4.24 (q, 2H), 6.75-7.21 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.18, 45.86, 60.29, 115.44, 128.26, 129.28, 145.81, and 170.89.

***p*-Me-Aniline,** ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 1.98 (s, 1H), 2.21 (s, 3H), 3.79 (s, 2H), 4.24 (q, 2H), 6.65-7.06 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.19, 20.33, 45.56, 60.27, 115.31, 129.47, 137.35, 143.96, and 171.18.

Table 1.2
(continued)

***p*-Cl-Aniline,** ^{1}H–NMR ($CDCl_3$), δ ppm 1.29 (t, 3H), 2.14 (s, 1H), 3.96 (s, 2H), 4.25 (q, 2H), 6.68-7.22 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.21, 46.72, 60.31, 116.23, 129.51, 133.33, 145.01, and 172.11.

Benzylamine, ^{1}H–NMR ($CDCl_3$), δ ppm 1.27 (t, 3H), 1.89 (s, 1H), 3.39 (s, 2H), 3.79 (s, 2H), 4.18 (q, 2H), 7.25 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.23, 50.08, 53.24, 60.52, 127.10, 128.22, 128.31, 139.52, and 172.43.

Phenethylamine, ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (t, 3H), 1.81 (s, 1H), 2.68 (t, 2H), 2.94 (t, 2H), 3.39 (s, 2H), 4.17 (q, 2H), 7.19 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.20, 43.85, 48.04, 54.01, 60.61, 126.03, 128.47, 128.85, 141.35, and 172.33.

***tert*-Butylamine,** ^{1}H–NMR ($CDCl_3$), δ ppm 1.27 (m, 12H), 1.93 (s, 1H), 3.38 (s, 2H), 4.16 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.16, 33.45, 56.74, 60.48, and 172.53.

Table S–1.3. NMR parameters for α-thio ethyl esters obtained from the thiols listed.

Ethanethiol. ^{1}H–NMR ($CDCl_3$), δ ppm 1.28 (m, 6H), 2.63 (q, 2H), 3.20 (s, 2H), 4.16 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.14, 14.15, 26.58, 33.31, 61.24, and 170.55.

Thiophenol. ^{1}H–NMR ($CDCl_3$), δ ppm 1.22 (t, 3H), 3.64 (s, 2H), 4.18 (q, 2H), 7.21-7.50 (m, 5H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.07, 36.72, 61.56, 126.96, 129.07, 130.01, 134.95, and 169.73.

1-Propanethiol. ^{1}H–NMR ($CDCl_3$), δ ppm 0.98 (t, 3H), 1.21 (t, 3H), 1.62 (m, 2H), 2.54 (q, 2H), 3.18 (s, 2H), 4.15 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 12.79, 14.10, 24.87, 32.73, 35.62, 61.51, 170.62.

sec-Butanethiol. ^{1}H–NMR ($CDCl_3$), δ ppm 0.95 (t, 3H), 1.20-1.72 (m, 8H), 2.91 (m, 1H), 3.15 (s, 2H), 4.16 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 11.43, 14.09, 25.11, 28.41, 32.60, 41.42, 61.22, 170.47.

1-Hexanethiol. ^{1}H–NMR ($CDCl_3$), δ ppm 0.85 (t, 3H), 1.19-1.77 (m, 11H), 2.61 (q, 2H), 4.09 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 13.97, 14.08, 22.59, 24.66, 28.23, 29.60, 32.69, 38.33, 61.18, 170.11.

4-Chlorothiophenol. ^{1}H–NMR ($CDCl_3$), δ ppm 1.21 (t, 3H), 3.68 (s, 2H), 4.16 (q, 2H), 7.13 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.06, 35.75, 61.54, 130.11, 131.93, 131.94, 136.43, 170.03.

4-Methoxybenzenethiol. ^{1}H–NMR ($CDCl_3$), δ ppm 1.21 (t, 3H), 3.37 (s, 2H), 3.74 (s, 3H), 4.12 (q, 2H), 6.83-7.37 (m, 4H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.07, 35.55, 55.26, 61.54, 115.73, 121.42, 133.14, 159.41, 169.66.

Table S–1.4. NMR parameters in $CDCl_3$ for the epoxides obtained from the specified aldehydes and ketones.

Benzaldehyde, ^{1}H–NMR ($CDCl_3$), δ ppm 1.32 (t, 3H), 3.49 (d, 1H), 4.08 (d, 1H), 4.27 (q, 2H), 7.28-7.42 (m, 5H).

n-Pr-CHO, ^{1}H–NMR ($CDCl_3$), δ ppm 0.98-1.20 (m, 6H), 1.42 (m, 2H), 1.72 (m, 2H), 3.56 (m, 1H), 4.15 (d, 1H), 4.11 (q, 2H).

n-Bu-C(O)-Me, Both GC/MS and ^{1}H–NMR ($CDCl_3$) show two epoxide products were formed. ^{1}H NMR ($CDCl_3$), δ ppm 0.90-1.54, **C**: 1.29 (s), 3.12(s), 4.18 (q); **D**: 1.33 (s), 3.10 (s), and 4.16(q). A/B=7.6 and **C** is *trans*-product.

i-Pr-C(O)-Me, also formed two epoxides. ^{1}H–NMR ($CDCl_3$), δ ppm **C**: 0.88 (d), 1.05 (d), 1.28 (t), 1.72 (m), 1.23 (s), 3.14(s), 4.18 (q); **D**: 0.96 (d), 1.02 (d), 1.21 (s), 1.30 (t), 1.52 (m), 3.12 (s), 4.17 (q). **C/D** ratio is 8.1.

Ph-C(O)-Me, two epoxide products were formed. ^{1}H–NMR ($CDCl_3$), δ ppm **C**: 1.22 (s), 1.26 (t), 3.11 (s), 4.16 (q) and 7.42 (m). **D**: 1.26 (t), 1.30 (s), 3.07 (s), 4.16 (q) and 7.42 (m). C/D ratio is 7.5.

Table S–1.5. NMR and MS data for the cyclopropanes formed from the alkenes listed, and the (presumably) 1-pyrazoline side products

---

2,3-Dimethyl-2-butene, ^{1}H–NMR ($CDCl_3$), δ ppm 1.18 (s, 12H), 1.24 (m, 4H), 4.07 (q, 2H); ^{13}C–NMR ($CDCl_3$), δ ppm 14.72, 16.88, 23.57, 29.89, 59.43, 172.11. MS (CI, NH_3) m/e: 171 ($M+H^+$) and 188 ($M+NH_4^+$).

cis-3-Hexene, ^{1}H–NMR ($CDCl_3$), δ ppm 0.71-1.70 (m, 16H), 3.90 (q, 2H). MS (CI, NH_3) m/e: 171 ($M+H^+$) and 188 ($M+NH_4^+$).

cis-3-Hexene, ^{1}H–NMR ($CDCl_3$), δ ppm 0.80-2.01 (m, 20H), 3.80 (q, 2H). MS (CI, NH_3) m/e: 199 ($M+H^+$) and 216 ($M+NH_4^+$).

Cyclohexene, ^{1}H–NMR ($CDCl_3$), δ ppm 0.95-2.12 (m, 14H), 4.00 (q, 2H). MS (CI, NH_3) m/e: 169 ($M+H^+$) and 186 ($M+NH_4^+$).

Styrene, ^{1}H–NMR ($CDCl_3$), δppm 0.96 (t, 3H), 1.47-2.12 (m, 4H), 4.18 (q, 2H), 7.00-7.36 (m, 5H). ^{13}C–NMR ($CDCl_3$), δ ppm 14.51, 16.89, 24.30, 26.41, 60.59, 126.59, 126.61, 129.03, 140.82, 172.12.

Byproduct (14% immediately, 2% after 3 days). **Isomer C:** δ/ppm: 1.48 (t, 3H), 1.74 (m, 1H), 2.50 (m, 1H), 4.30 (q, 2H), 5.48 (t, 1H, J = 8.4 Hz), 5.97 (t, 2H, J = 8.4 Hz), 7.19-7.45 (m, 5H); **Isomer T:** 0.96 (t, 3H), 1.90 (m, 1H), 2.06 (m, 1H), 4.15 (q, 2H), 4.99 (t, 1H, J = 10.5 Hz), 5.69 (t, 1H, J = 10.5 Hz), 7.22-7.53 (m, 5H). Ratio, T/C = 3.8:1.

Table S-1.5
(continued)

α-MeO-styrene, two isomers were formed. ^{1}H–NMR ($CDCl_3$), δ ppm **C**: 0.97 (t, 3H), 1.49 (dd, 1H), 1.81 (dd, 1H), 2.32 (dd, 1H), 3.14 (s, 3H), 3.88 (q, 2H) and 7.21-7.52 (m, 5H). **D**: 1.29 (t, 3H), 1.41 (dd, 1H), 1.52 (dd, 1H), 2.06 (dd, 1H), 3.22 (s, 3H), 4.22 (q,

2H), 7.20-7.52 (m, 5H). A/B about 1:1. MS (CI, NH_3) m/e: 221 ($M+H^+$) and 238 ($M+NH_4^+$).

2-MeO-propene, two isomers were formed. ^{1}H–NMR ($CDCl_3$), δ ppm **C**: 1.26 (t, 3H), 1.49 (s, 3H), 1.61 (m, 2H), 1.86 (dd, 1H), 3.29 (s, 3H), 4.14 (q, 2H). **D**: 0.95 (dd, 1H), 1.27 (t, 3H), 1.37 (m, 1H), 1.44 (s, 3H), 1.71 (m, 1H), 3.27 (s, 3H), 4.16 (q, 2H). **C/D** about 2:1. MS (CI, NH_3) m/e: 159 ($M+H^+$) and 176 ($M+NH_4^+$).

1-MeO-cyclohexene, two isomers were formed. ^{1}H–NMR ($CDCl_3$), δ ppm **C**: 1.27 (t, 3H), 0.8-2.2 (m, 9H), 2.21 (m, 1H), 3.24 (s, 3H), 4.10 (q, 2H). **D**: 1.27 (t, 3H), 1.2-2.2 (m, 10H), 3.28 (s, 3H), 4.14 (q, 2H). **C/D** about 2:1. MS (CI, NH_3) m/e: 199 ($M+H^+$) and 216 ($M+NH_4^+$).

Appendix. Derivation of the kinetic expression for Scheme 3. Let A = [Azine] and M = [Olefin (mostly maleate)], a = $[EDA]_0$, and $\kappa = k_2/k_3$. The ratio of the rates at which the azine and the maleate are formed is

$$\frac{dA}{dM} = \frac{k_2 E}{k_3} = \kappa E = \kappa\{a - 2A - 2M\} \qquad \text{(A-1.1)}$$

This is a first-order differential equation that can be solved by multiplying each side by the integrating factor, exp(2κM); integration between the limits 0 and ∞ then gives:

$$A_\infty e^{2\kappa M_\infty} = \frac{a}{2}\left(e^{2\kappa M_\infty} - 1\right) + \frac{1}{2\kappa}\left(e^{2\kappa M_\infty} - 1\right) - M_\infty e^{2\kappa M_\infty} \qquad \text{(A-1.2)}$$

Substitution of $A_\infty + M_\infty = a/2$, and rearrangement affords

$$a = \frac{1}{\kappa}\left(e^{2\kappa M_\infty} - 1\right) = \frac{1}{\kappa}\left(\exp^{2\kappa\left(\frac{a}{2} - A_\infty\right)} - 1\right) \qquad \text{(A-1.3)}$$

From this we find

$$A_\infty = \frac{a\kappa - \ln(a\kappa + 1)}{2\kappa} \qquad \text{(A-1.4)}$$

which is the form used to fit A_∞ as a function of a (= $[EDA]_0$), as shown in Figure 1.1. (Page 9)

References

(1) Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.

(2) Herrmann, W. A.; Ramao, C. C.; Kiprof, P.; Behm, J.; Cook, M. R.; Taillefer, J. *J. Organomet. Chem.* **1991**, *413*, 11.

(3) Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R.; Ramao, C. C. *Inorg. Chem.* **1992**, *31*, 4431.

(4) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Cat.* **1994**, *86*, 243.

(5) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1636.

(6) Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organomet.* **1994**, *13*, 4531.

(7) Zhu, Z.; Espenson, J. H. *J. Mol. Catal.* **1995**, in press.

(8) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157.

(9) Herrmann, W. A.; Scherer, W.; Fischer, R. W.; Blümel, J.; Kleine, M.; Mertin, W.; Gruehn, R.; Mink, J.; Boysen, H.; Wilson, C. C.; Ibberson, R. M.; Bachmann, L.; Mattner, M. *J. Am. Chem. Soc.* **1995**, *117*, 3231.

(10) Herrmann, W. A.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1995**, *485*, 243.

(11) Al-Ajlouni, A.; Espenson, J. H. *submitted for publication,*

(12) Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1993**, *32*, 4517.

(13) Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491.

(14) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326.

(15) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* in press.

(16) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272.

(17) Vaultier, M.; Carrie, R. *Tetrahedron* **1979**, *35*, 1357.

(18) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638.

(19) Al-Ajlouni, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243.

(20) Doyle, M. P.; Dorow, R. L.; Tamblyn, M. H. *J. Org. Chem.* **1982**, *47*, 4059.

(21) Pouchert, C. J.; Behnke, J. *The Aldrich Library of* ^{13}C *and* ^{1}H *FT-NMR Spectra;* 1993.

(22) Shankar, B. K. R.; Schechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277.

(23) Trahanovsky, W. S.; Bobins, M. D.; Smick, D. *J. Am. Chem. Soc.* **1971**, *93*, 2086.

(24) Nakajima, M.; Anselme, J. P. *J. Chem. Soc., Chem. Comm.* **1980**, 1796.

(25) Oshina, T.; Nagai, T. *Tetrahedron Lett.* **1980**, *21*, 1251.

(26) Bryson, A.; Davies, N. R.; Serjeant, E. P. *J. Am. Chem. Soc.* **1963,** *85,* 1933.

(27) Andrews, D. W. W.; Jeffrey, G. H.; Vogel, A. I. *J. Chem. Soc. (B)* **1966,** 1080.

(28) Chauveau, A.; Mathis-Noel, R. *Ann. Fac. Sci. Univ., Toulouse, Sci. Math. Sci. Phys.* **1963,** *25,* 147.

(29) Baret, P.; Buffet, H.; Pierre, J.-L. *Bull. Soc. chim. Fr.* **1972,** 2493.

(30) Field, L.; Carlile, C. G. *J. Org. Chem.* **1961,** *26,* 3170.

(31) Seyden-Penne, J.; Roux-Schmitt, M. C. *Tetrahedron* **1972,** *28,* 4965.

(32) Kraus, G. A.; Taschner, M. J. *Tetrahedron Lett.* **1977,** *52,* 4575.

(33) Tai, W. T.; Warnhoff, E. W. *Can. J. Chem.* **1994,** *42,* 1333.

(34) Mueller, E.; Huber-Emden, H. *Ann.* **1961,** *639,* 70.

(35) Regitz, M.; Maas, G. ; Academic Press: Orlando, 1986; Vol. Chapter 3.

(36) Espenson, J. H.; Pestovsky, O.; Huston, P.; Staudt, S. *J. Am. Chem. Soc.* **1994,** *116,* 2869.

(37) Hansen, P. J.; Espenson, J. H. *submitted for publication, Inorg. Chem.*

(38) Pestovsky, O.; vanEldik, R.; Huston, P.; Espenson, J. H. *J. Chem. Soc. Dalton Trans.* **1995,** 227.

(39) Doyle, M. P. *Chem. Rev.* **1986,** *86,* 919.

(40) Putala, M.; Lemenovskii, D. A. *Russ. Chem. Rev.* **1994,** *63,* 197.

(41) Chaloner, P. A. *Handbook of Coordination Catalysis in Organic Chemistry, Chapter 6;* Butterworth & Co.: Boston, 1986.

(42) Batterham, T. J. *NMR Spectra of Simple Heterocycles;* John Wiley & Sons: New York, 1973, pp 204.

(43) Herrmann, W. A.; Kriechbaum, G.; Ziegler, M. L.; Wulknitz, P. *Chem. Ber.* **1981**, *114*, 276.

(44) Boyer, J. H.; Hamer, J. *J. Am. Chem. Soc.* **1955**, *77*, 950.

(45) Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2438.

(46) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals;* 3d ed.; Butterworth-Heinemann: Oxford, 1988.

(47) Mass spectra used is NIST MS Library from Magnum, Finnigan MAT.: San Jose, CA.

(48) Kadentsev, V. I.; Chizhov, O. S.; Yanovskaya, L. A.; Kucherov, V. F. *isv* **1971**, *10*, 2207.

(49) Munshi, A. A.; Trivedi, J. P. *J. Ind. Chem. Soc.* **1966**, *43*, 277.

(50) Lemont, B. K.; Dhawan, D. *J. Pharm. Sci.* **1962**, *51*, 1058.

(51) Conti, L. *Boll. Chim. Farm.* **1967**, *106*, 47.

(52) Uyeda, Y.; Reid, E. E. *J. Am. Chem. Soc.* **1920**, *42*, 2388.

(53) Lown, J. W.; Maloney, T. W.; Dallas, G. *Can. J. Chem.* **1970**, *48*, 584.

(54) Pierre, J.-L.; Baret, P.; Arnaud, P. *Bull. Soc. chim. Fr.* **1971**, 3619.

(55) Mison, P.; Chaabouni, R.; Diab, Y.; Martino, R.; Lopez, A.; Lattes, A.; Wehrli, F. W.; Wirthlin, T. *Org. Magn. Resonance* **1976**, *8*, 79.

(56) Vandenbroucke, W.; Anteunis, M.; DeBruyn, A. *Bull. Soc. Chim. Belges* **1969**, *78*, 229.

(57) Roux-Schmitt, M. C.; Seyden-Penne, J. *Tetrahedron* **1972**, *28*, 4695.

(58) Valente, V. R.; Wolfhagen, J. L. *J. Org. Chem.* **1966**, *31*, 3509.

(59) Johnson, W. S.; Belew, J.; Chinn, L.; Hunt, R. *J. Am. Chem. Soc.* **1953**, *75*, 4995.

(60) Bachelor, W. S.; Basal, R. K. *J. Org. Chem.* **1969**, *34*, 3600.

(61) Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron* **1966**, *22*, 3393.

(62) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssie, P. *Synthesis* **1976**, 600.

(63) Subbotin, O. K.; Kozmin, A. S.; Grishin, Y. K.; Sergeev, N. M.; Bolesov, I. G. *Org. Magn. Resonance* **1972**, *4*, 53.

(64) Doyle, M. P.; Leusen, D. V.; Tamblyn, W. H. *Synthesis* **1981**, 787.

(65) Kaiser, C.; Weinstock, J.; Olmstead, M. P. *Org. Synthesis* **1963**, *50*, 94.

CHAPTER II. ORGANIC REACTIONS CATALYZED BY METHYLRHENIUM TRIOXIDE: DEHYDRATION, AMINATION AND DISPROPORTIONATION OF ALCOHOLS

A paper accepted by the *Journal of Organic Chemistry*

Zuolin Zhu and James H. Espenson

Abstract

Methylrhenium trioxide is the first transition metal complex in trace quantity to catalyze the direct formation of ethers from alcohols. The reactions are independent of the solvents used: benzene, toluene, dichloromethane, chloroform, acetone, and even the alcohols themselves. Aromatic alcohols gave better yields than aliphatic. Reactions between two different alcohols could also be used to prepare unsymmetric ethers, the best yields being obtained when one of the alcohols is aromatic. MTO also catalyzes the dehydration of alcohols to form olefins at room temperature, aromatic alcohols proceeding in better yield. When primary (secondary) amines were used as the limiting reagent, direct amination of alcohols, catalyzed by MTO gave good yields of the expected secondary (tertiary) amines at room temperature. Disproportionation of alcohols to alkanes and carbonyl compounds was also observed for aromatic alcohols in the presence of MTO. Based on the results of this investigation and a comparison with the interaction between MTO and water, a concerted process and a mechanism involving carbocation intermediates can be proposed.

Introduction

Methylrhenium trioxide (CH_3ReO_3 or MTO) catalyzes the epoxidation[1] and metathesis[2] of olefins, aldehyde olefination,[3] oxygen transfer,[4] as well as the transfer of carbene and nitrene groups from diazoalkanes and organic azides, respectively.[5] Many MTO-catalyzed oxidations of hydrogen peroxide have been reported, including the oxidations of alkenes,[1,6,7] cobalt thiolates,[8] organic sulfides,[9] anilines,[10] alkynes,[11] and phosphines.[12] We note this series of results, not because hydrogen peroxide is in any way involved with the transformations of alcohols described in this paper, but because the precursors to the rhenium peroxide intermediates from MTO and H_2O_2 can reasonably be used as models for them.

The dehydration of alcohols provides an important means of preparing ethers. The Williamson ether synthesis[13], one of the most widely used procedures, calls for the initial conversion of alcohols to halides or tosylates. Other synthetic methods have been reported, but they are not without limitations.[14-18] The method developed in this work is a direct one.

Another important transformation of alcohols is an elimination reaction to yield olefins. Known methods include heterogeneous and homogeneous reactions with a stoichiometric amount of dehydrating agent, such as anhydrous copper(II) sulfate,[19] copper(II) sulfate on silica gel,[20] ferric chloride on silica gel,[21] $SOCl_2/NEt_3$,[22] TsOH/PhH,[23] BF_3/OEt_2,[24] $Ph_3P/CCl_4/NEt_3$,[25] or Ph_3PBiBr_2/I_2.[26] The method reported here, which uses MTO as a catalyst for the dehydration of alcohols at room temperature in dry benzene, is more convenient.

Amines are of considerable practical importance, finding use as antioxidants in fuel oils, rubber stabilizers, medicinal drugs, detergents and herbicides.[27]

Generally, the alcohol used to form an amine must first be converted to a halide. The direct methods so far reported for the catalytic amination of alcohols require co-catalysts, such as these: $CuO/\gamma\text{–}Al_2O_3$,[28] $Al(OBu^t)_3$/Raney-Ni,[29] $CuO/Cr_2O_3/Na_2O/SiO_2/H_2O$,[27] $RuCl_2(PPh_3)_2/Ph_3P$,[30] and $Ph_3P^+NMeC_6H_4\ I^-$ /Bu^nNHMe/DMF.[31] We have developed a simpler procedure in which MTO is the sole catalyst.

Disproportionation of alcohols requires hydride transfer, and is usually done with Al_2O_3 at >300 °C,[32-34] or over HY-zeolite in refluxing carbon tetrachloride.[35] We have been able to cause disproportionation to occur at room temperature in benzene with a catalytic amount of MTO.

The shortcoming of the MTO procedures, however, is that the various transformations of alcohols take place concurrently and competitively, controlled largely by the structure of the alcohol. This aspect of the chemistry will be evident from the results obtained.

Results

Formation of ethers. Primary aliphatic alcohols in benzene gave low yields after two days: n-C_4H_9OH, ~7%; n-$C_5H_{11}OH$, ~8%; n-$C_6H_{13}OH$, ~8%. Further time did not increase the yield, as the process is limited by the buildup of water in the system, according to this equation:

$$2\ RCH_2OH \xrightarrow{MTO} RCH_2OCH_2R + H_2O \qquad (2.1)$$

The situation might be improved by employing a dehydrating agent, as it was in olefin-forming reaction referred to in the next section, but that prospect was not explored here.

Table 2.1. Yields [a] of symmetric ethers and of other products formed by alcohol dehydration catalyzed by methylrhenium trioxide.

R^1R^2CHOH,		Conv.,	Yield of	Other products
R^1 =	R^2 =	%	Ether, %	
Ph	H	36	30	~3% PhCHO, ~3% PhMe
Ph	Me	86	80[a]	~2% PhC(O)Me, ~2% PhEt
Ph	Et	89	79[b]	~3%PhC(O)Et, ~3% $PhCH_2Et$
Ph	Ph	100	100	
4-MeC_6H_4	Ph	100	90	~5% 4-$MeC_6H_4C(OH)Ph$
				~5% 4-$MeC_6H_4CH_2Ph$
4-ClC_6H_4	4-ClC_6H_4	10	10	
4-MeC_6H_4	H	42	34	~4% 4-MeC_6H_4CHO
				~4% 4-$MeC_6H_4CH_3$
4-$MeOC_6H_4$	H	48	36	~6% 4-$MeOC_6H_4CHO$
				~6% 4-$MeOC_6H_4CH_3$
1-Naphthyl	H		~4	~2% disproportionation
2-Naphthyl	H		~4	~2% disproportionation
n-C_4H_9	H		~7	
n-C_5H_{11}	H		~8	
n-C_6H_{13}	H		~8	

[a] Yields of the ethers were based on the alcohols; [b] Two isomers, in a 1:1 ratio.

Aromatic alcohols, especially secondary ones, gave higher conversions and greater yields of ethers. The addition of MTO to solutions of such alcohols in benzene gave rise to a yellow color; the nature of this intermediate will be considered subsequently. For alcohols of the general formula PhCH(OH)R, the conversion increased with the size of the group R, thus: R = H, 36%; Me, 86%; Et, 89%; Ph, 100%. If the aryl group has an electron withdrawing group attached, such as 4-NO_2, 4-Br, or 4-Cl, then no ether was formed, and the starting material remained unchanged. Although (4-$ClC_6H_4)_2CHOH$ has two electron withdrawing groups, it was converted to the ether in 10% yield with MTO in benzene. On the other hand, electron-donating groups improved the reaction only to a mild extent: for 4-$XC_6H_4CH_2OH$, the yields are R = H, 36%; Me,42%; R = MeO, 48%. In these cases meso and racemic ethers were produced in nearly equal amounts. Increasing the size of the aryl group decreased the conversion; with 1-naphthyl and 2-naphthyl groups, only 6% conversion was found. **Table 2.1** summarizes these data.

Inhibition by electron-withdrawing substituents reflects a powerful and remarkable electronic effect. It is not entirely eliminated with the use of electron-donating substitutents, as one might suppose, very likely because of the buildup of water, as noted previously.

When low molecular weight primary alcohols were used as the solvent, the aromatic alcohols reacted with them in the presence of MTO to form unsymmetric ethers in high yields, 69–95%. With a tertiary alcohol, however, such as tert-butanol, only 10% of the aromatic alcohol was converted to an unsymmetric ether under these conditions, the balance being the ether formed by the self-coupling of the aromatic ether. The results are given in **Table 2.2.**

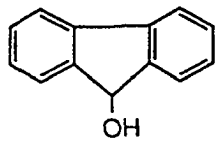
The successful strategy for unsymmetric aromatic ethers is based on using the more reactive aromatic alcohol at a much lower concentration than the aliphatic alcohol. Even then, some of the symmetric ether from the aromatic alcohol was formed. If the two alcohols used had similar reactivities, such as PhCH(OH)Me and PhCH(OH)Et, then three ethers were formed, $(PhCHMe)_2O$, $(PhCHEt)_2O$, and the unsymmetric ether PhCHMeOCH(Ph)Me. As it happened, the three were nearly equal in yield. In all the other cases, however, the unsymmetric ether was the major product. The findings are summarized in **Table 2.3.**

Table 2.2. Formation of unsymmetric ethers by coupling aromatic and aliphatic alcohols, catalzyed by MTO

Aromatic alcohol	Alipha·· alcohol	Yield, %[a]	Other product
Ph_2CHOH	EtOH	89	$(Ph_2CH)_2O$, 11%
Ph_2CHOH	*n*-C_3H_7OH	91	$(Ph_2CH)_2O$, 9%
Ph_2CHOH	*n*-C_4H_9OH	92	$(Ph_2CH)_2O$, 8%
Ph_2CHOH	*n*-$C_5H_{11}OH$	95	$(Ph_2CH)_2O$, 5%
Ph_2CHOH	*t*-Me_3COH	10	$(Ph_2CH)_2O$, 90%
$PhCH(OH)CH_3$	EtOH	69	$(PhMeCH)_2O$, 31%
$PhCH(OH)CH_3$	CH_2=$CHCH_2OH$	85	$(PhMeCH)_2O$, 15%

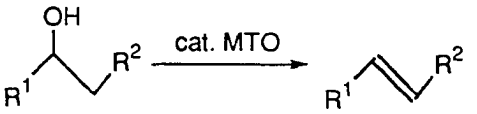
[a]Yields are based on the limiting amount of the aromatic alcohol, 10 mmol, dissolved in 15 mL of the dry aliphatic alcohol to which 0.2 mmol MTO was added.

Table 2.3. Yields of unsymmetric ethers from pairs of aromatic alcohols, catalyzed by MTO.

Alcohol A	Alcohol B	Ratio, A/B	Yield, %[a]
	$(4\text{-}MeOC_6H_4)_2CHOH$	3:1	93
PhCH(OH)Et	$(4\text{-}MeOC_6H_4)_2CHOH$	5:1	85
PhCH(OH)Me	$(4\text{-}MeOC_6H_4)_2CHOH$	10:1	90
PhCH(OH)Et	$(4\text{-}ClC_6H_4)_2CHOH$	1:15	83
Ph_2CHOH	$(4\text{-}ClC_6H_4)_2CHOH$	1:5	89
$PhCH_2OH$	Ph_2CHOH	10:1	100
PhCH(OH)Me	Ph_2CHOH	10:1	99
PhCH(OH)Et	Ph_2CHOH	10:1	96
PhCH(OH)Me	PhCH(OH)Et	1:1	34

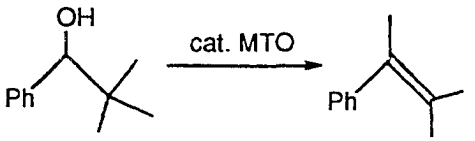
[a] Relative to the alcohol taken in limiting amount. 10 mmol of the limiting alcohol was used, with 0.2 mmol of MTO in 100 mL dry benzene.

Olefins from alcohol dehydration. The process in eq 2.2 was observed for the aliphatic alcohols, but the yields were quite low. With aromatic alcohols, however, the olefin yields were satisfactory, although accompanying amounts of ether and disproportionation products were formed. The data are given in **Table 2.4.**



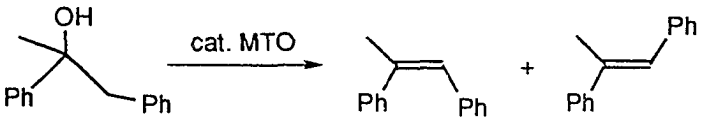
(2)

Some polymer formation, also MTO-catalyzed, accompanied these reactions. A solution of 0.2 mmol MTO in 25 mL of the alcohol was sealed in a 30-mL glass vial for one month, at which time 11% of the alcohol had ben converted to the polystyrene. Although attempts to synthesize the ether from 2,3-dimethyl-1-phenyl-1-propanol failed, an olefin was obtained after dehydration and rearrangement:



(2.3)

The tertiary aromatic alcohol, 1,2-diphenyl-2-propanol, yielded two olefins, Z- and E-methylstilbenes, in a 1:5 ratio:



(2.4)

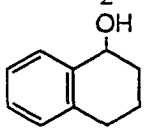
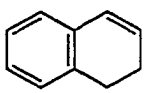
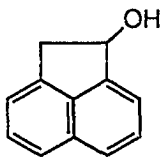
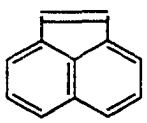
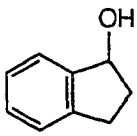
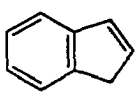
By way of comparison, dehydration with sulfuric acid, which occurs through a pure E_1 mechanism, gave a Z:E ratio of 1:18.[36]

Table 2.4. MTO–catalyzed dehydration of alcohols to form olefins.

Part A. Reactions with the alcohol as the solvent[a]

Alcohol	Product	Turnovers[b]
3-octanol	3-octene	40
1-dodecanol	1-dodecene	43
cyclo-octanol	cyclo-octene	76
c-$C_6H_{13}CH_2OH$	methylenecyclohexane	12
PhCH(OH)Me	$PhCH{=}CH_2$	100
PhCH(OH)Et	PhCH=CHMe	108
2-methyl-2-hexanol	$Pr^nCH{=}CMe_2$, $Bu^nCMe{=}CH_2$	66

Part B: Reactions in benzene[c]

Alcohol	Product	Yield, %[d]
$PhCH(OH)Bu^t$	$PhCMe{=}CMe_2$	11
$PhCMe_2OH$	$(Ph,Me)C{=}CH_2$	46
		71
		89
		64
$PhCH(OH)CHMe_2$	$PhCH{=}CMe_2$	33

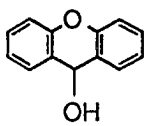
[a] MTO (0.2 mmol) was dissolved in 15 mL alcohol, and allowed to stand for three days. [b] Turnovers = mol of product/mol of catalyst, after three days. [c] The alcohol

(20 mmol) and MTO (0.2 mmol) were dissolved in 100 mL dry benzene and allowed to stand for three days. [d] Isolated yield.

Amination of aromatic alcohols. Secondary amines were obtained from primary aromatic alcohols and aliphatic or aromatic amines as in eq 2.5. These preparations were carried out by using the alcohol in excess in dry benzene.

$$ArCH(OH)R + R'NH_2 \xrightarrow{\text{cat. MTO}} ArCHRNHR' + H_2O \qquad (2.5)$$

Table 2.5. Yields of secondary amines from MTO-catalyzed aminations of alcohols, eq 2.5.

Alcohol	Amine	Yield, %[a]	Other products
Ph_2CHOH	$PhNH_2$	91 (26)[b]	$(Ph_2CH)_2O$
	$PhNH_2$	96	disproportionation
$(MeOC_6H_4)CHOH$	$PhNH_2$	>95	disproportionation
$(MeC_6H_4)PhCHOH$	$PhNH_2$	>95	MeC_6H_4CHOPh
$(MeOC_6H_4)CHOH$	n-$C_6H_{13}NH_2$	94	disproportionation
Ph_2CHOH	n-$C_6H_{13}NH_2$	92	$(Ph_2CH)_2O$

[a] Based on the amine in a reaction of 1 mmol amine and 3 mmol alcohol in 20 mL dry benzene to which 0.2 mmol MTO was added. [b] When 1 mmol amine and 3 mmol benzhydrol were used.

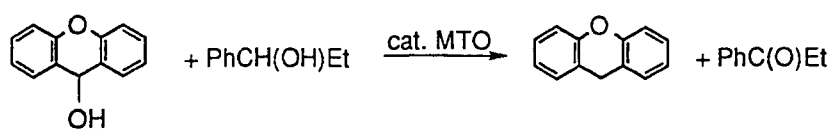
The yields (based on the limiting amines) were satisfactory, although considerable quantities of the ethers were also obtained. When the alcohol and amine were taken in equal quantity, however, the yields of secondary amine were considerably reduced. The data are summarized in **Table 2.5.**

Disproportionation of aromatic alcohols. Disproportionation of aromatic alcohols catalyzed by MTO, was observed for all the primary and secondary alcohols, except benzhydrol and those alcohols lacking an electron withdrawing group. These studies were carried out with 10 mmol alcohol and 0.2 mmol MTO in 100 mL dry benzene. 4,4'-Dimethoxybenzhydrol and 9-hydroxyxanthene undergo disproportionation only, eq 6; no ether was formed.

$$Ar^1Ar^2CHOH \xrightarrow{\text{cat. MTO}} Ar^1Ar^2C=O + Ar^1Ar^2CH_2 \qquad (2.6)$$

4-Methoxybenzhydrol gave both disproportionation (60% of the starting alcohol) and ether formation (40%). Mono-aryl alcohols, $ArCH_2OH$, underwent disproportionation to a much smaller extent: Ar = Ph, 6%; 4-MeC_6H_4, 8%; 4-$MeOC_6H_4$, 12%; 1-Naphthyl, 2%; 2-Naphthyl, 2%. Aryl,alkyl alcohols gave these percentages of disproportionation: PhCH(OH)Me, 4%; PhCH(OH)Et, 6%; 1,2,3,4-tetramethyl-1-naphthol, 11%.

Disproportionation was also observed between two different alcohols, 9-hydroxyxanthene and excess PhCH(OH)Et, which yielded only one set of products when the reaction was carried out in dry benzene, eq 2.7. No mixed ether was formed.

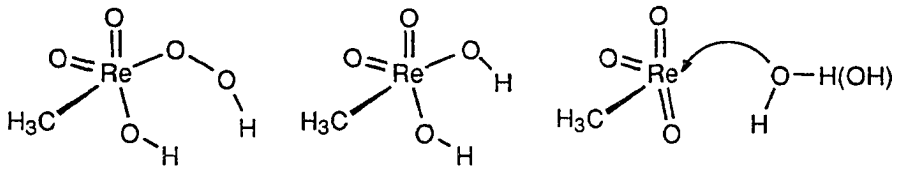


(2.7)

It should also be noted that no EPR signal was observed during the course of the disproportionation of 4,4'-dimethoxy-benzhydrol, even when the spectrum was recorded at 110 K in frozen C_6D_6.

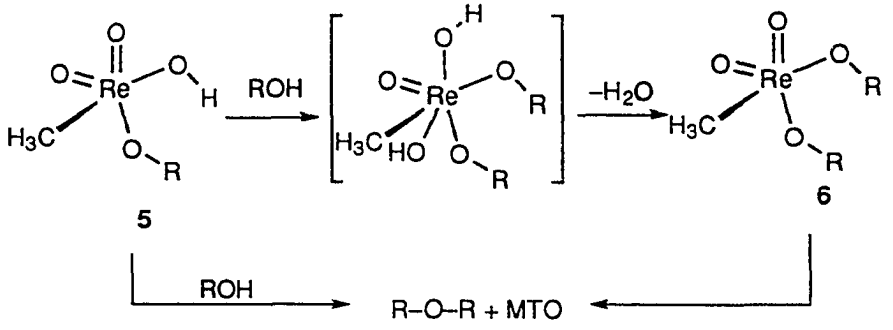
Discussion

The intermediates characterized and inferred during (a) the exchange of oxygen atoms between water and MTO and (b) the formation of the rhenium peroxides $CH_3Re(O)_2(\eta^2\text{–}O_2)$, **A**, and $CH_3Re(O)(\eta^2\text{–}O_2)_2(H_2O)$, **B**, may be pertinent to the present work. Intermediate **1** has been characterized as a precursor to **A**, and it thus seems highly likely that intermediate **2** serves as the vehicle for oxygen exchange between MTO and water. In both cases, nucleophilic attack by H_2O_2 or H_2O on the highly electropositive Re(VII) center, as shown in **3**, will generate the intermediates **1** and **2**.



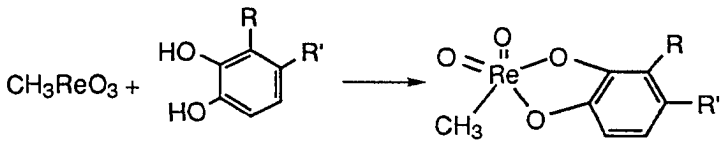
1 **2** **3**

From these comparisons, and since the rhenium diperoxide **B** is yellow, like the peroxorhenium complex, it is logical to infer that the reaction between MTO and aromatic alcohols proceeds through similar intermediates, with a single alcohol, **5**, and possibly with two, **6**. The second of these is less certain, since ethers could result instead from the attack of a second alcohol on **5**.



(2.8)

Attempts to isolate **5** and **6** were not successful; this is not unduly discouraging, however, since the OH analogues have not been directly seen. As an independent precedent, we note the condensation reaction between MTO and 1,2-dihydroxybenzene.[37]



(2.9)

Certain Lewis acids, such a zinc chloride,[18] catalyze the formation of ethers from alcohols, these are really stoichiometric reactions that are critically dependent on the solvent; the zinc chloride reaction, for example, is successful only in dichlorethane. MTO appears to be the first transition metal complex that leads to the direct formation of ethers from alcohols when used in catalytic amounts; this reaction can be carried out in benzene, toluene, dichloromethane, chloroform, acetone, and in the alcohols themselves.

Our findings that (a) no reaction occured with alcohols containing an electron-withdrawing group at the para position suchd as NO_2, Br, and Cl, (b) an olefin was formed from 2,2-dimethyl-1-phenyl-1-propanol, and (c) alcohols

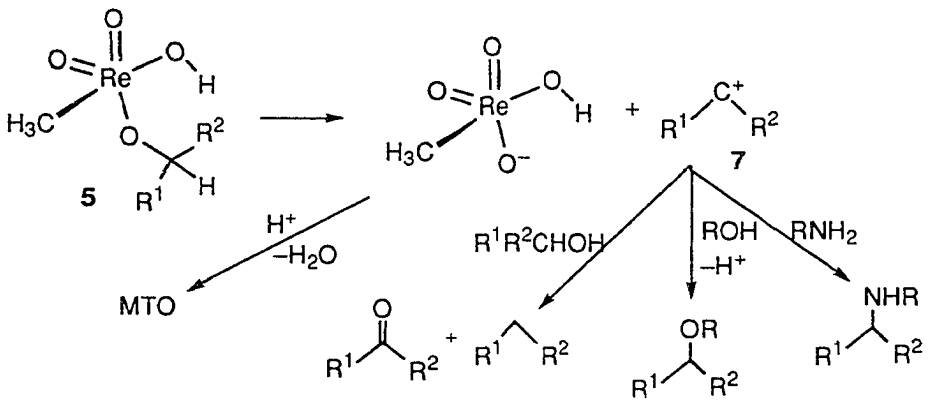
underwent disproportionation catalyzed by MTO lead us to suggest that these reaction occur through a carbocation intermediate **7**.

Two possible mechanisms can be suggested based on the results obtained. One of these is a concerted process. In it, the formation of the dialkoxide **6** is the first step, and this yields the ether, as in eq 2.10:

$$\mathbf{6} \rightarrow \text{MTO} + \text{R–O–R} \qquad (2.10)$$

This mechanism also explains why the smaller primary alcohols can form ethers, whereas the larger ones cannot: 1-dodecanol and 1-undecanol yield only the alkene by dehydration. This is due to the limited space in the coordination sphere of MTO. The dehydration reaction of 1,2-diphenyl-2-propanol should give a Z:E ratio of about 1:1 if the reaction is fully concerted. The observed ratio of Z:E::1:5 suggests that both concerted and carbonium ion pathways may contribute.

As far as the carbonium ion mechanism is concerned, formation of **6** is not necessary. After the first alcohol has been added, giving **5**, a carbocation intermediate **7** can be formed. Indeed, the ethers and the amines are formed by the nucleophilic addition of a second alcohol or of the amine to **5**.



Those alcohols that can generate a stable carbocation allow a second alcohol to react with it; this yields a ketone and and an alkane through disproportionation. Alternatively, the cation can be intercepted by the alcohol or by the amine. The results we have obtained suggest that the concerted process of eq 10 is the dominant one for the primary alcohols, whereas a carbocation intermediate provides the major pathway for the aromatic alcohols.

Eeperimental section

Materials. The chemicals were purchased commercially, and their purity was verified by GC-MS. The samples of methylrhenium trioxide used in this research were also purchased (Aldrich). The solvents were purified by standard procedures.[38]

Symmetric ethers. This is the general procedure: the alcohol (40 mmol) and MTO (0.2 mmol) were dissolved in 100 mL of dry benzene, and the solution allowed to stand at room temperature for two days. Much of the solvent was removed by rotary evaporation. Separation and purification of the ether was realized by vacuum distillation, recrystalization, or column chromatography using hexane/ethyl acetate (10:1 ~ 1:1) as the eluant. The products were identified by their NMR spectra, **Tables S-2.1 and S-2.2,** in comparison with literature data.[38,39]

Unsymmetric ethers. The alcohol (10 mmol) and MTO (0.2 mmol) were dissolved in 15 mL of the dry aliphatic alcohol, and allowed to stand at room temperature for two days. The crude products were obtained by removing the excess aliphatic alcohol and the symmetric ether using rotary evaporation. The pure ether was isolated by column chromatography using hexane/ethyl acetate

(10:1 ~ 1:1) as the eluant. When a pair of unsymmetric aromatic alcohols was used, the procedure was the same except that the two alcohols were used in 20 mL of dry benzene, the more reactive alcohol being taken in limiting quantity, 10 mmol, along with 0.2 mmol MTO.

Amination reactons. The alcohol (3 mmol), amine (1 mmol) and MTO (0.2 mmol) were dissolved in 20 mL dry benzene and allowed to stand for two days. The balance of the procedure was the same.

Olefin formation. The catalyst (0.2 mmol) was dissolved in 15 mL of the dry alcohol, and allowed to stand for three days. The olefins were isolated by distillation. For some of the aromatic alcohols, dry benzene with 20 mmol alcohol and 0.2 mmol MTO was used.

Identifications. The products were identified by their NMR spectra, **Tables S-2.1 and S-2.2**, in comparison with literature data.[38,39]

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.

Supporting Information

Organic Reactions Catalyzed by Methylrhenium Trioxide: Dehydration, Amination and Disproportionation of Alcohols

Zuolin Zhu and James H. Espenson

Table S-2.1. NMR data for the symmetric ethers formed from reactions of alcohols catalyzed by MTO.

Alcohol		^{1}H-NMR, δ	^{13}C-NMR, δ
$PhCH_2OH$	A	7.34 (m, 10H), 4.53 (s, 4H)	138.24, 128.37, 127.74, 127.59, 72.05
PhCH(OH)Me	A	7.26 (m, 10H), 7.24 (m, 10H) 4.48 (q, 2H), 4.21 (q, 2H), 1.44 (d, 6H), 1.36 (d, 6H)	144.11, 128.20, 127.10, 126.17, 74.36, 22.99, 144.20, 128.42, 127.34, 126.26, 74.57, 24.69.
PhCH(OH)Et	A	7.24 (m, 10H), 7.26 (m, 10H) 3.94 (t, 2H), 4.28 (t, 2H), 1.55 (m, 4H), 1.81 (m, 4H), 0.785 (t, 6H), 0.88 (t, 6H).	142.87, 127.90, 127.15, 126.77, 79.95, 29.71, 9.73, 142.96, 128.46, 127.34, 126.89, 80.54, 31.32, 10.44.
PhCH(OH)Ph	B	7.28 (m, 20H), 5.39(s, 2H)	142.19, 128.37, 127.41, 127.24, 79.95.
4-MeO-$PhCH_2OH$	A	7.21-6.94 (m, 8H), 4.28 (s, 4H), 3.54 (s, 6H).	159.11, 131.12, 128.54, 113.79, 68.63, 55.32.
4-Me-$PhCH_2OH$	A	7.15-7.25 (m, 8H), 4.50 (s, 4H), 2.35 (s, 6H)	137.26, 135.25, 129.05, 127.89, 71.75, 21.16.
2-Naphth-CH_2OH	C	7.48-7.83 (m, 14H), 4.77 (s, 4H)	138.30, 133.38, 132.96, 128.36, 127.90, 127.73, 126.21, 125.92, 125.45, 125.17, 72.22.
1-Naphth-CH_2OH	C	7.42-8.13 (m, 14H), 4.83 (s, 4H).	131.18, 128.29, 127.84, 127.67, 126.76, 125.75, 125.22, 125.12, 124.84, 124.18, 70.64.
4-Me-Ph-CH(OH)Ph	C	7.14-7.34 (m, 18 H), 5.35 (s, 2H), 2.33 (s, 6H). 7.15-7.36 (m, 18H), 5.36 (s, 2H), 2.34 (s, 6H).	142.44, 139.20, 136.99, 129.04, 128.28, 127.18, 127.16, 79.67, 21.12. 142.55, 139.32, 137.03, 129.06, 128.31, 127.21, 127.19, 79.68, 21.12.

Table S-2.1
(continued)

4,4'-$Cl_2C_6H_3$-CH(OH)Ph	C	7.29 (m, 16H), 5.28 (s, 2H).	140.79, 133.73, 128.83, 128.38, 78.98.
n-Bu-OH	A	3.39 (t, 4H), 1.56 (m, 4H), 1.37 (m, 4H), 0.92 (t, 6H).	70.67, 31.94, 19.51, 14.01.
n-Pentanol	A	3.38 (t, 4H), 1.24-1.61 (m, 12H), 0.91 (t, 6H).	71.04, 29.43, 28.54, 22.61, 14.02.
n-Hexanol	A	3.39 (t, 4H), 1.21-1.60 (m, 16H), 0.89 (t, 6H).	71.12, 31.87, 29.79, 26.00, 22.45, 14.00.

A: Separation was done by vaccum distillation, **B.** Isolation was done by recrystalization from benzene, water and ethanol. The product structure was identified using X-ray crystal analysis. **C.** Isolation was done by column chromatography using 10 :1 to 1:1 ratio of hexane to ethyl acetate as eluant.

Table S-2.2. NMR data for the unsymmetric ethers formed from reactions of alcohols catalyzed by MTO: one aromatic and one aliphatic alcohol

Aromatic Alcohol	Other Alcohol		^{1}H-NMR, δ	^{13}C-NMR, δ
PhCH(OH)Ph	ethanol	C	7.22 (m, 10H), 5.34 (s, 1H), 3.50 (q, 2H), 1.36 (t, 3H)	142.47, 127.27, 126.97, 126.40, 83.51, 64.45, 15.26
PhCH(OH)Ph	*n*-Pr-OH	C	7.22 (m, 10H), 5.33 (s, 1H), 3.40 (t, 2H), 1.64 (m, 2H), 0.94 (t, 3H).	142.63, 128.30, 127.28, 126.94, 83.52, 70.81, 23.09, 10.76
PhCH(OH)Ph	*n*-Bu-OH	C	7.20 (m, 10H), 5.33 (s, 1H), 3.43 (t, 2H), 1.36-1.67 (m, 4H), 0.90 (t, 3H)	142.63, 128.30, 127.27, 126.93, 83.55, 68.91, 31.97, 19.45, 13.93
PhCH(OH)Ph	*n*-Pentanol	C	7.21 (m, 10H), 5.32 (s, 1H), 3.41 (t, 2H), 1.26-1.61 (m, 6H), 0.90 (t,3H)	142.63, 128.30, 127.26, 126.93, 83.54, 69.62, 29.21, 28.49, 22.37, 13.99
PhCH(OH)Ph	*t*-Bu-OH	C	7.20 (m, 10H), 5.33 (s, 1H), 1.22 (s, 9H)	142.24, 128.48, 127.31, 126.52, 83.67, 72.44, 31.30
PhCH(OH)Me	ethanol	A	7.24 (m, 5H), 4.40 (q, 1H), 3.35 (q, 2H), 1.41 (d, 3H), 1.18 (t, 3H)	144.12, 128.23, 127.10, 126.18, 79.33, 64.51, 23.01, 15.12
PhCH(OH)Me	Allyl alcohol	A	7.25 (m, 5H), 6.11 (m. 1H), 5.20 (m, 2H), 4.41 (q, 1H), 3.89 (d, 2H), 1.44 (d, 3H).	144.11, 128.20, 127.08, 126.17, 137.85, 115.21, 82.08, 70.24, 24.33.

Table S-2.3. NMR data for the unsymmetric ethers formed from reactions of alcohols catalyzed by MTO: two aromatic alcohols

Aromatic Alcohol	Other Alcohol		^{1}H-NMR, δ	^{13}C-NMR, δ
9-Hydroxy-fluorene (3 ×)	4,4'($MeOC_6H_3$)$_2$ CHOH (1 ×)	C	7.61-6.80 (m, 16H), 5.70 (s, 1H), 5.59 (s, 1H), 3.75 (s, 6H)	158.83, 143.95, 140.55, 135.06, 128.69, 128.31, 127.29, 125.68, 119.73, 113.60, 81.23, 79.40, 55.21
PhCH(OH)Me (10 ×)	4,4'($MeOC_6H_3$)$_2$ CHOH (1 ×)	C	7.22-6.76 (m, 13H), 5.16 (s, 1H), 4.41 (q, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 1.38 (d, 3H)	158.89 (158.53), 143.79, 135.35 (134.14), 128.11, 129.95, (128.96), 127.33, 113.79 (113.47), 126.48, 79.09, 74.63, 55.14 (55.12), 24.18
PhCH(OH)Et (5 ×)	4,4'($MeOC_6H_3$)$_2$ CHOH (1 ×)	C	7.23-6.76 (m, 13H), 5.13 (s, 1H), 4.15 (t, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 1.65 (m, 2H), 0.86 (t, 3H)	158.90 (158.42), 142.79, 134.10 (132.84), 128.98, 129.67 (128.86), 128.17, 113.78, (113.73), 125.25, 80.00, 78.75, 55.15, (55.14), 31.11, 10.36
PhCH(OH)Et (1×)	4,4'(ClC_6H_3)$_2$ CHOH (15 ×)	C	7.25-7.13 (m, 13H), 5.14 (s, 1H), 4.12 (t, 1H), 1.69 (m, 2H),0.77 (t, 3H)	141.00, 139.88, 132.82, 128.94, 128.70, 128.48, 127.64, 126.61, 80.51, 78.27, 30.99, 10.24
PhCH(OH)Ph (1 ×)	4,4'(ClC_6H_3)$_2$ CHOH (5 ×)	C	7.38-7.23 (m, 18H), 5.34 (s, 1H), 5.33 (s, 1H)	143.73, 141.67, 140.22, 133.45, 128.83, 128.83, 128.69, 127.64, 127.11, 80.28, 78.70

Table S-2.3
(continued)

$PhCH_2OH$ (10 ×)	PhCH(OH)Ph (1 ×)	C	7.38-7.11 (m, 15H), 5.41 (s, 1H), 4.50 (s, 2H)	141.93, 138.18, 128.92, 128.30, 127.63, 127.45, 127.03, 125.19, 82.32, 70.35
PhCH(OH)Me (10 ×)	PhCH(OH)Ph (1 ×)	C	7.38-7.17 (m, 15H), 5.30 (s, 1H), 4.56 (q, 1H), 1.41 (d, 3H)	143.60, 142.73, 141.93, 128.10, 127.50, 127.04, 126.88, 126.48, 79.94, 74.90, 24.21
PhCH(OH)Et (10×)	PhCH(OH)Ph (1 ×)	C	7.33-7.15 (m, 15H), 5.22 (s, 1H), 4.18 (t, 1H), 1.68 (m, 2H), 0.87 (t, 3H)	143.02, 142.31, 141.89, 130.98, 128.47, 127.50, 127.43, 125.74, 80.21, 79.66, 31.12, 10.31
PhCH(OH)Me (1 ×)	PhCH(OH)Et (1 ×)	A	7.19 (m, 10H), [7.24 (m, 10H)] 4.43 (q, 1H), [4.52 (q, 1H)], 3.96 (t, 1H), [4.33 (t, 1H)] 1.69 (m, 2H), [1.82 (m, 2H)], 1.35 (d, 3H), [1.42 (d, 3H)] 0.65 (t, 3H), [0.82 (t, 3H)]	144.37, 144.04, 142.90, 128.41, 128.11, 127.14, 126.80, 126.22, 80.50, 74.47, 31.37, 24.62, 12.40 144.15, 143.98, 142.84, 128.22, 128.07, 126.89, 126.54, 125.80, 80.22, 70.22, 30.47, 22.21, 10.10

Table S-2.4. NMR data for the secondary amines formed from reactions of alcohols and primary amines, catalyzed by MTO

Alcohol	Amine		^{1}H-NMR, δ	^{13}C-NMR, δ
PhCH(OH)Ph	Aniline	C	7.33-6.58 (m, 15H), 5.71 (s, 1H), 3.11 (s,1H)	146.07, 143.78, 129.17, 128.36, 127.40, 126.47, 116.45, 115.18, 76.02
9-HO-xanthene	Aniline	C	7.26-6.59 (m, 13H), 5.15 (s, 1H), 3.29 (s, 1H)	151.02, 144.90, 136.79, 129.68, 129.61, 127.61, 124.96, 123.08, 116.37, 115.34, 43.43
4,4'-di-MeO-benzhydrol	Aniline	C	7.35-6.51 (m, 13H), 5.40 (s, 1H), 3.76 (s, 6H), 2.50 (s,1H).	158.68, 147.40, 135.36, 129.23, 128.43, 117.43, 113.75, 113.40, 61.64, 55.21
4-Me-Benzhydrol	Aniline	C	7.35-6.65 (m, 14H), 4.60 (s, 1H), 2.54 (s, 1H), 2.34 (s,3H)	146.21, 143.87, 140.88, 137.89, 137.29, 137.24, 129.23, 129.17, 128.29, 127.06, 118.60, 115.14, 61.12, 21.09
4,4'-di-MeO-benzhydrol	*n*-Hexylamine	C	7.77-6.92 (m, 8H), 5.44 (s, 1H), 3.85 (s, 6H), 2.47 (t, 2H), 1.49-1.17 (m, 9H), 0.88 (t, 3H)	162.76, 132.17, 128.24, 113.37, 75.02, 55.34, 41.72, 33.11, 31.54, 26.41, 22.53, 13.97.
PhCH(OH)Ph	*n*-Hexylamine	C	7.30 (m, 10H), 5.76 (s, 1H), 2.55 (t, 2H), 1.33(m, 9H), 0.88 (t, 3H)	144.07, 128.22, 127.35, 126.51, 75.97, 41.82, 33.31, 31.62, 26.48, 22.61, 14.04

References

(1) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Cat.* **1994**, *86*, 243.

(2) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1636.

(3) Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organomet.* **1994**, *13*, 4531.

(4) Zhu, Z.; Espenson, J. H. *J. Mol. Catal.* **1995**, in press.

(5) Zhu, Z.; Espenson, J. H. *submitted for publication*

(6) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157.

(7) Al-Ajlouni, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *in press*,

(8) Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1993**, *32*, 4517.

(9) Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491.

(10) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326.

(11) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* in press.

(12) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272.

(13) Barton, D.; Ollis, W. D. *Comprehensive Organic Chemistry*; Pergamon: Elmsford, 1979; Vol. 1, p 819.

(14) Curtin, D. Y.; Lescowitz, S. *J. Am. Chem. Soc.* **1951**, *73*, 2630.

(15) Traynellis, V. J.; Hergenrother, W. L.; Hanson, H. T.; Valicenti, J. A. *J. Org. Chem.* **1964**, *29*, 123.

(16) Emert, J.; Goldenberg, M.; Chiu, G. L.; Valeri, A. *J. Org. Chem.* **1977**, *42*, 2012.

(17) Noda, I.; Horita, K.; Oikawa, Y.; Yonemitsu, O. *Tetrahedron Lett.* **1986**, *27*, 1917.

(18) Kim, S.; Chung, K. N.; Yang, S. *J. Org. Chem.* **1987**, *52*, 3917.

(19) Trost, B. M.; Lautens, M.; Peterson, B. *Tetrahedron Lett.* **1983**, 4525.

(20) Nishiguchi, T.; Kamio, C. *J. Chem. Soc., Perkin Trans. I* **1989**, 707.

(21) Keinan, E.; Mazur, Y. *J. Org. Chem.* **1978**, *43*, 1020.

(22) Gaston, J. L.; Grundon, M. F.; James, K. J. *J. Chem. Soc., Perkin Trans. I* **1980**, 1136.

(23) Piers, E.; Karunaratne, V. *Can. J. Chem.* **1989**, 160.

(24) Posner, G. H.; -Roskes, E. M. S.; Chang, H. O.; Carry, J. C.; Green, J. V.; Clark, A. B.; Dai, H.; Anjeh, T. E. N. *Tetrahedron Lett.* **1991**, 6489.

(25) Saikia, A. K.; Barua, N. C.; Sharma, R. P.; Ghosh, A. C. *Synthesis* **1994**, 685.

(26) Dorta, R. L.; Suarez, E.; Betancor, C. *Tetrahedron Lett.* **1994**, *35*, 5035.

(27) Baiker, A.; Richarz, W. *Tetrahedron Lett.* **1977**, *18*, 1937.

(28) Baiker, A.; Richarz, W. *Synthetic Communications* **1978**, *8*, 27.

(29) Botta, M.; Angelis, F. D.; Nicoletti, R. *Synthesis* **1977**, 722.

(30) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y. *Tetrahedron Lett.* **1981**, *22*, 2667.

(31) Tanigawa, Y.; Murahashi, S. I.; Moritani, I. *Tetrahedron Lett.* **1975**, *16*, 2667.

(32) Jayamani, M.; Pillai, C. N. *Journal of Catalysis* **1989**, *119*, 8.

(33) Jayamani, M.; Pillai, C. N. *Journal of Catalysis* **1983**, *82*, 485.

(34) Jayamani, M.; Murugasen, N.; Pillai, C. N. *Journal of Catalysis* **1984**, *85*, 527.

(35) Climent, M. J.; Corma, A.; Garcia, H.; Iborra, S.; Primo, J. *J. Recl.Trav.Chim.Pays-Bas* **1991**, *110*, 275.

(36) Crummit, O.; Becker, E. I. *Org.Syn.Coll.* Vol 1.Wiley:New York **1963**, 771.

(37) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organomet.* **1990**, *9*, 782.

(38) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals;* 3d ed.; Butterworth-Heinemann: Oxford, 1988.

(39) Pouchert, C. J.; Behnke, J. *The Aldrich Library of* ^{13}C *and* ^{1}H *FT-NMR Spectra;* 1993.

CHAPTER III

METHYLRHENIUM TRIOXIDE AS CATALYST FOR OXIDATION WITH MOLECULAR OXYGEN AND OXYGEN TRANSFER

A paper in press in the *Journal of Molecular Catalysis*

Zuolin Zhu and James H. Espenson

Abstract

Methylrhenium trioxide (MTO) was found to be a good catalyst for the oxidation of tertiary phosphines by molecular oxygen at room temperature. Evidence is given that an intermediate Re(V) compound – CH_3ReO_2, or the adduct $CH_3ReO_2{\cdot}O{=}PPh_3$ – is involved. The deoxygenation of epoxides, sulfoxides, *N*-oxides, triphenylarsine oxide and triphenylstibine oxide at room temperature was also catalyzed by MTO, with triphenylphosphine as the oxygen acceptor. A plausible reaction mechanism involves phosphine attack at a compound formed between MTO and the epoxide or other oxygen-donor compound.

Key words: catalysis, phosphines, oxidation, rhenium, oxygen, oxides

Introduction

Transition metal–oxo complexes are of great relevance to many catalytic oxidation processes and to oxygen atom transfer between substrates [1].

Methylrhenium trioxide (CH_3ReO_3, abbreviated as MTO), is a stable compound prepared from dirhenium heptoxide and tetramethyltin [2]. It acts as an efficient homogeneous oxidation catalyst for hydrogen peroxide in both aqueous and organic solvents. With hydrogen peroxide as the oxidant, MTO catalyzes olefin epoxidations [3, 4], conversion of thiolatocobalt to sulfenatocobalt [5], oxidations of organic sulfides [6], phosphines, triphenylarsine, and triphenylstibine [7], and tertiary amines to the corresponding oxides [8], and for the conversion of aniline to nitrosobenzene. [8] With **S** representing such a substrate, all of these reactions can be abbreviated as:

$$S + H_2O_2 \xrightarrow{cat.\ MTO} S{=}O + H_2O \qquad (3.1)$$

Since both the activation of molecular oxygen and oxygen transfer are important industrially and biologically, the catalytic properties of many transition metal oxo complexes have been studied, including ruthenium(V) [9a], molybdenum(V) [9b], ruthenium(IV) [10], and rhenium(V) [11]. These oxo complexes and the hexanuclear carbonyl cluster $Rh_6(CO)_{16}$ [12] are capable of activating molecular oxygen or transferring an oxygen atom. This type of catalytic process for methylrhenium trioxide remains unexplored.

We have found that MTO catalyzes the oxidation of tertiary phosphines by molecular oxygen. Also, we have examined the transfer of the oxygen atom from epoxides, sulfoxides, aromatic tertiary amine oxides, triphenylarsine oxide, and triphenylstibine oxide. In each case the oxygen acceptor was triphenylphosphine.

Results

Catalyzed phosphine oxidation with molecular oxygen. The oxidation of tertiary phosphines was conducted in benzene at room temperature. Two different methods were used. First, the solutions containing MTO and the triarylphosphines were opened to air with stirring. One day later, substantial yields of phosphine oxides were recorded. The yields differ with the substrate, as given in **Table 3.1.**

TABLE 3.1. Product yields from the oxidation of triarylphosphines with air, catalyzed by MTO [a]

$(4\text{–}R\text{–}C_6H_4)_3P$, R =	% Yield	
	24 h	48 h
H	62	> 97
CH_3	71	100
Cl	53	> 96
CH_3O	80	100

[a] In benzene solution at room temperature, with phosphine : MTO ~ 10 : 1.

After two days, however, all of the phosphines had been converted to their oxides in yields of > 95%. Second, pure oxygen was used instead of air. In that case the reactions reached completion within six hours or less, with yields of > 95%. A independent reaction was carried out in which MTO was not used: triphenyl

phosphine was dissolved in benzene and exposed to air and stirred. After one week, triphenyl phosphine oxide was not detected from this reaction.

The reactions under pure oxygen at room temperature were monitored by ^{1}H–NMR. During the reaction the signal of the phosphine decreased as that of the oxide appeared. Without oxygen, only one signal from the rhenium present was seen at δ = 1.212 ppm. This corresponds to rhenium(V), perhaps [$CH_3ReO_2 \cdot OPPh_3$] or simply [CH_3ReO_2], [13], which will be abbreviated $\mathbf{V_A}$. A new peak appeared at δ 1.237 ppm after the solution was flushed with oxygen. Isolation of the latter species is in progress.

Oxygen transfer reactions. The reactions described in this section were catalyzed by MTO. This was confirmed by carrying out controls without MTO; in each case, no oxygen transfer reaction was observed even after one week.

Deoxygenation of epoxides. Treatment of an epoxide with triphenylphosphine in the presence of MTO under Ar at room temperature results in the deoxygenation of the epoxide and the formation of an olefin in high yield. The reaction preserves the relative stereochemistry about the C–C bond of the epoxide. The results are given in **Table 3.2**, which lists the epoxide taken, the olefin obtained, and its yield.

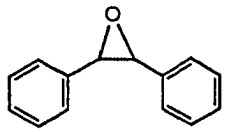
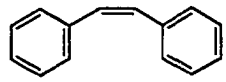
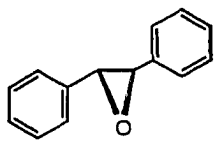
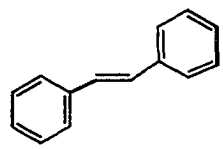
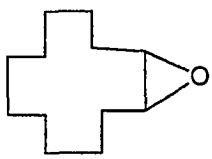
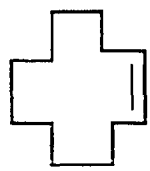
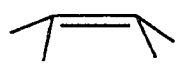
Oxygen abstraction from epoxides was also monitored by ^{1}H–NMR. Upon mixing the epoxide and MTO in benzene at room temperature, the signal corresponding to a dialkoxylrhenium complex (or rhenium glycolate) was observed. [14] Upon addition of triphenylphosphine, signals corresponding to Ph_3PO, olefin, and MTO were seen. Crystals were also isolated from the reaction

mixture. They had the same ^{1}H–NMR spectrum as the dialkoxylrhenium complex in solution. [14]

Deoxygenation of sulfoxides. Treated analogously in benzene, several sulfoxides reacted with triphenylphosphine at room temperature to give the sulfide as the only product. The reaction was studied by ^{1}H–NMR at room temperature. A 1:1 solution of the sulfoxide and MTO showed that the CH_3 group of rhenium after one hour had shifted downfield about 0.1 ppm. Upon addition of triphenylphosphine, the signals corresponding to triphenylphosphine oxide and sulfide appeared immediately. After the reaction has finished, MTO is still active. This was confirmed by the continuation of the catalytic process when more reactants were added.

Oxygen transfer from tertiary amine oxides. MTO also catalyzes oxygen transfer from tertiary amine oxides to triphenylphosphine, forming the amine and triphenylphosphine oxide. This reaction also occurs at room temperature under argon. The results are shown in **Table 3.4.** As for the epoxides, this reaction was investigated by ^{1}H-NMR, ^{13}C-NMR and GC-MS for *N,N*-dimethyl aniline *N*-oxide; see Eq. 3.2. GC-MS was employed in monitoring the reactions and for product identification for the other amine oxides. A mixture of MTO and the amine oxide in benzene at room temperature also shows a chemical shift about 0.1 ppm downfield of the methyl group of MTO which we believe is due to the effect of the substrates used.

Table 3.2. Deoxygenation of epoxides with triphenylphosphine, catalyzed by MTO [a]

Substrate	Olefin product	% Yield
Styrene epoxide	Styrene	83
Cyclohexene epoxide	Cyclohexene	71 [b]
		87
		85
		79
		81 [b]

[a] In benzene at room temperature with epoxide : MTO ~ 10 : 1.

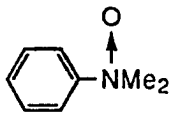
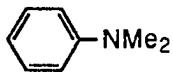
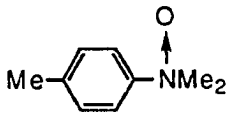
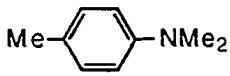
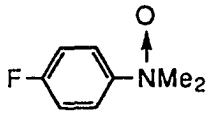
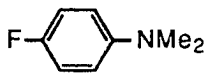
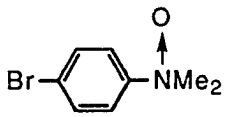
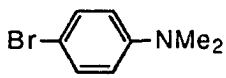
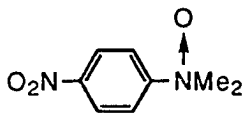
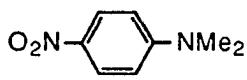
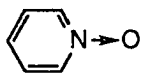
[b] Product yields were calculated from ^{1}H–NMR.

Table 3.3.. Deoxygenation of sulfoxides with triphenylphosphine, catalyzed by methylrhenium trioxide [a]

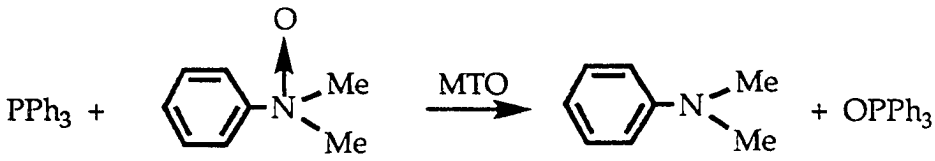
Substrate	Sulfide Produced	% Yield
$PhS(O)CH=CH_2$	$PhSCH=CH_2$	73
Ph_2SO	Ph_2S	66
PhS(O)Me	PhSMe	71
$(Pr^i)_2SO$	$(Pr^i)_2S$	75
$(Bu^n)_2SO$	$(Bu^n)_2S$	77
$(p\text{–}CH_3C_6H_4)_2SO$	$(p\text{–}CH_3C_6H_4)_2S$	65
$(p\text{–}ClC_6H_4)_2SO$	$(p\text{–}ClC_6H_4)_2S$	59

[a] In benzene at room temperature, with sulfoxide : MTO ~ 10 : 1.

Table 3.4.. Deoxygenation of tertiary amine oxides with triphenylphosphine, catalyzed by MTO [a]

Substrate	Amine product	% Yield
		78
		81
		74
		70
		65
		77

[a] In benzene at room temperature, with a mole ratio N–oxide : MTO ~ 10 : 1.



^{1}H-NMR /$CDCl_3$	7.925 ppm (m) 7.458 ppm (m) 3.844 ppm (s)	7.229 ppm (m) 6.714 ppm (m) 2.918 ppm (s)
^{13}C-NMR of Me/$CDCl_3$	61.467 ppm	40.753 ppm

(3.2)

Deoxygenations of triphenylarsine oxide and triphenylstibine oxide. Unlike the oxygen transfer reactions reported previously, the deoxygenations of triphenylarsine oxide and triphenylstibine oxide by Ph_3P are very fast when catalyzed by MTO. Both reactions were finished within 30 min. at room temperature under argon; triphenylarsine and triphenylstibine were formed almost quantitatively. The identities of these products were confirmed spectroscopically; see Eq. 3.3.

^{1}H-NMR /$CDCl_3$	7.85 ppm (m) 7.74 ppm (m)	7.35 ppm (m)	E = As
/C_6D_6		7.42 ppm 7.06 ppm	E = Sb

(3.3)

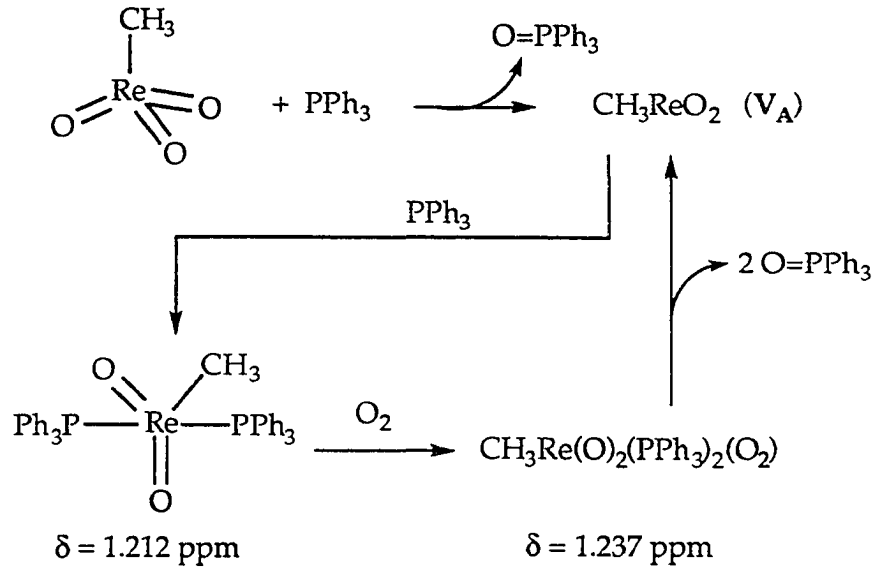
In the absence of triphenylphosphine, the ^{1}H–NMR signal of the methyl group of MTO shifted from 1.196 ppm to 1.390 (E = As) or 1.410 (E = Sb) after addition of excess triphenylarsine oxide or triphenylstibine oxide in benzene. These species are stable at room temperature under argon, where there is no change within three days. In addition about 2% of the MTO decomposed to methanol; but the extent of decomposition did not increase with time in the absence of triphenylphosphine.

Discussion

The oxidation of phosphines with molecular oxygen. The absence of an NMR signal for the methyl group of MTO or other possible oxidants during the reactions was noted. The well-known mono–η^2–peroxide, $CH_3Re(O)_2(O_2)$ **A**, and the bis–η^2–peroxide, $CH_3Re(O)(O_2)_2$ **B**, if present at all, remained undetected. This finding suggested a reaction pathway unlike that for catalytic oxidations that use hydrogen peroxide as the oxidant. [5, 7, 8, 13] In contrast, the oxidations of phosphines with molecular oxygen do not seem to occur by way of **A** or **B** formed from hydrogen peroxide. (Shortly, however, this statement will be revised so as to admit the possibility that **A** might be involved, but simply present at too low a concentration for detection.) From the ^{1}H–NMR data and results in the literature, [16] we suggest that this reaction may follow a mechanism that involves an oxygen-containing intermediate, Scheme I.

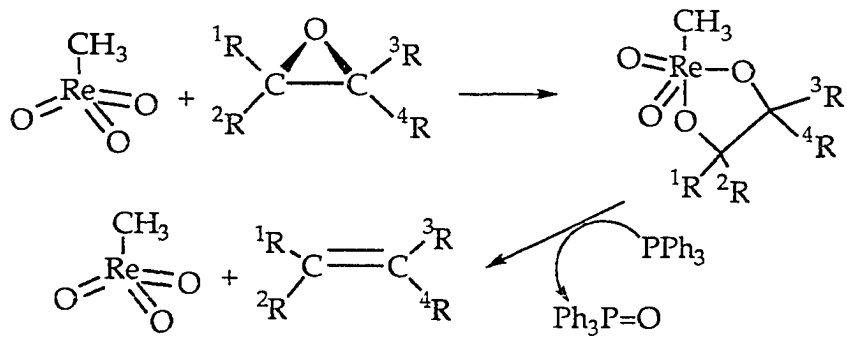
The incorporation into a substrate of an oxygen atom from molecular oxygen is important both industrially and biologically. Phosphines act as blood poisons, which may arise from the reaction with oxygen in the presence of some hemeproteins. [17] The in-depth study of this reaction may offer a ready explanation of the toxic effect.

Scheme I



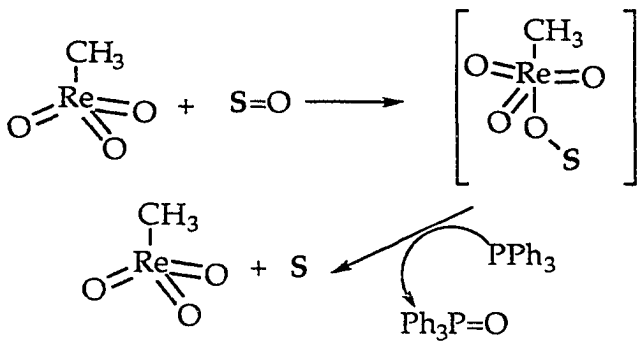
Deoxygenation of epoxides. This reaction is important in both synthesis and structural determinations. [18–21] It provides a simple (one pot) method that proceeds in high yield under mild conditions. This reaction is believed to occur by a mechanism that features the participation of a dialkoxylrhenium complex (or rhenium glycolate), as given in **Scheme II.**

Scheme II



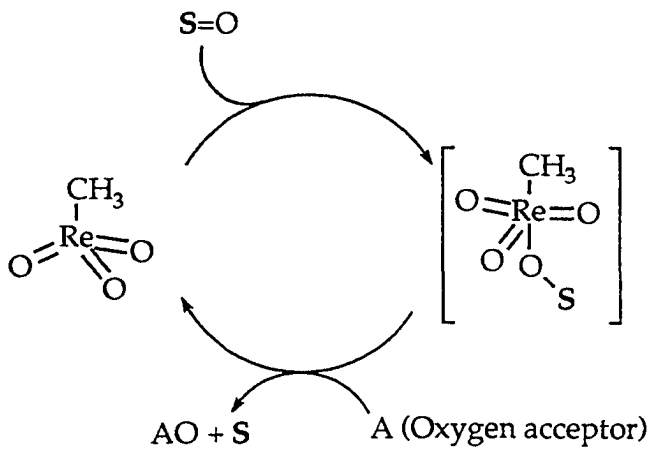
Deoxygenation of sulfoxides and tertiary amine oxides. Oxygen atom transfer reactions have received renewed attention in the last few years because of their importance in biological systems. [22] A number of methods have so far been developed for this purpose. [23, 24] Unlike the method given here, the previously-reported methods need either a long reaction time [25] or a higher temperature [26]. By analogy to the mechanism suggested for the deoxygenation of epoxides, the deoxygenation of sulfoxides and of N–oxides proceeds by a pathway in which the oxides first coordinate to MTO, and then (likely in >1 step) it transfers an oxygen atom to triphenylphosphine. This set of reactions is diagrammed in **Scheme III.**

Scheme III



Deoxygenation of triphenylarsine and triphenylstibine oxides. These reactions appear to follow a mechanism similar to that of the deoxygenation of sulfoxides and N–oxides. First, MTO coordinates $OAsPh_3$ or $OSbPh_3$, then PPh_3 reacts with this complex to form $AsPh_3$ or $SbPh_3$. The formation of methanol may arise from a very reactive oxidizing species in triphenylarsine oxide through an intermediate like "**A**', referred to previously.

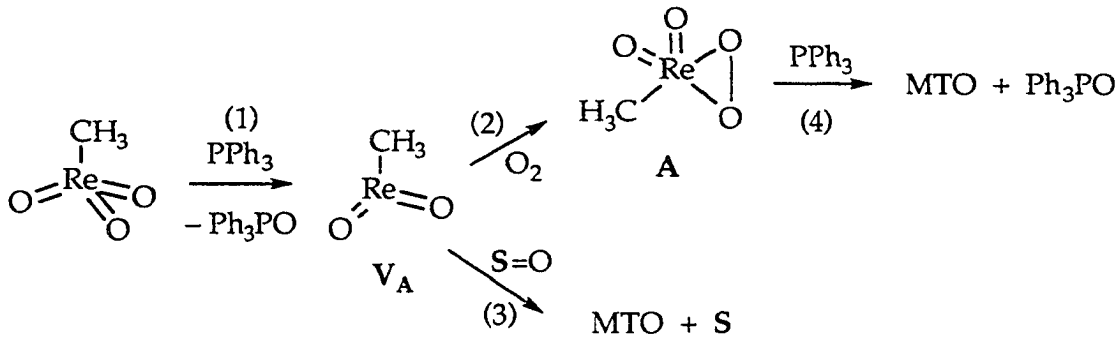
Scheme IV



These results point to MTO being an effective catalyst for several oxygen transfer reactions. The net stoichiometric scheme applicable to all of these reactions can be diagrammed as in **Scheme IV**.

We would also mention another set of reactions that may account for *all* of the processes reported herein. It entails a rhenium(V) intermediate $CH_3Re(O)_2$, which we shall abbreviate as $\mathbf{V_A}$ (a term arising from the role of this species in other reactions that will be reported independently). The actual formula of $\mathbf{V_A}$ might instead be $CH_3Re(O)_2{\cdot}OPPh_3$, a species referred to above. The postulate is this: $\mathbf{V_A}$ forms first, in a reaction between MTO and PPh_3. It partitions between alternative reactions, governed by the presence of oxygen or of the substrate–oxide. Included is a reaction known from earlier work [7], between the η^2–peroxorhenium complex, **A**, and the phosphine, shown as step (4) in **Scheme V**, which represents an alternative but reasonable picture for the general substrate S=O. At the present time, no clear resolution among these alternatives is at hand, although this and related chemistry remains an active endeavor.

Scheme V



These investigations have shown that MTO can act as an effective catalyst for a number of deoxygenation and oxygen transfer reactions, given a proper oxygen acceptor. Current studies are underway to extend the scope of this reaction.

Experimental section

Materials. The triarylphosphines, epoxides, sulfoxides, pyridine–N–oxide, and triphenylarsine oxide were purchased. The other N–oxides were obtained from our previous study. [8] 2,3–Dimethylbutene epoxide was prepared from 2,3–dimethyl–2–butene. [27] Triphenylstibine oxide was prepared by oxidizing triphenylstibine with hydrogen peroxide, catalyzed by MTO. [7] Methylrhenium trioxide was synthesized from dirhenium heptoxide and tetramethyltin in the presence of perfluoroglutaric anhydride. [2] Benzene was purified by a standard method. [28]

Oxidation of phosphines.

Method A. The tertiary phosphine (30 mmol) and MTO (3 mmol) were dissolved in 100 mL benzene, and the solution was stirred in air at room temperature. The reaction was monitored by TLC, ^{1}H–NMR, and ^{31}P–NMR; to do

this several drops of the reaction solution were dried in a stream of argon and the residue dissolved in C_6D_6 for NMR. After 48 h the solvent was removed under vacuum and the residue recrystallized from methanol.

Method B. The materials in the amounts described above were dissolved in 100 mL benzene, then flushed with oxygen at room temperature. The reaction was monitored as previously described. After 6 h, the solvent was removed and the products identified by MS, ^{1}H–NMR, or ^{31}P–NMR [29-33].

Triphenylphosphine oxide. ^{1}H–NMR/$CDCl_3$: δ 7.68 ppm (m), 7.43 ppm (m). MS (EI): m/e 278, (CI, ammonia); 279 ($M+H^+$) and 296 ($M+NH_4^+$).

(*p*-Me-Ph)$_3$PO. ^{1}H–NMR/$CDCl_3$: δ 7.26 ppm (m), 7.533 ppm (m) and 2.38 ppm (s). MS (EI) m/e 320, (CI, ammonia), m/e 321 ($M+H^+$) and m/e 338 ($M+NH_4^+$).

(*p*-MeO-Ph)$_3$PO. ^{1}H–NMR/$CDCl_3$: δ 7.55 ppm (m), 6.97 ppm (m) and 3.84 ppm (s). MS (EI): m/e 368, (CI, ammonia), m/e 369 ($M+H^+$) and m/e 386 ($M+NH_4^+$).

(*p*-Cl-Ph)$_3$PO. ^{1}H–NMR/$CDCl_3$: δ 7.56 ppm (m), 7.61 ppm (m) and ^{31}P–NMR/$CDCl_3$ 29.4 ppm (neat H_3PO_4 as external reference). MS (EI): m/e 380 (^{35}Cl), 382 (^{37}Cl); (CI, ammonia) 381 (^{35}Cl), 383 (^{37}Cl) ($M+H^+$); 398 (^{35}Cl), 400 (^{37}Cl) ($M+NH_4^+$).

General procedure for deoxygenation of epoxides. The epoxide (30 mmol) and MTO (3 mmol) were dissolved in 100 mL benzene. A triphenylphosphine (31 mmol in 100 mL benzene) was added dropwise over 6 h with stirring under Ar, which was continued for another 12 h. The olefins were isolated by distillation under reduced pressure. The products were identified spectroscopically.

Cyclododecene, ^{1}H–NMR/$CDCl_3$: δ 1.33 ppm (m), 2.06 ppm (m) 5.38 ppm (m). Unsaturated ^{13}C–NMR/$CDCl_3$ at δ 130.23 ppm and 131.78 ppm (two isomers from cis and trans isomers of the starting epoxide). GC-MS: m/e 166 (cyclododecene); 278 ($OPPh_3$).

Cyclohexene, ^{1}H–NMR/$CDCl_3$: δ 1.61 ppm (m), 1.99 ppm (m) 5.68 ppm (m). GC-MS:m/e 82 (cyclohexene); 278 ($OPPh_3$).

trans-Stilbene, ^{1}H–NMR/$CDCl_3$: δ 7.09 ppm (m), 7.22 ppm (m), 7.32 ppm (m), 7.48 ppm (m). GC-MS: m/e 180 (*trans*-stilbene); 278 ($OPPh_3$).

cis-Stilbene, ^{1}H–NMR/$CDCl_3$: δ 6.58 ppm (m), 7.19 ppm (m). GC-MS: m/e 180 (*cis*-stilbene); 278 ($OPPh_3$).

Styrene, ^{1}H–NMR/$CDCl_3$: δ 5.20 ppm (d), 5.71 ppm (d), 6.68 ppm (dd), 7.29 ppm (m). GC-MS: m/e 104 (styrene); 278 ($OPPh_3$).

2,3-Dimethyl-2-butene, ^{1}H–NMR/$CDCl_3$: δ 1.65 ppm (s). GC-MS: m/e 84 (2,3-dimethyl-2-butene); 278 ($OPPh_3$).

Deoxygenation of sulfoxides. The general procedure used for the epoxides was used.

PhSMe, ^{1}H–NMR/$CDCl_3$: δ 7.23 ppm (m), 7.12 ppm (m) and 2.44 ppm (s). ^{13}C–NMR/$CDCl_3$ of methyl is 15.84 ppm. GC-MS: m/e 124 (PhSMe); 278 ($OPPh_3$)

Ph_2S, ^{1}H–NMR/$CDCl_3$: δ 7.28 ppm (m). GC-MS: m/e 186 (Ph_2S); 278 ($OPPh_3$).

$PhSCH{=}CH_2$, ^{1}H–NMR/$CDCl_3$: δ 7.30 ppm (m), 6.54 ppm (dd) and 5.32 ppm (m). GC-MS: m/e 136 ($PhSCH{=}CH_2$); 278 ($OPPh_3$).

(*p*-Me-Ph)$_2$S, ^{1}H–NMR/$CDCl_3$: δ 7.11 ppm (m), 6.88 ppm (m) and 2.25 ppm (s). GC-MS: m/e 214 ((*p*-Me-Ph)$_2$S); 278 ($OPPh_3$).

(n-Bu)$_2$S, ^{1}H–NMR/$CDCl_3$: δ 2.49 ppm (q), 1.58 ppm (m), 1.40 ppm (m) and 0.92 ppm (t). GC-MS: m/e 146 ((n-Bu)$_2$S); 278 ($OPPh_3$).

(*iso*-Pr)$_2$S, ^{1}H–NMR/$CDCl_3$: δ 2.99 ppm (m) and 1.27 ppm (d). GC-MS: m/e 118 ((*iso*-Pr)$_2$S); 278 ($OPPh_3$).

(p-Cl-Ph)$_2$S, GC-MS: m/e 255 ((p-Cl-Ph)$_2$S); 278 ($OPPh_3$).

Deoxygenation of N-oxides. $PhNMe_2$. GC-MS: m/e 121 (2,3-Dimethyl-2-butene); 278 ($OPPh_3$) and likewise the other tertiary amines formed from the *N*-oxides. p-Me-$PhNMe_2$, 135; p-F-$PhNMe_2$, 139; p-Br-$PhNMe_2$, 200; p-NO_2-$PhNMe_2$, 166 and pyridine, 79.

Acknowledgment. This research was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

References

(1) R. H. Holm, *Chem. Rev.*, *87* (1987) 1401.

(2) W. A. Herrmann, F. E. Kuhn, R. W. Fischer, W. R. Thiel and C. C. Ramao, *Inorg. Chem.* , *31* (1992) 4431.

(3) W. A. Herrmann, R. W. Fischer and D. W. Marz, *Angew. Chem. Int. Ed. Engl.* , *30* (1991) 1638.

(4) W. A. Herrmann, R. W. Fischer, M. U. Rauch and W. Scherer, *J. Mol. Cat.* , *86* (1994) 243.

(5) P. L. Huston, J. H. Espenson and A. Bakac, *Inorg. Chem., 32* (1993) 4517.

(6) K. A. Vassell and J. H. Espenson, *Inorg. Chem., 34* (1995) 5491.

(7) M. M. Abu-Omar and J. H. Espenson, *J. Am. Chem. Soc. , 117* (1995) 272.

(8) Z. Zhu and J. H. Espenson, *J. Org. Chem., 60,* (1995) 1326.

(9) (a) M. T. Kahn, A. P. Rao, S. A. Samad, D. Chatterjee, S. D. Bhatt and R. R. Merchant, *Proc. Indian Acad Sci. 102* (1990) 231; (b) B. E. Schultz, S. F. Gheller, M C. Muetterties, M. J. Scott and R. H. Holm, *J. Am. Chem. Soc. , 115* (1993) 2714.

(10) B. A. Moyer, B. K. Sipe and T. J. Meyer, *Inorg. Chem. , 20* (1981) 1475.

(11) W. K. Rybak and A. Zagicek, *J. Coord. Chem. , 26* (1992) 79.

(12) D. M. Roundhill, M. K. Dickson, N. S. Dixit, and B. P. Sudha-Dixit, *Adv. Chem. Ser. , 196* (1982) 291.

(13) J. Takacs, M. R. Cook, P. Kiprof, J. G. Kuchler and W. A. Herrmann, *Organometallics,* **1991**, *10,* 316.

(14) W. A. Herrmann, P. Watzlowik and P. Kiprof, *Chem. Ber.* **1991**, *124,* 1101.

(15) M. T. Khan, A. P. Rao, S. A. Samad, D. Chatterjee, S. D. Bhatt and P. R. Merchant, *Proc. Indian Acad Sci , 102* (1990) 231.

(16) W. A. Herrmann, P. W. Roesky, M. Wang and W. Scherer, *Organometallics, 13* (1994) 4531.

(17) M. Q. Chaudry and N. R. Price, *Pesticide Biochem. Physiol.*, *36* (1990) 14, and references therein.

(18) S. Rauher, K. W. Chi, K. J. Hwang and J. E. Burks, *J. Org. Chem.*, *51* (1986) 5503.

(19) W. R. Roush and S. Russo-Rodriguez, *J. Org. Chem.*, *51* (1987) 598.

(20) E. J. Corey and W. G. Su, *J. Am. Chem. Soc.*, *109* (1987) 7534.

(21) D. B. Borders, P. Shu and J. E. Lancaster, *J. Am. Chem. Soc.*, *94* (1972) 2540.

(22) R. Sato and T. Omura, *Cytochrome P–450*; Kodansha, Tokyo, 1987.

(23) J. Drabowicz, H. Togo, M. Mikolajczyk and S. Oae, *Org. Prep. Proceed. Int*, *16* (1984) 171.

(24) M. Malinowski, *Synthesis* (1987) 732.

(25) H. Arzoumanian, D. Nuel and J. Sanchez, *J. Mol. Catal.*, *65* (1991) L9.

(26) X. Lu, J. Sun and X. Tao, *Synthesis* (1982) 185.

(27) F. Camps, J. Coll, A. Messeguer and M. A. Pericas, *Tet. Lett.*, *22* (1981) 3859.

(28) D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 1988, 3rd ed, Pergamon Press

(29) C. J. Pouchert, *The Aldrich Library of NMR Spectra;* 2nd ed.; 1983.

(30) C. J. Pouchert, *The Aldrich Library of FT-IR Spectra;* 1st ed.; 1985.

(31) R. F. Hudson, *Structure and Mechanism in Organophosporus Chemistry;* Academic Press: New York, 1965.

(32) V. Munyejabo, P. Guillaume and M. Postel, *Inorg. Chem. Acta., 221* (1994,) 133, and references therein.

(33) C. W. Lee and J. S. Lee, *J. Mol. Catal. 80* (1993) 31.

CHAPTER IV.
THE OXIDATION OF ALKYNES BY HYDROGEN PEROXIDE CATALYZED BY METHYL RHENIUM TRIOXIDE

A paper accepted by the *Journal of Organic Chemistry*

Zuolin Zhu and James H. Espenson

Abstract

The oxidation of alkynes with hydrogen peroxide is catalyzed by methylrhenium trioxide. The reactions can be rationalized by postulating that an oxirene intermediate is formed between a rhenium peroxide and the alkyne. Internal alkynes yield α-diketones and carboxylic acids, the latter from the complete cleavage of the triple bonds. Rearrangement products were observed only for aliphatic alkynes. Terminal alkynes gave carboxylic acids and their derivatives and α-ketoacids as the major products, but their yields varied with the solvent used.

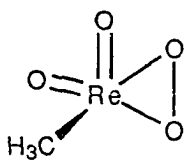
Introduction

The stoichiometric oxidation of alkynes has been widely studied with reagents such as organic peracids,[1-3] thallium nitrate,[4] ruthenium[5] and osmium[6] tetroxides, permanganate,[7,8] peroxomonophosphoric acid,[9] peroxomolybdenum complexes,[10] and dioxiranes.[11,12] Examples of catalytic oxidations are fewer.[13-16]

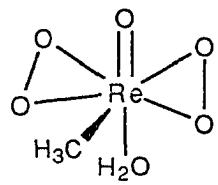
The oxidation of terminal and internal alkynes usually yields different products. Terminal alkynes usually give carboxylic acids, coupling products, carboxylic acids with one carbon less, or α-keto carboxylic acids.[17] Internal alkynes, on the other hand, usually form α,β-unsaturated ketones, α-diketones or cleavage products of the triple bond. The products formed depend on the nature of the oxidizing agent and the reaction conditions.[18-21]

Methylrhenium trioxide (CH_3ReO_3 or MTO) catalyzes the epoxidation of alkenes with hydrogen peroxide.[22-25] In addition, this rhenium compound catalyzes other oxygen-transfer reactions of hydrogen peroxide, such as the conversion of anilines to nitrosobenzenes and *N,N*-dimethylanilines to the amine oxides,[26] phosphines, arsines and stibines to their oxides,[27] organic sulfides to sulfoxides,[28] thiolatocobalt to the sulfenatocobalt complex,[29] and so on.

Two active forms of the catalyst have been identified, with 1:1 and 1:2 ratios of rhenium to peroxide. The formulas are $CH_3Re(O)_2(O_2)$, **A**, and $CH_3ReO(O_2)_2$, **B**, which has been characterized crystallographically.[23]



A



B

We have found that the oxidation of both terminal and internal alkynes by hydrogen peroxide is also catalyzed by MTO. These findings can be rationalized on the basis of an oxirene intermediate.

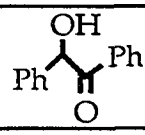
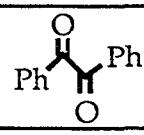
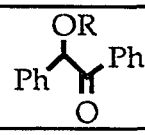
Results

Internal alkynes. Three internal alkynes were used: diphenylacetylene, 4-octyne, and 4,4-dimethyl-2-pentyne. The reactions were carried out in homogeneously in acetone and in various alcohols, and heterogeneously, in a two-phase system, methylene chloride-water. The products formed depend to some extent on the choice of solvent. None of the alkynes reacted with hydrogen peroxide in 48 hr. but all of them were oxidized when the rhenium compound was added.

Diphenylacetylene is resistant to oxidation by common organic peracids,[1,2] which afford complex product mixtures with poor yields and low conversions. With MTO–hydrogen peroxide, however, the reactions can be carried to a satisfactory conversion (>84%) in homogeneous solution. The products formed in twelve alcohol solvents, with excess hydrogen peroxide and 10% MTO, are summarized in **Table 4.1.** The product is principally benzil in acetone and methanol.

In the biphasic system CH_2Cl_2–water, on the other hand, over-oxidation evidently occurs, and mainly benzoic acid is produced. Rearrangement products were not observed in any of these solvents. In methanol a small amount of the α-methoxy ketone was formed, and a trace of benzoic acid was also observed in acetone and methanol. The product is also principally benzil in the two-phase system. These results are similar to those obtained with trifluoroperacetic acid,[30] with benzil the major product and benzoic acid the minor one. In contrast, with dimethyldioxirane, ketene-derived products predominated.[11] Aromatic alkynes are less reactive under these conditions than aliphatic alkynes, which showed >95% conversion. The aliphatic alkynes led to more complex mixtures of products,

Table 4.1. Product yields[a,b] from the oxidation of diphenylacetylene by hydrogen peroxide catalyzed by MTO in different alcohols.

		Product			
Alcohol	Conv. %	PhCOOH			
MeOH	87	7	–	79	4
EtOH	91	8	–	80	6
n-PrOH	90	10	–	74	7
n-BuOH	86	11	–	76	6
n-Amyl-OH	84	14	–	78	–
$PhCH_2OH$	86	16	6	75	–
2-BuOH	90	20	7	69	–
s-Amyl-OH	88	18	8	72	–
Cyclopentanol	89	19	7	71	–
$PhCH(CH_3)OH$	87	17	11	70	–
t-BuOH	86	16	12	72	–
t-Amyl	87	17	10	72	–

[a] Protocol: 1.78 g (10 mmol) diphenylacetylene, 1 mmol MTO, and 30 mmol hydrogen peroxide were used in 15 mL alcohol.

[b] Minor products, <10%, are from GC-MS, others are isolated yields.

Table 4.2. Product yields[a] from the homogeneous oxidation of alkynes by hydrogen peroxide, catalyzed by CH_3ReO_3

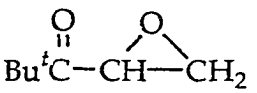
Alkyne	Acetone	Methanol
PhC≡CPh (% conversion)	(69%)	(87%)
PhC(O)C(O)Ph	57%	79%
PhCH(OMe)C(O)Ph	–	4
$PhCO_2H$	tr.	7
$PhCO_2Me$		9
$Pr^nC{\equiv}CPr^n$	(>97%)	(>97%)
$Pr^nC(O)C(O)Pr^n$	43	41
$(Pr^n)_2CH_2CO_2H$	24	–
$Pr^nC(O)CH{=}CHCH_3$	11	17
Pr^nCO_2Me	–	15
$Bu^tC{\equiv}CMe$	(>99%)	(>99%)
Bu^tCO_2H	86	58
$Bu^tC(O)C(O)Me$	~3	16
	~2	~2
$Bu^tC(O)CH{=}CH_2$	~1	~2
Bu^tCO_2Me	–	12
$Bu^tC(O)CH(OMe)CH_3$	–	~4

Table 4.2
(continued)

$CH_3(CH_2)_6C{\equiv}CH$	(>96%)	(>96%)
$CH_3(CH_2)_6CO_2H$	95	18
$CH_3(CH_2)_6CO_2Me$	–	81
$PhC{\equiv}CH$	(88%)	(84%)
$PhCH_2CO_2H$	65	~2
$PhCH_2CO_2Me$	–	95
$PhC(O)CO_2H$	11	–

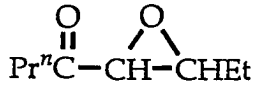
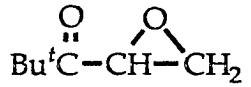
[a] Isolated yields, except minor products, <10%, from the GC-MS.

however; in acetone and methylene chloride, the α-diketone, the α-unsaturated ketone, the α-hydroxyketone, and the α,β-epoxy ketone were found, along with the carboxylic acid from rearrangement or cleavage of the triple bond. Thus, 4-octyne gave 2-4% of butyric acid in all three solvents. Other products, all minor, were also detected; see **Table 4.2** for homogeneous reactions and **Table 4.3** for the results under heterogeneous conditions.

Terminal alkynes. Phenylacetylene and 1-nonyne were also included in this study. Compared to the internal alkynes, the products from the terminal alkynes were much simpler. The results are summarized in **Tables 4.3-4.5**. Oxidation of phenylacetylene in alcohols give satisfactory conversions. In primary alcohols, the major products are the esters, but they become minor in secondary alcohols (except cyclopentanol), and are not formed in tertiary alcohols. The major products are the carboxylic acids in acetone, the esters in methanol, and the α-ketocarboxylic acid in the biphasic methylene chloride-water system. Not detected were the alkyne dimers, formed by the oxidation of the terminal alkyne, and the carboxylic acid from C–C cleavage.

The ratio of MTO to alkyne did not affect the product distribution, but it did alter the substrate conversion in a given reaction time. Oxidation of 10 mmol diphenylacetylene with 30 mmol hydrogen peroxide in methanol with varying quantities of MTO gave different conversions. MTO at 5% of Ph_2C_2 gave 65% conversion (80% benzil, 17% benzoic acid and ester); at 10% the conversion after 2 days was 87% (79% benzil, 14% benzoic acid and ester).

Table 4.3. Product yields[a] from the oxidation of alkynes by hydrogen peroxide, catalyzed by CH_3ReO_3 in the biphasic solvent.

Alkyne	Conversion (%)	Yield (%)
PhC≡CPh	73	
PhC(O)C(O)Ph		67
$PhCO_2H$		17
$Pr^nC{\equiv}CPr^n$	92	
$Pr^nC(O)C(O)Pr^n$		41
$Pr^nC(O)CH(OH)Pr^n$		24
		21
$Bu^tC{\equiv}CMe$	94	
Bu^tCO_2H		~2
$Bu^tC(O)C(O)Me$		38
		~2
$Bu^tC(O)CH{=}CH_2$		14
$(CH_3)_2C{=}C(CH_3)C(O)CH_3$		31
$CH_3(CH_2)_6C{\equiv}CH$	>95	
$CH_3(CH_2)_7CO_2H$		31
$CH_3(CH_2)_6C(O)CO_2H$		47
PhC≡CH	89	
$PhCH_2CO_2H$		21
$PhC(O)CO_2H$		68

[a] Minor products, <10%, are from the GC-MS, others are isolated yields.

Table 4.4. Products from the oxidation of phenylacetylene by hydrogen peroxide catalyzed by MTO in primary alcohols.

Alcohol	Conversion (%)	Products (%)	
		Ester	Acid
MeOH	88	96	tr.
EtOH	87	96	tr.
n-PrOH	85	95	~3
n-BuOH	90	94	~4
n-Amyl-OH	87	85	10
$PhCH_2OH$	86	60	33
$PhCH_2CH_2OH$	82	47	50

[a] Protocol: 1.03 g (10 mmol) phenylacetylene, 1 mmol MTO, and 30 mmol hydrogen peroxide were used in 15 mL alcohol.

[b] Minor products, <10%, are from GC-MS, others are isolated yields.

Limiting peroxide. The data in the preceding sections pertain to experiments in which the alkynes were the limiting reagents with excess peroxide, the natural emphasis being the conversion of the alkynes. On the other hand, given the side-products observed, it became necessary to learn whether they are an immediate consequence of a complex pattern of reactions, or whether they more simply arise from the over-oxidation of the primary and initial product, the α-diketone. Toward this end, we carried out experiments with diphenylacetylene, with excess diphenylacetylene (1 mmol), limiting peroxide (0.5 mmol), and 40 mg MTO (0.16 mmol). Data were obtained for the conversion of the acetylene in the three different solvents and for the product yields; the effective conversion relative

Table 4.5. Product yields[a,b] from the oxidation of phenylacetylene by hydrogen peroxide catalyzed by MTO in secondary and tertiary alcohols.

Alcohol	Conversion	Product (%)			
		$PhCO_2H$	$PhCH_2CO_2H$	$PhCO_2R$	$PhCH_2CO_2R$
2-BuOH	84%	38	17	8	30
s-Amyl-OH	87	40	15	11	30
Cyclopentanol	85	trace	10	–	84
$PhCH(CH_3)OH$	83	47	41	–	5
t-BuOH	79	23	74	–	–
t-Amyl-OH	84	22	71	–	–

[a] Protocol: 1.03 g (10 mmol) phenylacetylene, 1 mmol MTO, and 30 mmol hydrogen peroxide were used in 15 mL alcohol.

[b] Minor products, <10%, are from GC-MS, others are isolated yields.

to peroxide can also be obtained by calculation. These are the results:

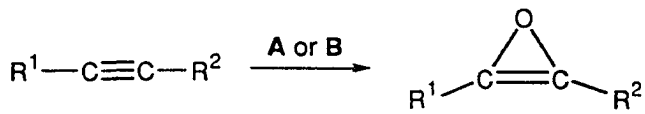
Solvent	%Conversion of Ph_2C_2	%Conversion of H_2O_2 (calcd)	PhC(O)C(O)Ph	$PhCO_2H$/ $PhCO_2Me$
Acetone	12	50	87	11
Methanol	24	90	88	10
CH_2Cl_2	24	96	100	–

The reaction produces entirely benzil in methylene chloride, and nearly so in the other solvents. The data also illustrate that the reaction is the slowest in acetone, where peroxide remains even after the five days at ambient temperature allowed for these reactions.

Discussion

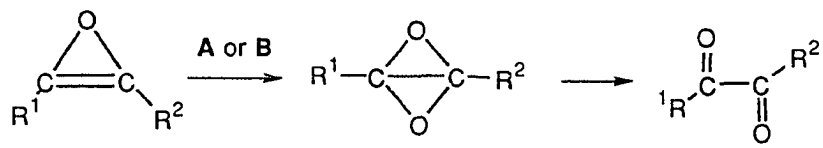
Because the reactions were carried out with excess hydrogen peroxide, **B** was the predominant form of the catalyst given the equilibrium constants for peroxide binding to MTO.[26] From the kinetic data, both **B** and dimethyldioxirane (DMDO)[11] have similar reactivities towards alkenes.[31] This evidently holds as well for alkynes. DMDO gives predominantly ketene-derived products, whereas MTO yields α-diketones as the major products from internal alkynes. In the biphasic solvent mixture, MTO proved more reactive than peroxotungstophosphate, which gave <50% conversion of diphenylacetylene.[32]

The results obtained for alkyne oxidations, along with comparisons with the reactions in which alkenes are converted to epoxides by MTO/H_2O_2, lead us to suggest that the reaction proceeds initially with the formation of an oxirene intermediate. These elusive species have been alluded to previously.[33,34] The initial step may be as shown in eq 4.1:



(4.1)

The ruthenium tetroxide-catalyzed reaction[35] serves as a precedent for this reaction. No mechanism was suggested, however, although it seems reasonable that the pathway is analogous to that of osmium tetroxide.[36] Following that step, it is further reasonable to propose yet another epoxidation step, such that a "double epoxide", intermediate **I**, would intervene on the path to the major product, the diketone:



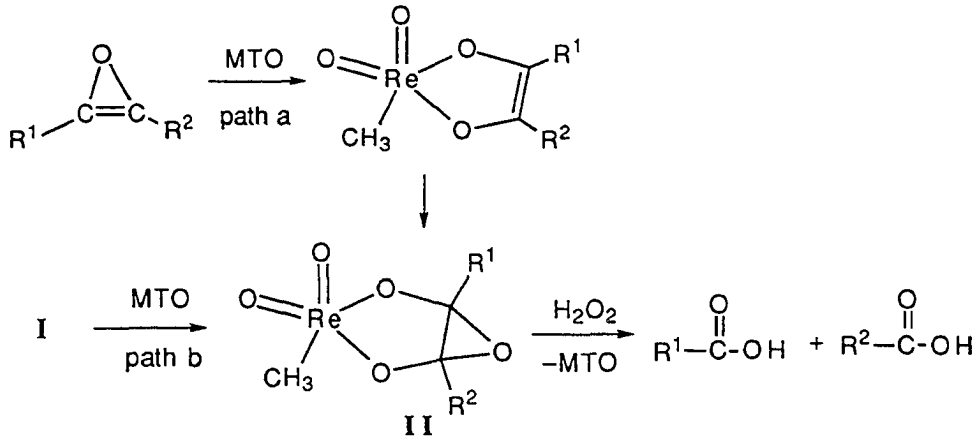
I

(4.2)

Accepting this proposed pathway provisionally, we ask about the subsequent steps. Either the formation of **I** follows a concerted mechanism, such that an oxirene intermediate does not form, or the rearrangement of the oxirene to form a ketone (or a ketene, as shown subsequently) occurs more slowly than oxygen transfer from **A** or **B** to the oxirene double bond.

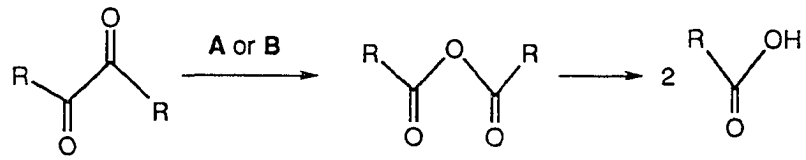
The carboxylic acids are formed by cleavage of the triple bond, for which two pathways can be explored. First, and similar to the mechanism we reported for the reaction between CH_3ReO_3 and epoxides,[37] a possible pathway involves the

reaction of the oxirene with MTO to form a "bisalkoxy" complex whose C=C double bond is then converted to an epoxide with **A** or **B**; we call this path "a", and note that it will form a second intermediate, **II**. Oxidation of **II** yields the carboxylic acid upon cleavage of the C–C bond. An alternative is presented by path "b", which allows **II** to be formed from MTO and **I**, eq 4.3:



(4.3)

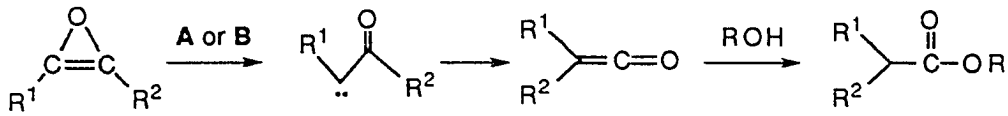
Alternatively, a pathway that may also be possible that involves the typical conversion of an α-diketone to two carboxylic acids by a Baeyer-Villiger oxidation, eq 4.4.[38]



(4.4)

Cleavage of an alkyne triple bond to give two carboxylic acids is well known using metal oxides.[39] The mechanism by which **A** and **B** may act is very likely similar to that proposed for permanganate,[7,8] ruthenium tetroxide,[5] and thallium(III) nitrate.[4]

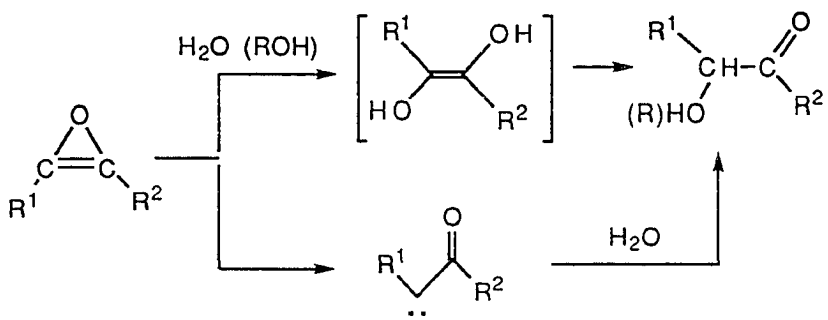
The carboxylic acids, or their methyl esters in methanol, were possibly formed from both terminal and internal alkynes by a ketene rearrangement. The following equations depict the oxidation of the alkyne to an oxirene by **A** or **B**. The oxirene then rearranges to a ketene which adds water (or methanol) to generate the acid (or ester), as in eq 4.5.



(4.5)

The conversion of the carbene to a ketene, the photochemical Wulff rearrangement, finds precedent.[40] Unlike other secondary alcohols, the oxidation of phenylacetylene in cyclopentanol gives a higher yield of the ester. As a result, we suggest the competition between water and alcohols is subject to a steric influence, as the relatively inflexible structure of cyclopentanol offers less steric demand than the other, freely-rotating alcohols.

The α-hydroxy (or methoxy) ketones, we believe, form directly from the oxirene intermediate. Two possible schemes are illustrated by eq 4.6:

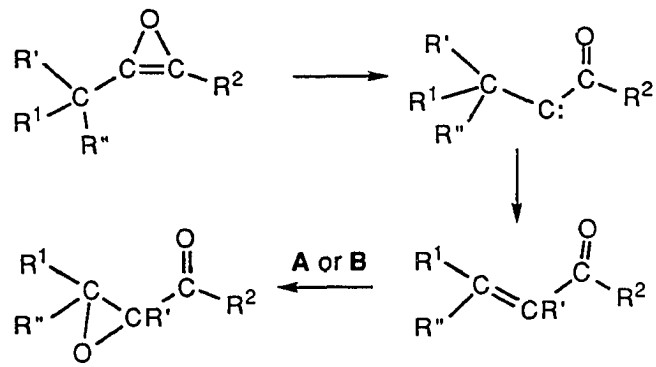


(4.6)

According to this, the oxirene either undergoes nucleophilic attack by water, giving an intermediate that then rearranges to the α-hydroxy ketone (as suggested by the

ring-opening reaction of epoxides with water[41]), or it rearranges to an oxocarbene which then undergoes an insertion reaction with water.[9]

The α,β–unsaturated products were obtained only for the internal alkynes. These products are believed to result from an intermediate that arises from rearrangement of an oxirene. *α,β*–Epoxy ketones are formed by the direct oxidation of *α,β*–unsaturated products with **A** or **B**. That is depicted by this equation sequence in which R′ is Me for 4,4-dimethyl-2-pentyne and R′ is H for all the others:



(4.7)

The final step in this reaction, the conversion of an *α,β*-unsaturated ketone to an *α,β*-epoxy ketone, can be carried out by MCPBA[3] and hydrogen peroxide.[42] This conversion requires alkaline conditions, and utilized HOO^-. It is possible, based on this precedent, that ring-opened forms of **A** or **B** are responsible for the final step in eq 4.7.

Experimental section

Materials. The alkynes were obtained from commercial sources, and the purity of each was verified by GC-MS before use. The solvents were purified by standard methods.[43] Hydrogen peroxide (30%, Fisher) was used without further

treatment. Methylrhenium trioxide[44] was prepared from Re_2O_7 and $Sn(CH_3)_4$ according to the literature procedure.[45]

Procedures for the oxidation of alkynes. The alkyne (30 mmol) was dissolved in 300 mL of acetone or methylene chloride, then CH_3ReO_3 (10 mol% of the alkyne) was added. After the solid had dissolved, a moderate excess of hydrogen peroxide (100 mmol) was added. The reaction vessel was closed, and the solution was stirred for two days at room temperature, during which time the reaction was monitored by GC-MS. The excess of peroxide was decomposed by adding a little manganese dioxide. After filtration, most of the solvent was removed under vacuum, and then the solution was extracted with ether three times. The ether was removed, the residue dried over magnesium sulfate, and the products separated by fractional distillation under vacuum.

The known products from 4-octyne and 4,4-dimethyl-2-pentyne were identified by comparison to data in the literature.[7,12]. Spectroscopic data and the results of elemental analysis are given in **Table 4.6** and **Table** 4.7.

When an alcohol was used as the solvent, only 10 mmol of diphenylacetylene and phenylacetylene, 1 mmol MTO, and 30 mmol H_2O_2 were used. After decomposition of the excess hydrogen peroxide with MnO_2, the products were separated by distillation under reduced pressure or vacuum. Benzil obtained from the distillation was recrystallized from ethanol. The products were identified by ^{1}H–NMR, ^{13}C–NMR and by mass spectroscopy in comparison with the results from NMR and MS libraries; see **Table 4.8**.[46,47]

Table 4.6. Spectral and analytical data for the oxidation products of 4-octyne[a]

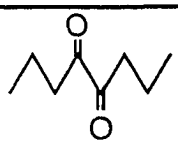
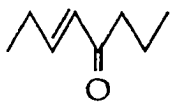
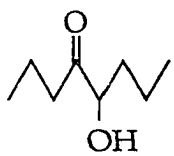
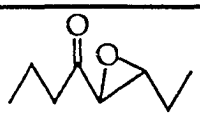
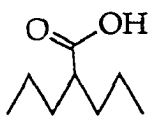
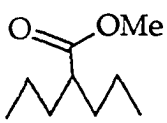
Compound	^{1}H–NMR	^{13}C–NMR	Mass Spec.	Elemental Analysis
	0.91 (t), 1.59 (m), 2.78 (t)	13.2, 17.6 29.7, 249.8	142 (0.35), 124 (1.77), 112 (28.85), 71 (100), 57 (10.37), 43 (87.63)	Found (Calcd.) C: 67.80 (67.57) H: 9.94 (9.92)
	0.91 (m), 1.58 (m), 2.02 (m), 2.71 (t), 6.12 (m), 6.83 (m)	13.3, 16.4, 17.6, 26.5, 28.8, 128.3, 154.7, 198.8	126 (12.41), 96 (23.42), 82 (100), 67 (4.66), 55 (37.04), 41 (15.42)	C: 76.15 (76.14) H: 11.30 (11.18)
	0.91 (m), 1.59 (m), 1.97 (t), 2.73 (t), 3.57 (br), 4.48 (t)	13.4, 14.1, 17.8, 19.4, 29.7, 39.7, 72.8, 247.7	144 (4.32), 126 (1.55), 114 (5.22), 101 (41.99), 73 (100), 57 (14.44), 55 (21.37), 41 (23.82)	C: 66.89 (66.63) H: 11.18 (11.18)

Table 4.6
(continued)

	0.91 (m), 0.97 (t), 1.41 (q), 1.58 (m), 2.72 (t)	12.8, 13.4, 17.7, 20.2, 34.5, 44.3, 45.4, 206.5	142 (1.91), 128 (3.23), 112 (1.38), 97 (5.96), 82 (16.83), 71 (100), 57 (13.29), 55 (13.57), 43 (75.25)	C: 67.34 (67.57) H: 9.83 (9.92)
	0.92 (t), 1.34 (m), 1.61 (m), 2.47 (m), 12.21 (s)	11.7, 21.8, 25.4, 46.2, 183.1	144 (1.78), 129 (3.42), 114 (1.67), 86 (47.34), 72 (100), 55 (5.56), 43 (32.50)	C: 66.89 (66.63) H: 11.24 (1.18)
	0.92 (t), 1.34 (m), 1.61 (m), 2.45 (m), 3.64 (s)	11.7, 21.8, 25.4, 45.9, 51.2, 174.3	158 (2.26), 128 (3.70), 115 (21.11), 96 (8.76), 86 (100), 69 (6.02), 57 (22.07), 41 (21.05)	C: 68.32 (68.31) H: 11.58 (11.46)

[a] NMR spectra were recorded in $CDCl_3$.

Table 4.7. Spectral and analytical data for the oxidation products of 4,4-dimethyl-2-pentyne.

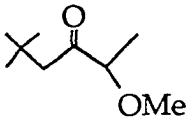
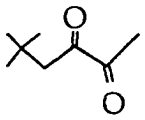
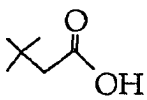
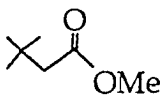
Compound	^{1}H–NMR	^{13}C–NMR	Mass Spec.	Elemental Analysis
	1.19 (d), 1.23 (s), 3.51 (s), 4.27 (q)	14.7, 17.8, 25.4, 59.7, 77.4, 234.5	144 (2.52), 129 (1.04), 113 (0.76), 87 (100), 85 (16.45), 72 (60.77), 57 (79.04), 41 (66.98)	Found (Calcd.) C: 66.74 (66.63) H: 11.37 (11.18)
	1.21 (s), 2.39 (s)	22.7, 25.1, 43.4, 242.7, 243.9	129 (1.30), 112 (1.27), 110 (3.27), 86 (8.49), 84 (2.13), 83 (2.98), 69 (1.94), 67 (1.35), 57 (100), 43 (25.14)	C: 65.60 (65.60) H: 9.48 (9.44)
	1.19 (s), 12.5 (s)	25.2, 43.7, 184.3	102 (0.64), 87 (1.22), 72 (14.63), 57 (100), 42 (54.13)	C: 58.92 (58.80) H: 10.10 (9.87)
	1.18 (s), 3.57 (s)	25.2, 43.5, 56.7, 172.8	117 (0.53), 116 (4.05), 101 (1.37), 85 (2.03), 75 (9.75), 56 (100), 41 (54.13)	C: 62.09 (62.04) H: 10.52 (10.41)

Table 4.8. Spectral data for the oxidation products of phenylacetylene and diphenylacetylene in alcohols.

Product	^{1}H–NMR (δ/ppm)	^{13}C–NMR (δ/ppm)
$PhCH_2CO_2$-Amyl^n	7.28 (m, 5H); 4.05 (q, 2H); 3.60 (s, 2H); 1.24-1.75 (m, 6 H); 0.90 (t, 3H)	174.05, 134.18, 129.22, 128.50, 126.99, 65.01, 41.46, 34.10, 28.43, 22.54, 13.93
$PhCH_2CO_2CH_2Ph$	7.20-7.39 (m, 10H); 4.28 (s, 2H); 3.64 (s, 2H)	170.67, 138.27, 134.15, 129.19, 128.55, 128.51, 127.77, 127.63, 126.96, 63.34, 41.39
$PhCH_2CO_2CH_2CH_2Ph$	7.12-7.30 (m, 10H); 4.30 (t, 2H); 3.58 (s, 2H); 2.79 (t, 2H)	171.53, 137.71, 134.20, 129.56, 129.27, 128.54, 128.45, 128.20, 127.04, 65.33, 41.40, 40.54
$PhCH_2CO_2$-c-Pentyl	7.27 (m, 5H); 4.34 (m, 1H); 3.56 (s, 2H); 1.57-1.76 (m, 8H)	171.44, 134.28, 129.32, 128.45, 126.90, 77.52, 41.70, 32.55, 23.63

Table 4.8
(continued)

$PhCH_2CO_2$-Amyl^s	7.29 (m, 5H); 4.11 (m, 1H); 3.61 (s, 2H); 1.11-2.16 (m, 10H)	171.74, 134.15, 129.23, 128.45, 127.00, 63.59, 43.54, 37.23, 25.03, 22.41, 11.16
$PhCH_2CO_2$-Bu^n	7.29 (m, 5H); 4.09 (t, 2H); 3.62 (s, 2H); 1.59 (m, 2H); 1.33 (m, 2H); 0.90 (t, 3H)	174.76, 134.17, 129.20, 128.49, 126.98, 64.73, 41.43, 30.55, 19.02, 13.62
$PhCH_2CO_2Et$	7.25 (m, 2H); 4.13 (q, 2H); 3.59 (s, 2H); 1.24 (t, 3H)	171.26, 134.03, 129.11, 128.28, 127.02, 60.79, 41.37, 14.10
$PhCH_2CO_2$-Pr^n	7.29 (m, 5H); 4.05 (t, 2H); 3.63 (s, 2H); 1.63 (m, 2H); 0.89 (t, 3H)	172.93, 134.13, 129.15, 128.43, 126.93, 66.38, 41.36, 21.83, 10.22
$PhCO_2$-Bu^n	7.39-8.51 (m, 5H); 4.32 (t, 2H); 1.74 (m, 2H); 1.47 (m, 2H); 0.98 (t, 3H)	166.66, 132.81, 130.67, 129.54, 128.23, 64.87, 30.92, 19.41, 13.84

References

(1) McDonald, R. N.; Schwab, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 4866.

(2) Stille, J. K.; Whitehurst, D. D. *J. Am. Chem. Soc.* **1964**, *86*, 4871.

(3) Ciabattoni, J.; Campbell, R. A.; Renner, C. A.; Concannon, P. W. *J. Am. Chem. Soc.* **1970**, *92*, 3826.

(4) Mckilklop, A.; Oldenziel, O. H.; Swan, B. P.; Taylor, E. C.; Robey, R. L. *J. Am. Chem. Soc.* **1973**, *95*, 1296.

(5) Muller, P.; Goday, A. J. *Helv. Chim. Acta* **1981**, *64*, 2531.

(6) Schroder, M.; Griffith, W. P. *J. Chem. Soc. Dalton Trans.* **1978**, 1599.

(7) Lee, D. G.; Chang, V. S. *J. Org. Chem.* **1979**, *44*, 2726.

(8) Lee, D. G.; Chang, V. S.; Chandler, W. D. *J. Org. Chem.* **1985**, *50*, 4306.

(9) Ogata, Y.; Sawaki, Y.; Ohno, T. *J. Am. Chem. Soc.* **1982**, *104*, 216.

(10) Ballistreri, F. P.; Failla, S.; Timaselli, G. A.; Curci, R. *Tet. Lett.* **1986**, *27*, 5139.

(11) Curci, R.; Fiorentino, M.; Fusco, C.; Mello, R.; Ballistreri, F. P.; Failla, S.; Tomaselli, G. A. *Tet. Lett.* **1992**, *33*, 7929.

(12) Murray, R. W.; Singh, M. *J. Org. Chem.* **1993**, *58*, 5076.

(13) Kropf, H.; Schröder, R. *Liebigs Ann. Chem.* **1976**, 2325.

(14) Balllistreri, F. P.; Failla, S.; Tomaselli, G. A. *J. Org. Chem.* **1988**, *53*, 830.

(15) Ballistreri, F. P.; Failla, S.; Spina, E.; Tomaselli, G. A. *J. Org. Chem.* **1989**, *54*, 947.

(16) Sakaguchi, S.; Watase, S.; Katayama, Y.; Sakata, Y.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1994**, *59*, 5681.

(17) Ando, W.; Moro-oka, Y. *The Role of Oxygen in Chemistry and Biochemistry*; Elsevier: Amsterdam, New York, 1988; Vol. 33, pp 341.

(18) Warig, A. J. *Comprehensive Organic Chemistry*, eds. Barton, D.; Ollis, W. D. Pergamon Press: Oxford, 1979; Vol. 1; pp 1027-1104.

(19) Plesnicar, B. *The Chemistry of Peroxide*, ed. Patai, S. Wiley-Interscience: 1983; pp 536-539.

(20) Hudlicky, M. *Oxidations in Organic Chemistry*, American Chemical Society: Washington, D. C., 1990; pp 90-92.

(21) Muzart, J.; Piva, O. *Tet. Lett.* **1988**, *29*, 2321.

(22) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638.

(23) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157.

(24) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Cat.* **1994**, *86*, 243.

(25) Al-Ajlouni, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243.

(26) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326.

(27) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272.

(28) Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491.

(29) Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1993**, *32*, 4517.

(30) Emmons, W. D.; Pagano, A. S. *J. Am. Chem. Soc.* **1955**, *77*, 80.

(31) Al-Ajlouni, A.; Espenson, J. H. *submitted for publication,*

(32) Ishii, Y.; Sakata, Y. *J. Org. Chem.* **1990**, *55*, 5545.

(33) Lewars, E. G. *Chem. Rev.* **1983**, *83*, 519.

(34) Vacek, G.; Galbraith, J. M.; Yamaguchi, Y.; Schafer, H. F.; Nobes, R. H. *J. Phys. Chem.* **1994**, *98*, 8660-8665.

(35) Gopal, H.; Gordon, A. J. *Tet. Lett.* **1971**, *31*, 2941.

(36) Collin, R. J.; Jones, J.; Griffith, W. P. *J. Chem. Soc. Dalton Trans.* **1974**, 1094.

(37) Zhu, Z.; Espenson, J. H. *J. Mol. Catal.* **1995**, in press.

(38) Leffler, J. E. *J. Org. Chem.* **1951**, *16*, 1785.

(39) Raphael, R. A. *Acetylenic Compounds in Organic Synthesis*; Butterworths: London, 1955, pp 31.

(40) Lewars, E. G. *Chem. Rev.* **1983**, *83*, 524.

(41) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.

(42) House, H. O.; Wasson, R. L. *J. Am. Chem. Soc.* **1957**, *79*, 1488.

(43) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals;* 3d ed.; Butterworth-Heinemann: Oxford, 1988.

(44) Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.

(45) Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R.; Ramao, C. C. *I norg. Chem.* **1992**, *31*, 4431.

(46) Pouchert, C. J.; Behnke, J. *The Aldrich Library of* ^{13}C *and* ^{1}H *FT-NMR Spectra;* 1993.

(47) Mass spectra used is NIST MS Library from Magnum, Finnigan MAT.: San Jose, CA.

CHAPTER V

THE KINETICS AND MECHANISM OF OXIDATION OF ANILINES BY HYDROGEN PEROXIDE AS CATALYZED BY METHYLRHENIUM TRIOXIDE

A paper published in *Journal of Organic Chemistry* *

Zuolin Zhu and James H. Espenson

Abstract

The oxidation of anilines by hydrogen peroxide in methanol is catalyzed by methylrhenium trioxide, CH_3ReO_3. The major product of the oxidation of aniline at room temperature is nitrosobenzene. For 4–substituted *N,N*–dimethylanilines, the *N*–oxide is the only product. The rate constants for the oxidation of 4–substituted *N,N*–dimethylanilines follow a linear Hammett relationship with $\rho = -1.19$. The rate constants for the reaction between $CH_3Re(O)_2(O_2)$, referred to as **A**, and 4-X-$C_6H_5NMe_2$ are: 4–Me, 24.5; 4–H, 18.4; 4–F, 12.7; 4–Br, 8.7 and 4–NO_2, 1.9 L mol^{-1} s^{-1}. This shows that electron withdrawing substituents inhibit the reaction. The corresponding rate constant for the oxidation of aniline is 2.04 ± 0.11 L mol^{-1} s^{-1}, whereas it is 178 ± 11 L mol^{-1} s^{-1} for the oxidation of *N*–phenylhydroxylamine to nitrosobenzene. A mechanism has been assigned on the basis of the kinetics and product yields. The data are consistent with the attack of the nucleophilic nitrogen

---

* Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326.

atom on the peroxidic oxygen atom of **A**. The kinetics of the reaction of CH_3ReO_3 and hydrogen peroxide in methanol were also investigated. The formation of the 1:1 peroxide compound **A** is characterized by an equilibrium constant $K_1 = 261 \pm 6$ L mol^{-1}. The equilibration occurs rapidly: $k_1 = 1150 \pm 60$ L mol^{-1} s^{-1} and $k_{-1} = 4.4 \pm 0.4$ s^{-1} at 25.0 °C. The bis-peroxide compound, $CH_3Re(O)(O_2)_2(H_2O)$, **B**, forms more slowly. The rate constant is $k_2 = 308 \pm 16$ L mol^{-1} s^{-1}, and the equilibrium constant is $K_2 = 814 \pm 14$ L mol^{-1} at 25.0 °C in methanol. **B** reacts with the anilines, but much more slowly than **A**.

Introduction

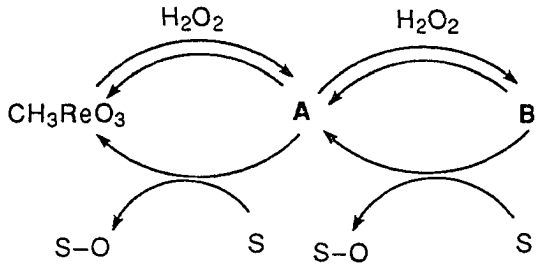
Various reagents, including metal compounds, organic peroxides and hydrogen peroxide, have been used to form oxygen–containing derivatives of anilines. Sometimes the reagents are used in combination for greater efficiency. The oxidation of anilines by chromium(VI) compounds leads to benzoquinones.[2] In the presence of manganese dioxide, substituted anilines form symmetrically substituted azobenzenes.[3] Anilines are readily converted to azo compounds by nickel peroxide,[4] and are slowly oxidized to azobenzenes by silver carbonate on Celite.[5] The oxidation of *N*–arylhydroxylamines with lead tetraacetate gives the corresponding nitroso compounds.[6] Anilines are oxidized to azoxybenzenes by hydroperoxides, catalyzed by Ti(IV),[7] and to azobenzenes by hydrogen peroxide, catalyzed by cetylpyridinium heteropolyoxometalates.[8]

The current environmental imperatives require the substitution of a 'greener' oxidizing agent for those that produce wastes, salts, or other by-products. Hydrogen peroxide is potentially an important substitute, since its only reduction product is water. This and other advantages have been cited.[9,10]

In general, however, hydrogen peroxide reactions are characterized by high activation energies, which result in slow reactions.[11] For all practical purposes a catalyst is required. In addition to the kinetic acceleration the catalyst will provide, the enhancement of the desired electrophilic activity of peroxide will minimize the importance of free radical pathways which are undesirable owing to the mixture of products.

Methylrhenium trioxide, CH_3ReO_3, is a homogeneous catalytic activator of hydrogen peroxide in both organic solvents and water. It can also be used heterogeneously on Al_2O_3–SiO_2 as a catalyst support.[12] The oxygen is transferred to the substrate from either of the two peroxides that result from CH_3ReO_3 and hydrogen peroxide. This reaction forms rhenium peroxides having 1:1 and 1:2 ratios of metal to peroxide.[13] These compounds are $CH_3Re(O)_2(O_2)$ and $CH_3Re(O)(O_2)_2(H_2O)$, referred to as **A** and **B**.[13] Scheme **I** presents the catalytic cycles for the oxidation of a general substrate **S**, allowing for both **A** and **B** to be effective catalysts.

Scheme I

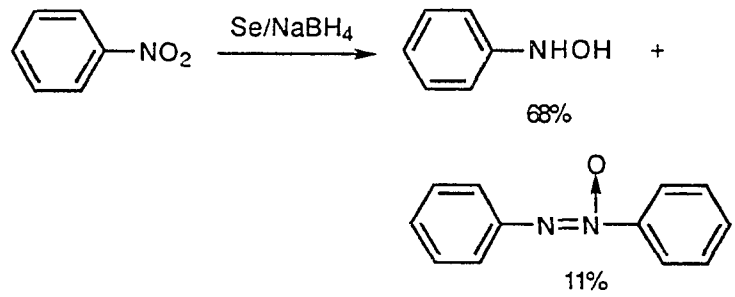


This general scheme is, for example, representative of the oxidation of thiolatocobalt(III) complexes in aqueous solutions of dilute perchloric acid,[14] and of organic sulfides[15] and phosphines[16] in acetonitrile–water. It may also apply to olefin epoxidation in *tert*–butanol.[17]

Since the oxidation of amines by methylrhenium trioxide with hydrogen peroxide has not been reported to date, we undertook a study that included both 4–substituted *N,N*–dimethylanilines and some ring–substituted anilines. The tertiary anilines afford the *N*–oxides predominately, whereas aniline itself yields primarily nitrosobenzene. The kinetics of these reactions will give more information about the mechanism by which the rhenium catalyst operates. Since the data suggested that the oxidation of aniline might occur *via* *N*–phenylhydroxylamine, the kinetics of its rhenium catalyzed oxidation with hydrogen peroxide, was also investigated.

Experimental section

Materials. *N*–Phenylhydroxylamine was synthesized from nitrobenzene.[18] This product was obtained as colorless needles (m.p. 83–84 °C), and in the process we also obtained another, previously unreported but relatively minor product. It was identified as azoxybenzene [M.S. 77(100) 91(30) 105(26) 51(25) 65(22) 170(20) 198(19) 64(17)] and m.p. 87–89 °C.



4–Methyl–*N,N*–dimethylaniline and 4–fluoro–*N,N*–dimethylaniline were prepared according to the literature with these minor changes:[19] (1) The system containing the aniline and trimethyl phosphate was heated only gently until the

exothermic reaction was completed, before being brought to reflux. (2) The solution containing base was extracted with 1:1 ether–hexane instead of ether only.

Methylrhenium trioxide was prepared from Re_2O_7 and $Sn(CH_3)_4$.[20] The organorhenium peroxide **B**, $CH_3Re(O)(O_2)_2(H_2O)$, was prepared from methylrhenium trioxide.[21] Methanol and hexanes were purified by standard methods.[22] The anilines and other reagents used in this study were obtained commercially.

General procedure for synthesis of nitrosobenzene. 1.0 mL of $ArNH_2$ was dissolved in 10 mL methanol, mixed with 3.0 mL 30% hydrogen peroxide, after which 50 mg CH_3ReO_3 was added. The solution was stirred at room temperature for 2 hours, and then extracted three times with methylene chloride. The combined extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The product was purified by column chromatography on silica gel using 1:5–10 ethyl acetate–hexane as the eluent. The product from each aniline was identified spectroscopically by comparison to literature values.[23]

General procedure for the synthesis of *N*–oxides. A mixture of 2–4 g of the 4–substituted *N,N*–dimethylaniline ($ArNMe_2$), 200 mg of CH_3ReO_3 and 10 mL of 30% hydrogen peroxide in 10 mL methanol was stirred at room temperature for 2–5 hours. The product obtained after the solvent had been evaporated under vacuum was recrystallized from methylene chloride. Each product was identified by comparison of its spectra and melting point with those recorded in the literature.[24]

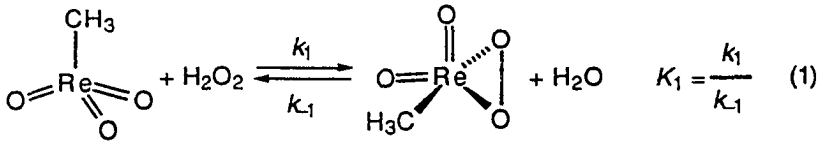
Kinetic studies. The progress of the reaction was monitored spectrophotometrically, using a Shimadzu UV–2101PC spectrophotometer and a Sequential DX–17MV stopped–flow instrument from Applied Photophysics Ltd.,

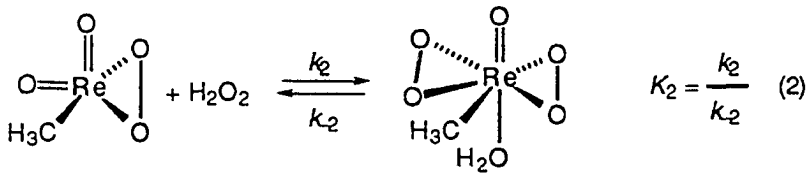
depending on the time scale of a given experiment. Kinetic studies were carried out by monitoring the disappearance of *N,N*–dimethylaniline at 251 nm, the disappearance of 4–bromo–*N,N*–dimethylaniline at 265 nm , the disappearance of 4–fluoro–*N,N*–dimethylaniline at 315 nm, and the accumulation of 4–nitro–*N,N*–dimethylaniline *N*–oxide at 231 nm, and 4–methyl *N,N*–dimethylaniline *N*–oxide at 265 nm. The kinetics with excess *N,N*–dimethylaniline for measurement of rate constant of the formation of **A** (the 1:1 peroxide of CH_3ReO_3 and hydrogen peroxide) was studied by monitoring the decrease in absorbance at 328 nm.

Reaction mixtures were prepared with hydrogen peroxide added last. The order of addition is important, since the steady-state analysis of the kinetic system applied most precisely when the compounds **A** and **B** were not allowed to accumulate prior to the start of the oxidation.

Results

Equilibrium measurements. It was necessary to remeasure the equilibrium constants of the reactions between CH_3ReO_3 and hydrogen peroxide in methanol. As cited above, this interaction results in the reversible formation of peroxides with 1:1 and 1:2 ratios rhenium to peroxide, as given in eq 1–2. Their equilibrium constants K_1 and K_2 were determined from the equilibrium absorbances in the range of 345–400 nm in experiments in which no aniline was present.





The values of the constants K_1 and K_2 were obtained by the nonlinear least-squares fitting of the data to the following equation:[13]

$$\frac{\mathrm{Abs}_\lambda}{[\mathrm{Re}]_T} = \frac{\varepsilon_0 + \varepsilon_A K_1[H_2O_2] + \varepsilon_B K_1 K_2 [H_2O_2]^2}{1 + K_1[H_2O_2] + K_1 K_2 [H_2O_2]^2} \qquad (5.3)$$

The total concentration of CH_3ReO_3, $[Re]_T$, was 0.52 mM and the concentration of hydrogen peroxide was varied over a range 1.2–76 mM, using eight concentrations. The equilibrium absorbance was recorded at 345, 360, 380 and 400 nm. The absorbance readings obtained as a function of hydrogen peroxide concentration were fitted to eq 3 by means of the program GraFit that allowed a global fit of all the multiwavelength spectra simultaneously. The data and fitting at one wavelength are shown in **Figure 5.1.**

The equilibrium constants obtained are $K_1 = 261 \pm 6$ L mol^{-1} and $K_2 = 814 \pm 14$ L mol^{-1}. The values are considerably larger than th0se in water,[13] which are 7.7 L mol^{-1} and 145 L mol^{-1}; the system in methanol is still cooperative (i.e. $K_2 > K_1$), although to a lesser extent than in water.

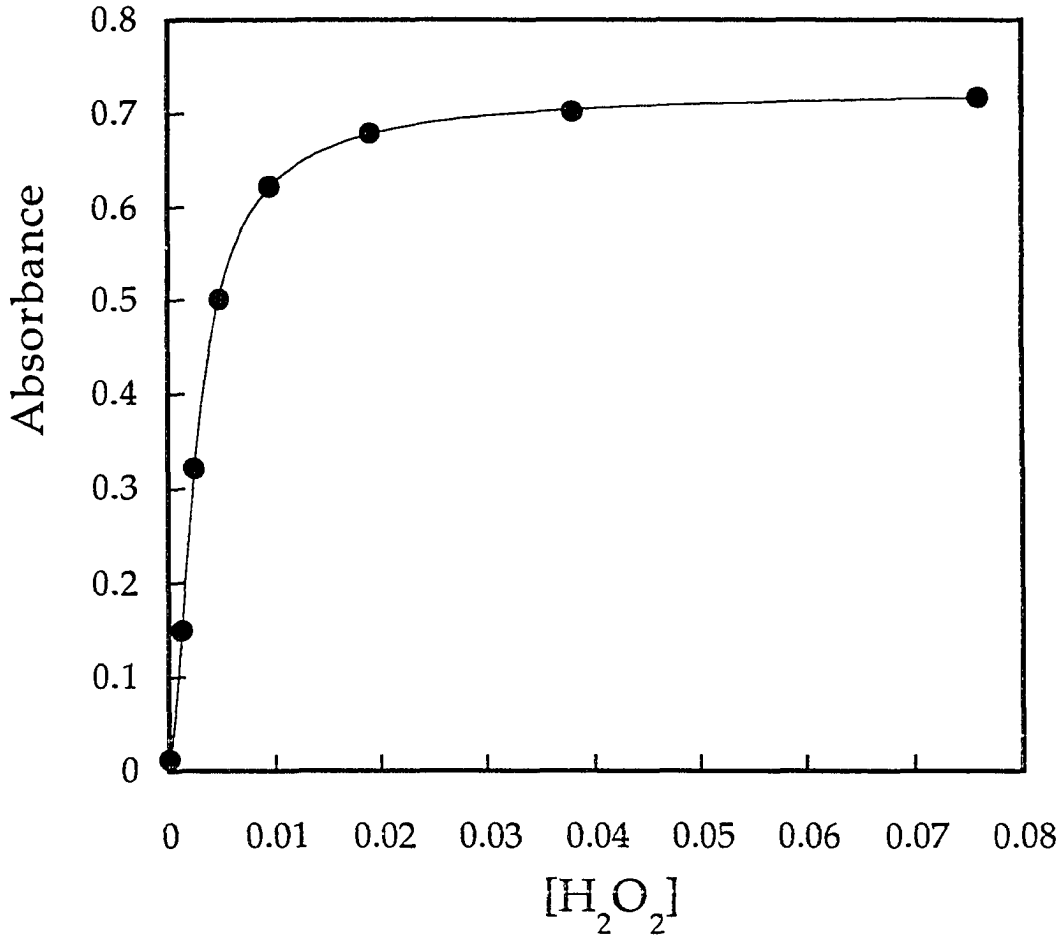


Figure 5.1. A plot showing the increases in absorbance at 345 nm that result from the formation of two rhenium peroxides in a 0.52mM solution of CH_3ReO_3 as a function of the concentration of hydrogen peroxide in methanol. This curve and similar ones at other wavelengths were used to evaluate the equilibrium constants K_1 and K_2 for the stepwise binding of peroxide ions.

The initial presence of a small concentration of water in the reaction did not shift the equilibrium, nor did the addition of a small concentration (2–20 mM) of water after the peroxides were formed. This is significant, since it bears on the question of the coordination of solvent to the peroxide **B**, and perhaps to **A**. Were the coordinated solvent methanol, or were the solvent not coordinated at all, then a change in the concentration of water, which itself would then be a reaction product free in solution, would shift the equilibrium position.

Experiments showed that this was not the case under the reaction conditions employed. We take this as evidence that water is the ligand coordinated to rhenium in moist methanol, despite the fast that the activity of methanol is higher than that of water. In other words, the peroxide compounds **A** and **B** are the same species here as they are in water or mixed water–organic solvents. Although the binding of water in **B** could be confirmed in THF by the use of ^{1}H nmr,[21] this was not possible in the hydroxylic solvent CD_3OD, where the formation of D_2O, coordinated or not, eliminates a measurable proton nmr signal.

Rate constants. The kinetics of reactions 1 and 2 were then examined in methanol. It proved impossible, however, to find conditions where only one of the reactions could be studied. The two were therefore studied together, although the accuracy was less than if each could have been studied separately. The kinetic data consisted of absorbance–time traces that were taken at 300 nm where the absorbance decreases with the reaction progress since CH_3ReO_3 itself has a larger molar absorptivity than **A** or **B** at this wavelength. The concentrations used were $[CH_3ReO_3]_T$ = 1.6 mM, and $[H_2O_2]$ was varied in the range 9.8–98 mM.

If we postulate that the equilibrium reactions that produce compounds **A** and **B** also describe the kinetics, the rate equations are:

$$\frac{d[\mathbf{A}]}{dt} = k_1[CH_3ReO_3][H_2O_2] - k_{-1}[\mathbf{A}] - k_2[\mathbf{A}][H_2O_2] + k_2[\mathbf{B}] \quad (5.4)$$

$$\frac{d[\mathbf{B}]}{dt} = k_2[\mathbf{A}][H_2O_2] - k_{-2}[\mathbf{B}] \quad (5.5)$$

where the possibility that water plays a specific role in the mechanism is ignored for the meantime; we shall return to that point later. These equations were solved for the case $[H_2O_2] >> [Re]_T$, such that $[H_2O_2]$ remained essentially constant in each experiment. The resulting expressions for **[A]** and **[B]** are the sums of two exponentials, but the two relaxation times are not simply those for the separate reactions in isolation. Rather, both relaxation times are complex functions of the four separate rate constants.[25-27] The buildup of **[B]** is given by:

$$[\mathbf{B}]_t = [Re]_T\left\{1 + \frac{\lambda_3}{\lambda_2 - \lambda_3}\exp(-\lambda_2 t) - \frac{\lambda_2}{\lambda_2 - \lambda_3}\exp(-\lambda_3 t)\right\} \quad (5.6)$$

where the two observed rate constants are related to the parameters of the kinetic scheme. The approach to the solution is best made through certain combinations of the two rate constants. The expressions for their sum and their product are useful; the equations are:

$$\lambda_2 + \lambda_3 = (k_1 + k_2)[H_2O_2] + k_{-1} + k_{-2} \quad (5.7)$$

$$\lambda_2 \times \lambda_3 = k_1k_2[H_2O_2]^2 + k_1k_{-2}[H_2O_2] + k_{-1}k_{-2} \quad (5.8)$$

This pair of equations was used for the analysis of the kinetic data, which consisted of ten experiments at five concentrations of hydrogen peroxide in the range 0.01–0.10 M. The absorbance buildup followed biexponential kinetics, characterized by the two rate constants λ_2 and λ_3, in accord with this model. The absorbance–time traces were fitted to a double exponential function with a floating

end–point. **Figure 5.2.** depicts a typical absorbance–time trace obtained from stopped–flow experiments, and superimposed on it the biexponential fit. The close fit of the data lends credence to this model.

The analysis of the data was done according to eq 5.7–5.8. To obtain numerical results the value of k_{-1} was replaced k_1/K_1, and that of k_{-2} by k_2/K_2, with the equilibrium constants K_1 and K_2 set at their known values. The data fit gave the values of two of the rate constants;[28] the rate constants for the reverse reactions were then calculated from the equilibrium constants. The results are as follows, with the aqueous values shown in parentheses:

$k_1 = 1150 \pm 60$ (Aq. 77) L mol^{-1} s^{-1} $\qquad$ $k_{-1} = 4.4 \pm 0.4$ (Aq. 9.0) s^{-1}

$k_2 = 308 \pm 16$ (Aq. 5.2) L mol^{-1} s^{-1} $\qquad$ $k_{-2} = 0.38 \pm 0.06$ (Aq. 0.04) s^{-1}

The addition of up to 10 mM water, when hydrogen peroxide is in excess, did not change the rate in methanol; higher concentrations of water caused the rate to decrease appreciably. A few experiments were also carried out in acetonitrile, where the kinetic retardation of added water was evident even at the lowest concentrations. The "forgiving" nature of methanol with respect to the concentration of water was the major reason for choosing methanol as the solvent. Since water is present in the peroxide solutions, roughly 4–5 mol per mol of hydrogen peroxide, and more is produced in the reaction, its effect on the rates of reaction in solvents where the rate is very sensitive to water would have greatly complicated a quantitative kinetic study.

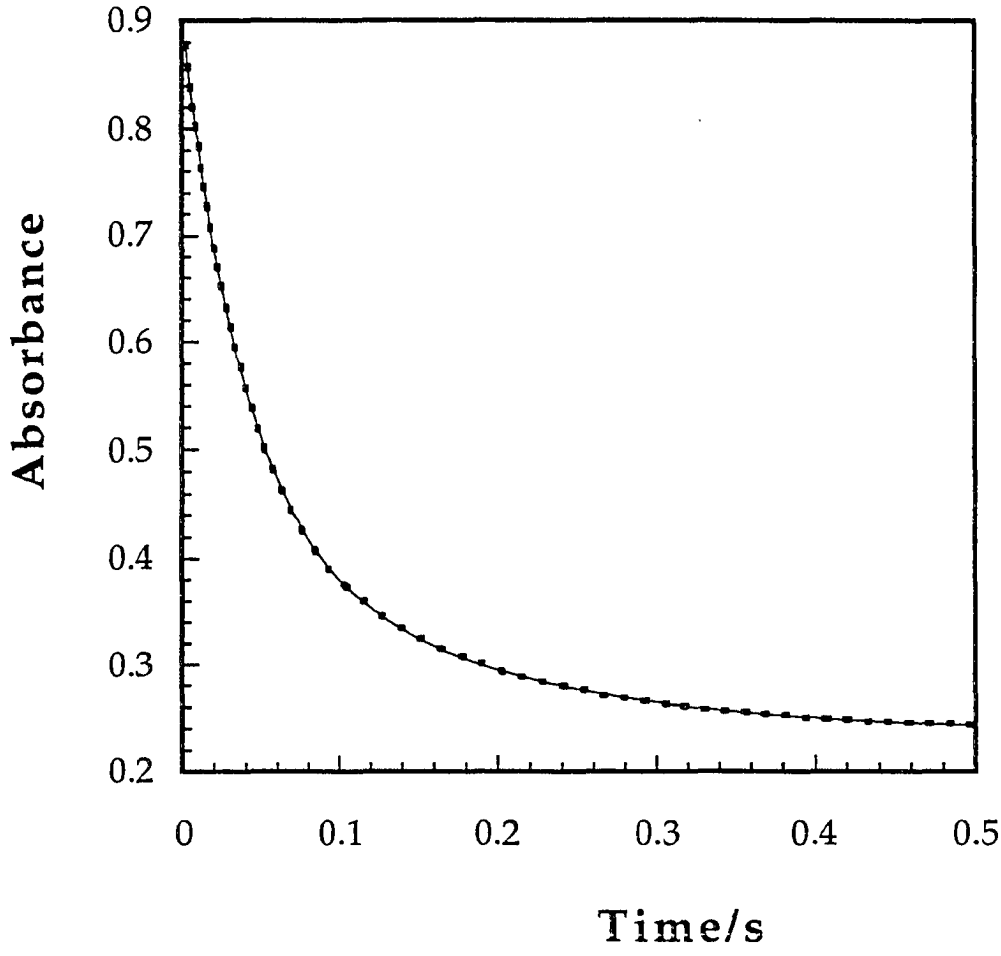


Figure 5.2. A typical absorbance–time trace at 300 nm from a stopped–flow experiment in methanol, in which 1.6 mM CH_3ReO_3 and 19.6 mM hydrogen peroxide form an equilibrium mixture of the rhenium peroxides **A** and **B**. The smooth curve shows the fitting of the data to a bi-exponential rate equation.

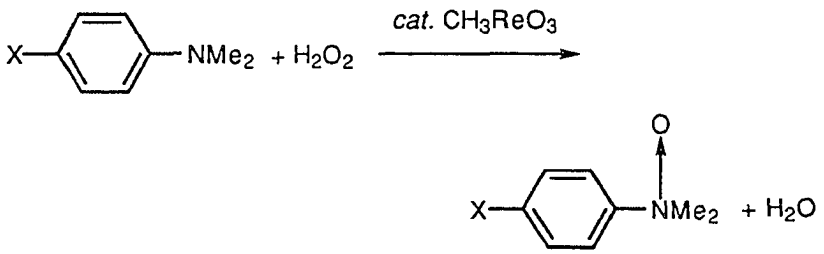
It should be added that the involvement of water might have been taken into account more explicitly, by relating [H_2O] to [H_2O_2], and then including it explicitly in the expressions for the thermodynamic and kinetic data. We opted not to follow this course, however, since to do so would require defining the role of water more precisely than the data allow.

***Para*–substituted *N,N*–dimethylanilines.** The oxidation of these anilines with hydrogen peroxide is strongly catalyzed by CH_3ReO_3. In methanol $ArNMe_2$ forms only the *N*–oxide at room temperature according to eq 9. The individual substrates studied and the yields of the product isolated from each are given in **Table 5.1**.

Table 5.1. Isolated yields of the N-oxide from the oxidation of *para*–substituted dimethylanilines by hydrogen peroxide, as catalyzed by CH_3ReO_3. [a]

para substituent:	CH_3	H	F	Br	NO_2
% Yield:	87	92	85	89	88

[a] In MeOH at room temperature, with an approximate mole ratio of aniline : peroxide : rhenium of 20 : 50 : 1.



(5.9)

The yields of this reaction were >85%. This convenient reaction may be used for the preparation of aromatic amine *N*–oxides. The product yields for the compounds with the different para substitutents did not differ significantly although it was suggested that electron-withdrawing groups will inhibit the reaction.[29] The catalyzed reactions might, however, be subject to kinetic influences, in that those with electron withdrawing groups might take longer reach completion. To explore the kinetic requirements in this practical sense, and also to gain insight into the molecular mechanism, we undertook a study of the reaction kinetics.

The kinetics of the oxidation of 4–substituted *N,N*–dimethylanilines. As the reaction was clean, forming only the *N*–oxide, it was straightforward to study the kinetics. These anilines do not react with hydrogen peroxide without the rhenium catalyst. **Figure 5.4** shows the absorbance changes without and with the catalyst.

The kinetics of the reactions catalyzed by CH_3ReO_3 were evaluated by the initial rate method. The data showed that the reaction is first–order with respect to both CH_3ReO_3 and aniline. Plots were made (see **Figure 5.5**) of $v_i = (-d[\text{Aniline}]/dt)_i$ versus $[Re]_T$ at constant $[PhNMe_2]_0$ and of v_i versus $[\text{Aniline}]_0$ at constant $[Re]_T$. The rate constants were obtained from the slopes of the plots.

For $PhN(CH_3)_2$ a series of experiments was carried out at five values of $[H_2O_2]$, in the range of 1.6–10.0 mM, with 69 μM $PhN(CH_3)_2$ and 10.6 μM CH_3ReO_3. The values of v_i were constant at $(1.26 \pm 0.01) \times 10^{-8}$ L mol^{-1} s^{-1}, proving the zeroth-order dependence on $[H_2O_2]$ under these conditions.

In a separate series, the rate was determined under conditions where the formation of **A** governed the rate. Thus this would constitute an independent

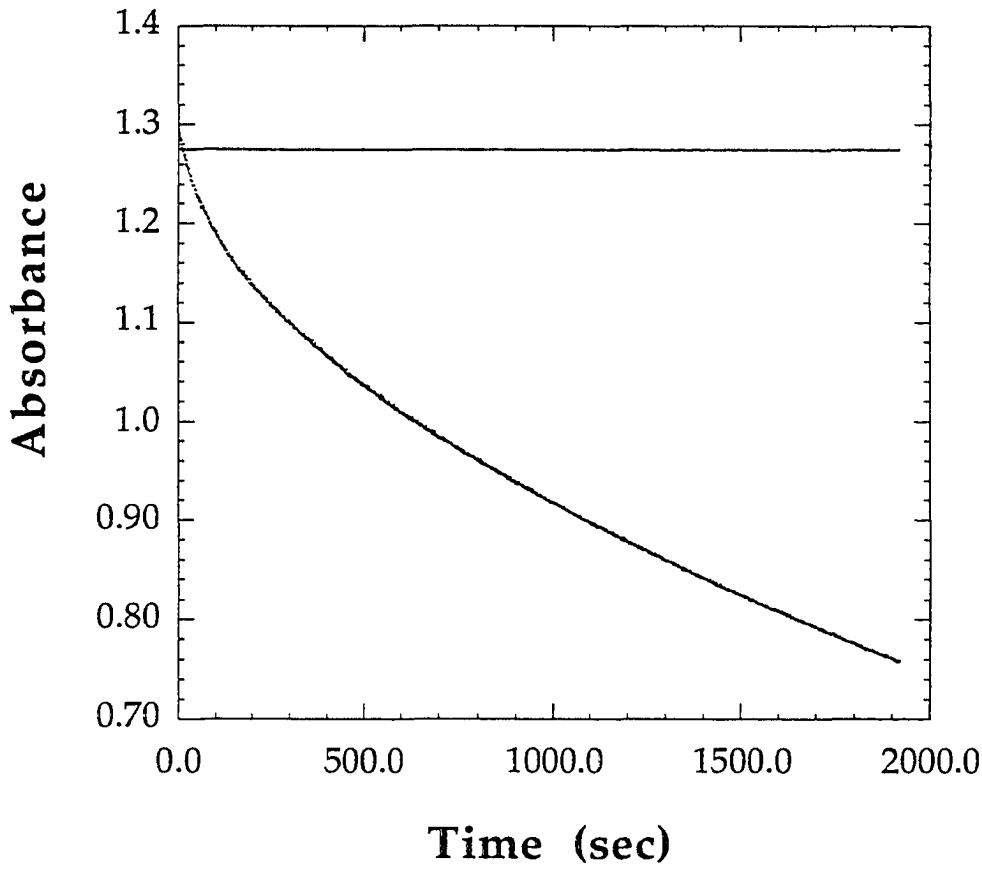


Figure 5.4. Typical absorbance–time kinetic traces at 251 nm for the oxidation of $PhNMe_2$ in methanol by hydrogen peroxide with and without CH_3ReO_3. The concentrations in MeOH were 13.3 μM CH_3ReO_3, 7.8 mM H_2O_2, and 0.11 mM [$PhNMe_2$].

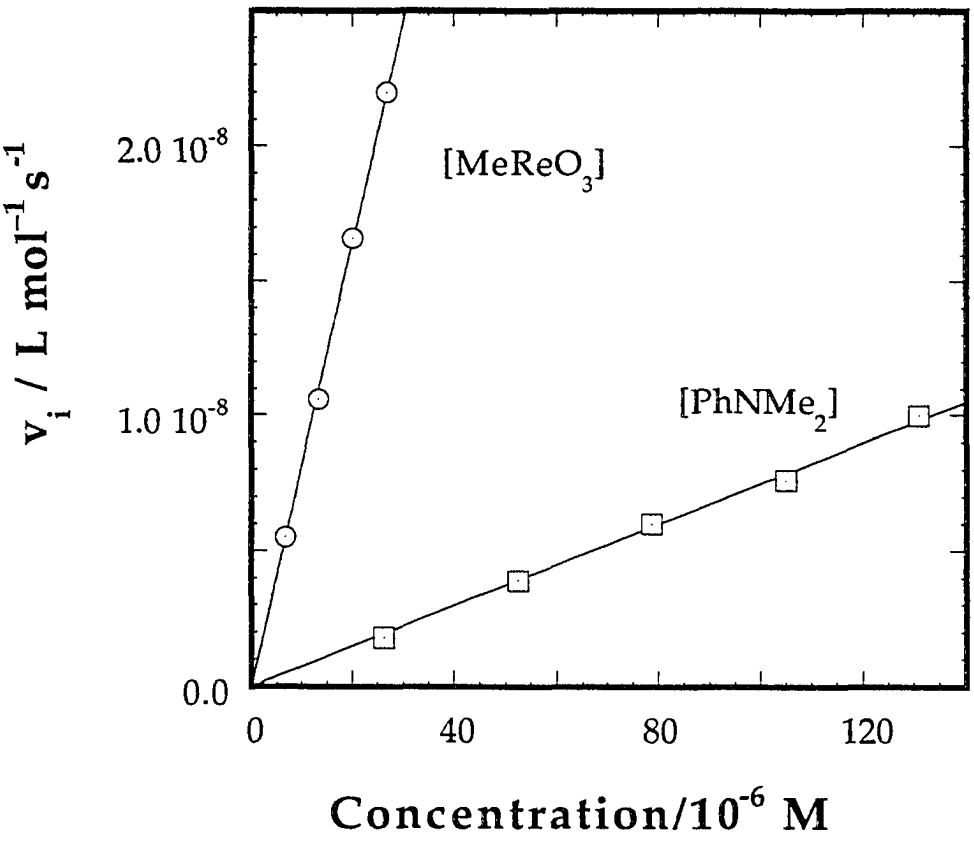
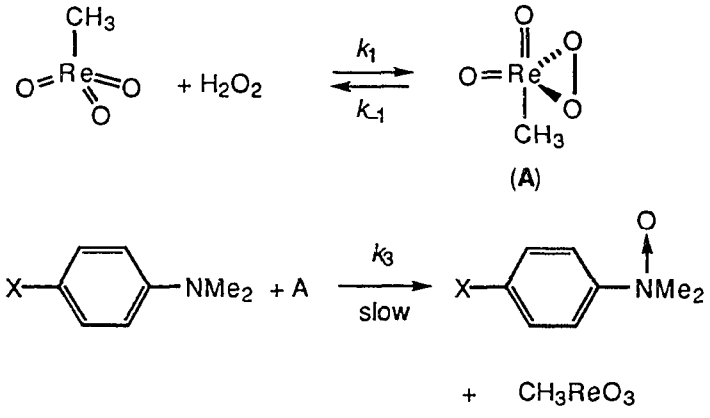


Figure 5.5. The variation of initial rate of reaction of dimethylaniline with a constant and excess $[H_2O_2]$, 2.76 mM, as a function of $[Re]_T$ at 45 μM $PhNMe_2$, and $[PhNMe_2]$ at 4.15 μM CH_3ReO_3.

determination of k_1, and also validate the reaction scheme. So that the kinetic term in k_1 would be the dominant one, an excess of the aniline was used. In the initial stage of the reaction, only **A** was formed. With high [$PhNMe_2$], however, the subsequent oxidation reaction proceeded more rapidly, and the k_1 step was nearly rate–controlling.

The initial rates from stopped–flow experiments were fit to the equation $v_i = k_1[Re]_T[H_2O_2]$. These determinations were carried out with a constant concentration of CH_3ReO_3 and a varying hydrogen peroxide concentration, the progress of the reaction being monitored at 328 nm where $\Delta\varepsilon$ = 105 L mol^{-1} cm^{-1}. The plot of v_i vs. [H_2O_2] was linear. The slope gave $k_1 = (1.18 \pm 0.06) \times 10^3$ L mol^{-1} s^{-1}. This value agrees well with that obtained from the double exponential curve fitting of the peroxide reactions alone, which gave $k_1 = 1.15 \times 10^3$ L mol^{-1} s^{-1}. Based on above observations, we suggest that the reaction follows the pathway shown in **Scheme II**.

Scheme II



The oxidation of *N,N*-dimethyl aniline by **B** was studied with **B** in excess. The reaction was investigated with [**B**] varying in the range of 1.5–7.5 mM, while

[$PhNMe_2$] was kept constant at 11 μM; then [**B**] was kept constant at 1.5 mM, and [$PhNMe_2$] varied in the range of 5.5–28 μM. The reaction proved to be first-order with respect to [**B**] and [$PhNMe_2$]. The rate constant was obtained from the plot of initial rate of the reaction versus [**B**] or [$PhNMe_2$] is $(1.14 \pm 0.07) \times 10^{-2}$ L mol^{-1} s^{-1}. In comparison, the oxidation of N,N-dimethyl aniline by **A** has $k_3 = 18.4$ L mol^{-1} s^{-1}. Clearly, the reactivity of **B** towards the oxidation of *N,N*-dimethylanilines is negligible compared to that of **A**.

The steady–state approximation for [**A**] and [CH_3ReO_3] gives the rate equation assuming that Scheme II is operative:

$$-\frac{d[\text{Aniline}]}{dt} = \frac{k_3[\text{Re}]_T[H_2O_2][\text{Aniline}]}{\frac{k_{-1} + k_3[\text{Aniline}]}{k_1} + [H_2O_2]} \tag{5.10}$$

With excess hydrogen peroxide, such that $(k_{-1} + k_3[\text{Aniline}])/k_1 << [H_2O_2]$,

$$-\frac{d[\text{Aniline}]}{dt} \cong k_3[\text{Re}]_T[\text{Aniline}] \tag{5.11}$$

This form agrees with the results reported above, in which the orders with respect to catalyst and aniline are unity, whereas that with respect to hydrogen peroxide is zero. From initial rate experiments, we obtained values for the rate constants k_3 for the reactions of 4–methyl–*N,N*–dimethylaniline, 4–fluoro–*N,N*–dimethylaniline, 4–bromo–*N,N*–dimethylaniline, *N,N*–dimethylaniline and 4–nitro–*N,N*–dimethylaniline at 25.0 °C in methanol. The values are given in **Table 5.2.**

Table 5.2. Rate constants for the oxidation of *para*–substituted dimethylanilines [a,b]

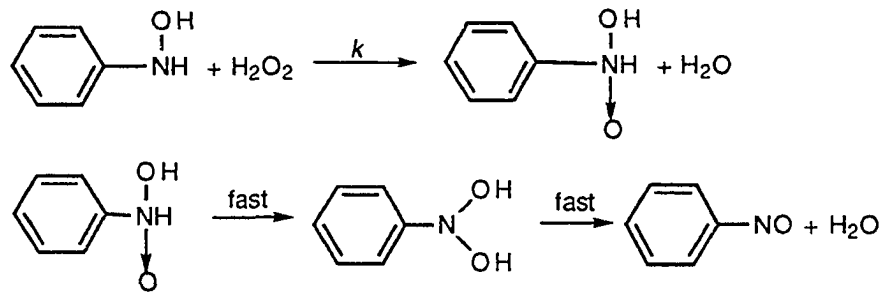
Para substituent:	CH_3	H	F	Br	NO_2
k_3/L mol^{-1} s^{-1}:	24.5	18.4	12.7	8.7	1.9

[a] In MeOH at 25.0 °C. The rate constants were calculated from initial rate determinations carried out with high concentrations of hydrogen peroxide.
[b] The value of k_3 is given by eq 5.11.

Oxidation of *N*–phenylhydroxylamine. This compound was examined because we came to believe that it might be an intermediate in the reaction of aniline itself. The reaction in the absence of CH_3ReO_3 was examined with [PhNHOH] = 53–160 μM and [H_2O_2] in the range of 1.04–5.02 mM. The reaction gave nitrosobenzene in about 88% yield. The reaction is first–order with respect to both *N*–phenylhydroxylamine and hydrogen peroxide, as represented by eq 11. The rate constant for the rate–controlling step in **Scheme III** is k = 0.78 ± 0.04 L mol^{-1} s^{-1}.

$$-\frac{d[\text{PhNHOH}]}{dt} = k[\text{PhNHOH}][H_2O_2] \qquad (5.12)$$

Scheme III



***N*–Phenylhydroxylamine: Catalysis by CH_3ReO_3.** The catalyzed reaction was investigated with $[Re]_T$ = 14.5–58.4 μM, $[H_2O_2]$ = 1.5–10 mM, and [PhNHOH] in the range of 58.4–233 μM. The reaction with added CH_3ReO_3 proved to be much faster than the uncatalyzed reaction. Under these condtions, with excess hydrogen peroxide, the catalyzed reaction was first–order with respect to both CH_3ReO_3 and phenylhydroxylamine, and nearly independent of $[H_2O_2]$. For reasons of simplicity, the initial rate method was used to study the catalyzed reaction. The rate constant for the catalyzed reaction of PhNHOH is $k_3 = 178 \pm 11$ L mol^{-1} s^{-1}. The data suggest that **Scheme II** also applies, with phenylhydroxylamine in place of the aniline. The rate law is the same as that for the oxidation of anilines, as given by eq 10. With a sufficient excess of hydrogen peroxide, such that $[H_2O_2] >> (k_{-1} + k_3[PhNHON])/k_1$, the expression for the reaction rate reduces to the experimental result expressed by eq 5.11.

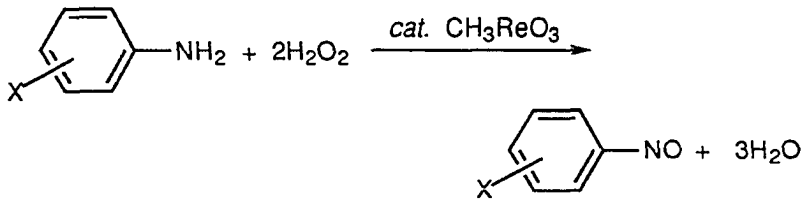
Oxidation of anilines of the formula $ArNH_2$. The major product of the oxidation of aniline by hydrogen peroxide catalyzed by CH_3ReO_3 is nitrosobenzene, according to eq 5.13. The product yields are listed in **Table 5.3.**

Table 5.3. Yields of the nitrosoarenes from the oxidation of substituted anilines by hydrogen peroxide, as catalyzed by CH_3ReO_3. [a]

substituent:	*o*–CH_3	H	*m*–CH_3	*p*–CH_3	*p*–OCH_3	*p*–c-hexyl	*p*–Cl
% Yield:	78	86	79	82	89	73	52

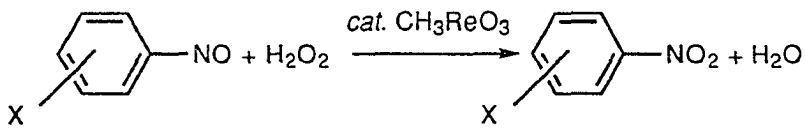
[a] In MeOH at room temperature, with an approximate mole ratio of aniline : peroxide : rhenium of 20 : 500 : 1.

The data suggest that the product yields may be lower for electron–withdrawing substituents.



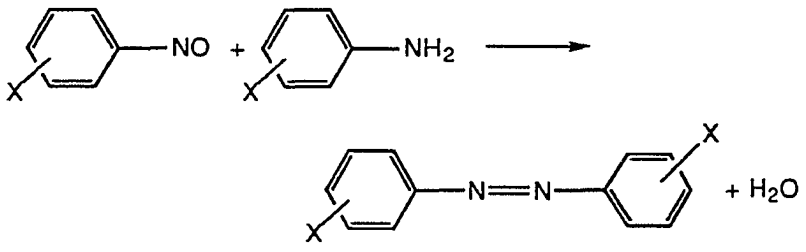
(5.13)

The GC–MS results showed that small amounts of the nitroarenes and traces of the azobenzenes were formed as well. The nitroarenes probably come from the further oxidation of nitroso compound. We used nitrosobenzene itself as starting material, and confirmed the occurence of eq 5.14, a much slower and therefore minor reaction, under the same conditions.



(5.14)

The azobenzene may come about from the condensation of nitrosobenzene with aniline. We mixed nitrosobenzene and aniline together in methanol, and showed that the major product was azobenzene, which did not require the rhenium catalyst.



(5.15)

Kinetics of the catalyzed oxidation of $PhNH_2$. The reaction was monitored by the buildup of nitrosobenzene at 320 nm where the $\Delta\varepsilon$ is 5000 L mol^{-1} cm^{-1}. The initial rate was calculated from the initial slopes of the absorbance–time curves; dAbs/dt values were converted to the reaction rates, $-d[PhNH_2]/dt$, by division by $\Delta\varepsilon$.

The kinetic study was carried out in two parts. In the one, we maintained $[Re]_T$ constant and varied $[PhNH_2]$, and vice–versa; see **Figure 5.6**. The results together were used to prove that eq 5.10 applied here as well.

With a large excess of hydrogen peroxide, the reaction became first–order with respect to both $[Re]_T$ and $[PhNH_2]_0$, consistent with the limiting form shown in eq 5.11. Plots of v_i vs $[Re]_T$ and v_i vs. $[Aniline]_0$ were linear. The rate constant for $PhNH_2$ was $k_3 = 2.04$ L mol^{-1} s^{-1}.

The oxidation of aniline by **B** was also studied with **B** in excess. The reaction was investigated with [**B**] varying in the range of 2.0–10.0 mM, while [Aniline] was kept constant at 12 μM; then [**B**] was kept constant at 2.0 mM, and [Aniline] varied in the range of 6–30 μM. The reaction proved to be first-order with respect to [**B**]

and [Aniline]. The rate constant was obtained from the plot of initial rate of the reaction versus [**B**] or [Aniline] is $(3.34 \pm 0.15) \times 10^{-4}$ L mol^{-1} s^{-1}. As in the case of N,N-dimethyl aniline, the reactivity of **B** towards the oxidation of aniline is also negligible compared to that of **A**.

It can be seen from **Table 5.3** that the anilines with an electron donating group (e.g. *p*–anisidine) gave higher yields. Based on the product yields and on the kinetic study of *para*–substituted *N,N*–dimethylanilines, *N*–phenylhydroxylamine and aniline, the assumption that the *N*–phenylhydroxylamine is the intermediate in this MTO cataltzed oxygen transfer reaction is reasonable. We suggest that this reaction occurs as shown in **Scheme IV.**

Discussion

The oxidation of *para*-substituted *N,N*-dimethyl aniline is inhibited by electron-withdrawing groups. The rate constants from Table 2 follow a linear Hammett relationship. The reaction constant $\rho = -1.19$, suggesting that the rate-controlling step is the nucleophilic attack of nitrogen lone-pair electrons of anilines on a peroxidic oxygen of **A.**

Electron-donating groups attached to the nitrogen atom of aniline also increase the rate constant. For example, the k_3 for aniline of 2.04 L mol^{-1} s^{-1} increases for $PhNMe_2$ by about ninefold, to 18.4 L mol^{-1} s^{-1}.

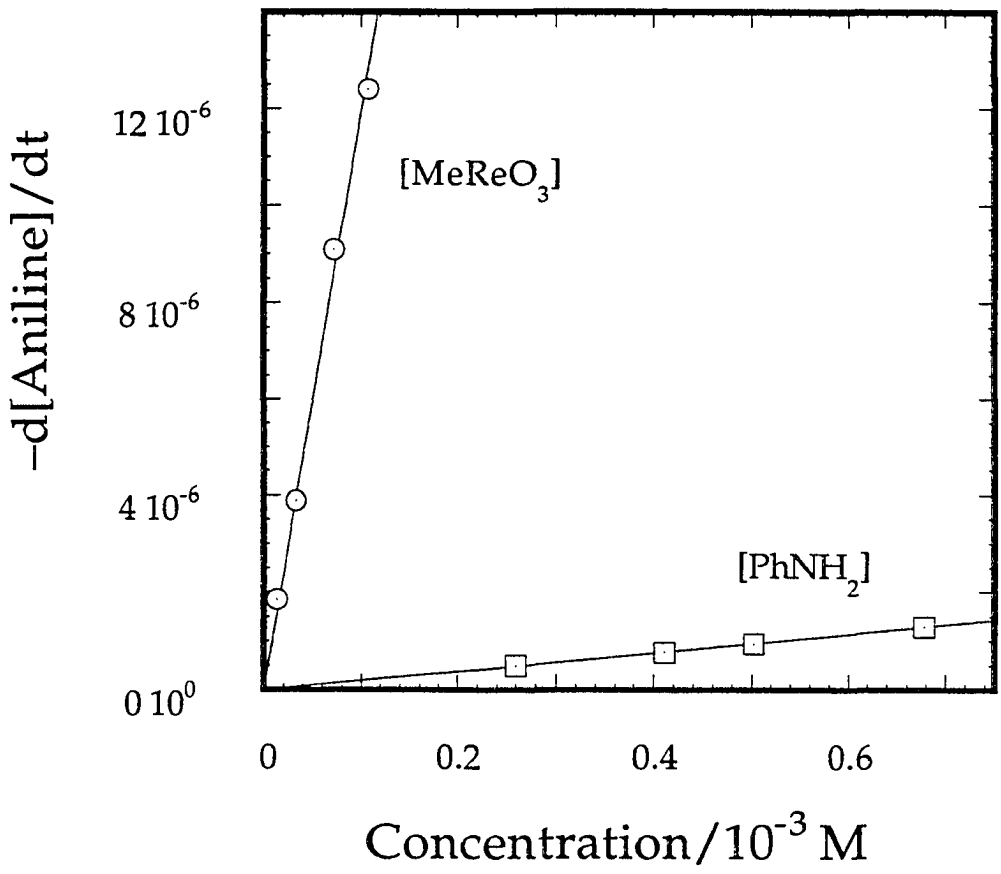
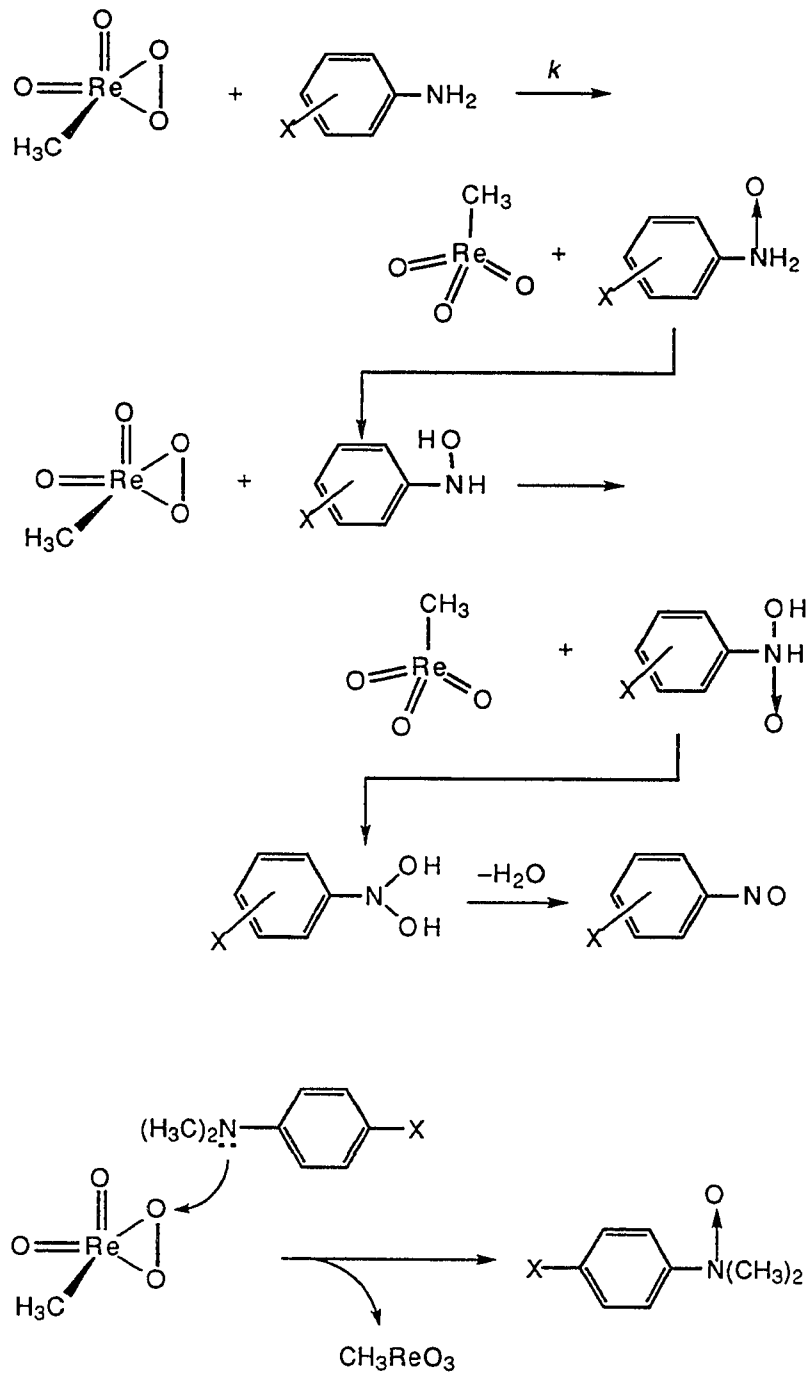


Figure 5.6. Variation of initial rate of oxidation of $PhNH_2$ at constant $[H_2O_2]$ = 1.96 mM, as a function of $[Re]_T$ at 0.973 mM $PhNH_2$, and as a function of $[PhNH_2]_0$ at $[Re]_T$ = 15 μM.

N-Phenylhydroxylamine has an OH group attached to nitrogen. As a result the rate constant, 178 L mol^{-1} s^{-1}, is about 90 times larger than that of aniline. As it is known that aniline oxidation by peroxyacids proceeds to nitrosobenzene by the way of hydroxylamine as the intermediate,[30] So we suggested that the hydroxylamines may be intermediates in this rhenium-catalyzed oxidation of anilines to the nitrosobenzenes. Since the second step is about 90 times faster than the first, it is difficult to detect the existence of *N*-phenylhydroxylamine directly. The postulate that ArNHOH are intermediates does allow a ready explanation for the formation of the observed products.

The rate constant for the formation of **A** from CH_3ReO_3 in methanol is much larger than that in pH 1 aqueous media (MeOH: k_1 = 1150 L mol^{-1} s^{-1}; H_2O: 77 L mol^{-1} s^{-1}) This suggests that **A** might be stablized in methanol, perhaps because the activity of water is so much lower in methanol. As we mentioned earlier, the addition of more than a trace of water to the reaction of *N*,*N*-dimethylaniline decreased the rate of the formation of the *N*-oxide. The stabilization by methanol can also explain why the equilibrium constant for the reaction of CH_3ReO_3 and H_2O_2, K_1 = 261 L mol^{-1} in methanol, is almost 40 times larger than that in water at pH 1, K_1 = 7.7.

Scheme IV



The oxidations of tertiary amines to *N*-oxides by peroxy acids also show negative rho values. For example, ρ = –2.35 for the oxidation of substituted pyridines.[31] It would be interesting to know if the oxygen of peroxy acids is more electrophilic than the oxygen of **A**.

Although anilines $ArNH_2$ can be oxidized to the corresponding nitroso compounds with peroxyacetic acid,[32] they need either long reaction times (48 hours) or heating. With the rhenium catalyst, a reaction time of one hour at room temperature suffices.

Acknowledgement. This research was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-W-Eng-82.

References

(1) Sakaue, S.; Tsubakino, T.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1993**, *58*, 3633.

(2) Costain, W.; Terry, B. W. H. *Germ. Offen. Brit.* **1971**, 041171; *Chem. Abstr.* **1971**, *76*, 33964.

(3) Wheeler, O. H.; Gonzalez, D. *Tetrahedron*, **1964**, *20*, 189.

(4) Nakagawa, K.; Tsuji, T. *Chem. Pharm. Bull.* **1963**, *11*, 296.

(5) Ross, L.; Barclay, C.; Dust, J. M.; Brownstein, S.; Gabe. E. J. *Organic Magn. Res.* **1981**, *17*, 175.

(6) Baumgarten, H. E.; Staklis, A.; Miller, E. M. *J. Am. Chem. Soc.* **1965**, *87*, 1203.

(7) Kosswig, K. *Justus Liebigs Ann. Chem.* **1971**, *749*, 206.

(8) Ciminale, F.; Camporeale, M.; Mello, R.; Troisi, L.; Curci, R. *J. Chem. Soc. Perkin Trans. II*, **1989**, 417.

(9) Sheldon, R. A. Topics in Chemistry, **1993**, *164*, 21–44.

(10) Strukul, G. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant* Kluwer Academic Publishers, Dordrecht **1992**.

(11) Kahr, K.; Beetha, C. *Chem. Ber.* **1960**, *93*, 132.

(12) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem. Int. Ed. Eng.* **1991**, *30*, 1636.

(13) Yamazaki, S.; Espenson, J. H.; Huston, P. *Inorg. Chem.* **1993**, *32*, 4683.

(14) Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1993**, *32*, 4517.

(15) Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 5491.

(16) Abu–Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272.

(17) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem. Int. Ed. Eng.* **1991**, *30*, 1638.

(18) Yanada, K.; Yamaguchi, H.; Meguri, H.; Uchida, S. *J. Chem. Soc. Chem. Commun.* **1986**, 1655.

(19) Billman, J. H.; Radike, A.; Mundy, B. W. *J. Am. Chem. Soc.* **1942**, *64*, 2977.

(20) Herrmann, W. A.; Kuhn, F. E.; Fischer, R. W.; Thiel, W. R.; Romo, C. C. *Inorg. Chem.* **1992,** *31,* 4431.

(21) Herrmann, W. A.; Fisher, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem. Int. Ed. Engl.* **1993,** *32,* 1157.

(22) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals,* **1988,** 3rd edition, Pergamon Press: Jordan Hill.

(23) Baumgarten, H. E.; Staklis, A.; Miller, E. M. *J. Org. Chem.* **1965,** *30,* 1203.

(24) Khuthier, A. H.; Al–Kazzaz, A. K.; Al–Rawi, J. M.; Al–Iraqi, M. A. *J. Org. Chem.* **1981,** *46,* 3634, and references therein.

(25) Bernasconi, C. F. *Chemical Relaxation,* Academic Press, New York, 1976, pp 23-29.

(26) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms,* 2nd Ed. McGraw-Hill, New York, 1995.

(27) Bernasconi, C. F. in *Investigations of Rates and Mechanisms of Reaction,* Part I: *General Considerations and Reactions at Conventional Rates,* C. F. Bernasconi, Ed., [which is Volume VI of *Techniques of Chemistry,* A. Weissberger, series editor], 4th Ed., Wiley-Interscience, John Wiley & Sons, New York, 1986, pp 435-443.

(28) The form of the kinetic equations allows the interchange of k_1 with k_2, and of k_{-1} with k_{-2}. The values were assigned on the basis of other chemical evidence.

(29) Mijs, W. J.; De Jonge, C. R. H. I. *Organic Syntheses by Oxidation with Metal Compounds*, **1986**, 206, Plenum Press: New York.

(30) Panda, A. K.; Mahapatro, S. N.; Panigrahi, G. P. *J. Org. Chem.* **1981.** *46*, 4000. and references therein.

(31) Dondoni, A.; Modena, G.; Todesco, P. E. *Gazz. Chim. Ital.* **1961**, *91*, 613.

(32) Holmes, R. R.; Bayer, R. P. *J. Am. Chem. Soc.* **1960,** *82*, 3454.

CHAPTER VI

A CONVENIENT SYNTHESIS OF BIS(ALKOXY)RHENIUM(VII) COMPLEXES

A paper submitted to the *Inorganic Chemistry*

Zuolin Zhu, Ahmad M. Al-Ajlouni and James H. Espenson

Abstract

Compounds of the general formula $CH_3Re(O)_2(OCR_2CR_2O)$ were prepared from the reaction between CH_3ReO_3 (MTO) and the epoxide in dry methylene chloride, and were characterized spectroscopically. The compounds are bis(alkoxides), containing a chelating diolate dianion. The diolates react with triphenylphosphine to form the alkene and regenerate MTO. Mechanisms of these reactions are suggested.

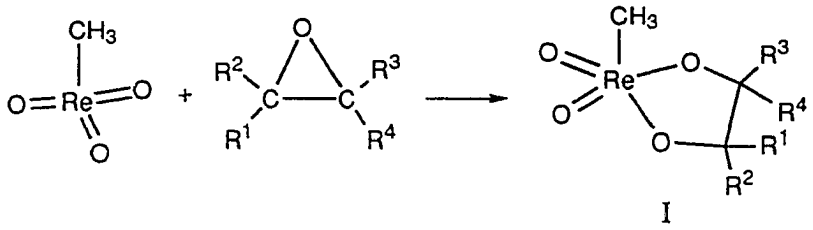
Introduction

The study of high oxidation state organorhenium compounds has been a field of continuing activity, thanks to the success of methylrhenium trioxide (CH_3ReO_3 or MTO) in catalytic processes. This catalyst is effective in oxidations[1-3], olefin metathesis,[4] the olefination of aldehydes,[5] and in the preparation of other compounds with three-membered rings.[6] The syntheses of some rhenium compounds derived from MTO have been reported.[5] Epoxide formation is a key reaction,[7-9] and it bears directly on these findings, as we now report.

Re(VII) complexes containing a chelated bis(diolate) ligand can be synthesized by refluxing MTO with 2,3-dimethyl-2,3-diol.[10] Here we report a more convenient method for this preparation. A different series of related compounds consists of chelated bis(diolates) of the Cp*Re-oxo series, Cp*ReO(diolate).[11,12]

Results and discussion

The reaction between MTO and an epoxide, eq 1, leads to diolate complexes. Five epoxides were used in this study: 2,3-dimethyl-2-butene epoxide, styrene epoxide, cis–cyclododecane epoxide, cis–stilbene oxide and trans–stilbene oxide. All except the last react with methylrhenium trioxide to give the corresponding bis(alkoxy)rhenium(VII) compounds (**I**) in nearly quantitative yield.

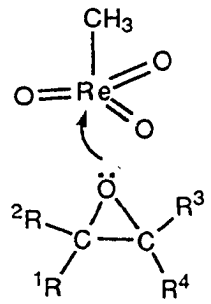


I (6.1)

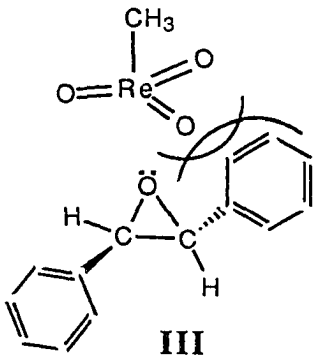
We suggest that the first step is the approach of the oxygen atom of the epoxide to the rhenium atom, at a site remote from the Re–C bond (**II**). Steric reasons may account for the failure of trans–stilbene oxide to react with MTO, since a similar approach would be impeded by the disposition of the phenyl groups (**III**).

The bis(alkoxy)rhenium(VII) complexes react with triphenylphosphine in dry benzene at room temperature to yield MTO, triphenylphosphine oxide, and olefin:

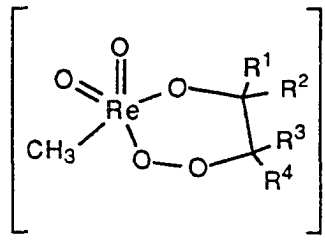
$$CH_3Re(O)_2(OCR_2CR_2O) + PPh_3 \rightarrow CH_3ReO_3 + Ph_3P{=}O + CR_2CR_2 \qquad (6.2)$$



II

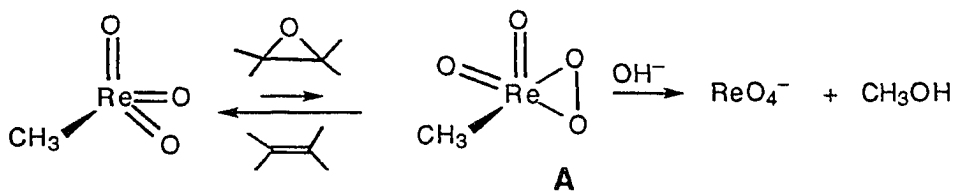


III



IV

Release of an alkene is strongly enhanced by the phosphine, and it occurs essentially upon mixing. Without phosphine, alkenes are released only slowly, if at all, from these Re(VII) derivatives; if heated, the MTO is destroyed. In wet acetonitrile, the reactions of styrene epoxide and 2,3-dimethyl-2-butene epoxide with MTO also gave bis(alkoxy)rhenium(VII) complexes in the presence and in the absence of H_2O_2. The yield (~10–15%) was much less than that obtained in dry benzene or in chloroform. In the absence of hydrogen peroxide, alkenes were released slowly over 3–5 days at room temperature. In addition, perrhenate ions and methanol were formed as decomposition products of the monoperoxo-Re(VII) species, **A**.[13] Because epoxides are also formed from the reaction of **A** with alkenes, the first step in eq 6.3 is reversible.



A (6.3)

The reaction of the diperoxo-Re(VII), **B**, ([H_2O_2] = 0.5 M and [MTO] = 0.02 M) with styrene was complete in 3-4 hours. Under the same conditions, in the

absence of H_2O_2, the ^1H–NMR spectrum showed that less than 50% of the styrene oxide had reacted with MTO after 5 days. Because **A** and **B** exhibit similar reactivity toward the epoxidation of olefins,[9] these results indicate that the reverse rate constant in eq 3 is much larger than the forward one and so the equilibrium constant for the first step is much less than unity. In the presence of H_2O_2, **A** and **B** are present, so any alkene formed reacts rapidly with **A** or **B** and can not be observed. Oxygen is transferred from styrene epoxide (0.1 M) to 2,3-dimethyl-2-butene (0.1 M) in acetonitrile in the presence of MTO (0.02 M). The reaction produced styrene and 2,3-dimethyl-2-butene epoxide in ~ 5-10% yield, eq 4. After three day, only ~20% of styrene epoxide and 2,3-dimethyl-2-butene were consumed. Other products, 1-phenyl-1,2-ethanediol, 2,3-dimethyl-2,3-butanediol and bis(alkoxy)rhenium-(VII) complexes were also observed. In the absence of MTO no styrene or 2,3-dimethyl-2-butene epoxide were observed, clearly substantiating the need for a catalyst.

(6.4)

2,3-Dimethyl-2-butene epoxide most probably results from the reaction of 2,3-dimethyl-2-butene with **A**, formed from styrene epoxide with MTO as shown in eq 6.4. We have not explored the unimolecular reactions that lead to alkene release. On the other hand, the literature reports the slow unimolecular release of alkene from rhenium(V) diolates.[12,14]

The most substantial difference between Re(V) and Re(VII) diolates is not so much the oxidation state of the metal, but the nature of the rhenium compound that remains when each diolate dissociates an alkene. The Re(V) compound produces R-

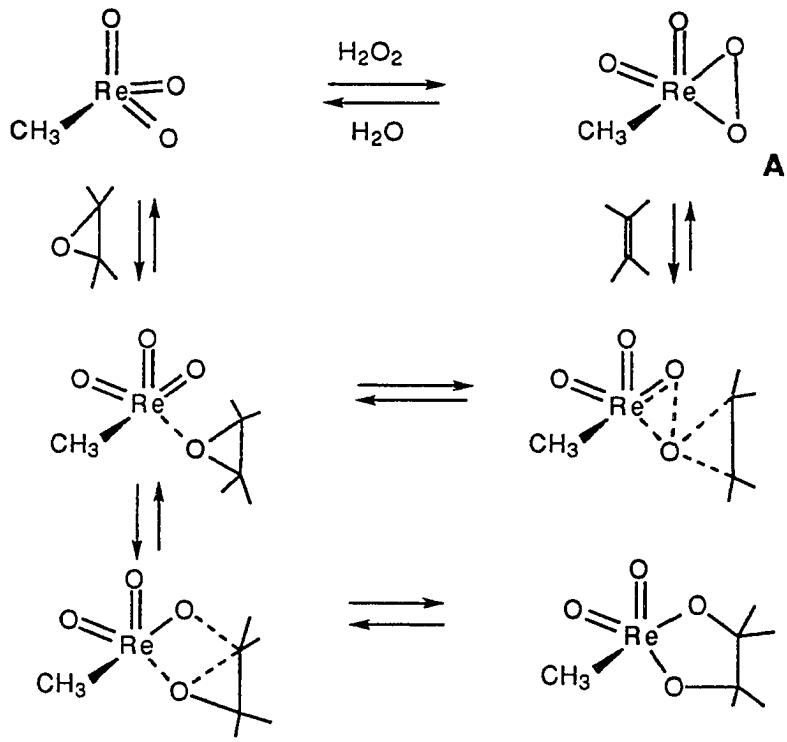
ReO_2, and Re(VII) gives R-ReO_3. The latter is a very stable substance, whereas the former, although known,[5,15,16] is not particularly stable. That difference must surely influence the transition state energies, favoring the Re(VII) compound.

There is, we believe, a close interrelation of three processes: (a) alkene epoxidation with hydrogen peroxide catalyzed by MTO that proceeds through the peroxorhenium compound $CH_3Re(O)_2(O_2)$, **A**; (b) diolate formation from an epoxide with MTO as described herein; and (c) alkene release from the diolate which has been better characterized for Re(V).[12,14,17,18]

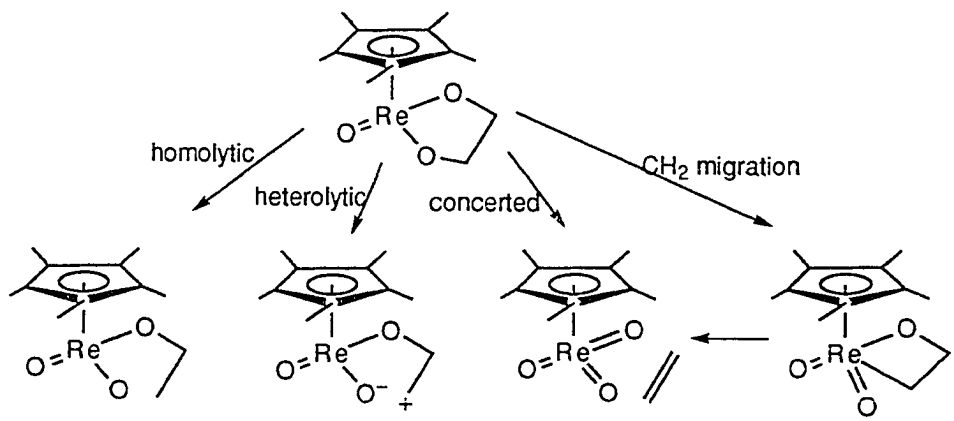
The interrelationship between these processes, in part conjectural, is diagrammed in **Scheme 1.** This diagram depicts the epoxidation occuring via the peroxide **A**, proceeding through one or more intermediates either to the epoxide or the diolate. In practice epoxidation is very rapid, as is the conversion of MTO to **A** by reaction with hydrogen peroxide. Although not depicted, the diperoxo rhenium complex **B** would be expected to react in a parallel fashion. Thus diolate formation is of minimal importance until the supply of peroxide is exhausted (assuming the alkene was taken in excess); alternatively, as in the procedure described here, no peroxide was used, allowing the transformation of the epoxide to the diolate. Hydrogen peroxide accelerates the MTO-catalyzed ring opening reaction of epoxycyclohexane in tert-butanol–water solutions;[19] with MTO alone, ring opening is catalyzed but the reaction is slower.

Certain possiblities for the excission of an alkene from a rhenium(V) diolate are shown in **Scheme 2.**[14,17,18] In particular, Hammett correlations have been used to rule out some possibilities, and CH_2 migration is the avenue suggested. By the same token, CH_2 migration (to O, not Re, see **IV**) may provide the avenue for the reaction under discussion here.

Scheme 1



Scheme 2



Eeperimental section

Synthetic procedure. A solution of methylrhenium trioxide (250 mg, 1mmol) in 15 mL dry methylene chloride was treated with the desired epoxide (1.2 mmol). After one day at room temperature, during which time the solution changed from colorless to yellow to deep red, the solvent was removed under vacuum. The light yellow bis(alkoxy)rhenium(VII) compounds were purified by vacuum sublimation. These procedures were carried out under argon. 2,3-Dimethyl-2-butene epoxide was prepared as described[20] and the other epoxides, available commercially, were purified using standard methods. [21]

Spectroscopic data

Spectroscopic data for the isolated products in $CDCl_3$ are as follows:

(a) For $R_1 = R_2 = R_3 = R_4 =$ Me, ^{1}H–NMR: $\delta = 2.38$ (3H), $\delta = 1.34$ (12H); ^{13}C–NMR: $\delta = 96.45$ (C–Me_2), $\delta = 42.70$ (Me–Re), $\delta = 25.75$ (C–Me2). ^{1}H–NMR in CD_3CN : $\delta = 2.39$ (3H), $\delta = 1.36$ (12 H);

(b) for $R_1 = R_2 = R_3 = H$, $R_4 =$ Ph, ^{1}H–NMR: $\delta = 2.44$ (3H), $\delta = 4.15$ (1H), $\delta = 4.52$ (1H), $\delta = 5.35$ (1H), $\delta = 7.05$ (5H); ^{13}C–NMR: $\delta = 136.54$, $\delta = 129.52$, $\delta = 128.85$, $\delta = 126.31$, $\delta = 87.18$, $\delta = 85.25$ and $\delta = 42.83$. ^{1}H–NMR in CD_3CN : $\delta = 2.45$ (s, 3H), $\delta = 4.78$ (dd, 1H), $\delta = 5.23$ (t, 1H), $\delta = 5.54$ (dd, 1H), $\delta = 7.32$ (m, 3H), $\delta = 7.47$ (m, 2H);

(c) for the reaction between MTO and cyclododecane epoxide, ^{1}H–NMR: $\delta = 2.41$ (3H), $\delta = 4.24$ (2H), $\delta = 2.17$ (4H), $\delta = 1.82$ (4H), $\delta = 1.35$ (8H), $\delta = 1.01$ (4H); ^{13}C–NMR: $\delta = 94.54$, $\delta = 42.07$, $\delta = 31.22$, $\delta = 28.73$, $\delta = 28.73$, $\delta = 26.18$, $\delta = 24.75$ and $\delta = 22.83$;

(d) reaction between MTO and cis–stilbene, ^{1}H–NMR: δ=2.47 (3H), δ=4.31 (2H), δ= 7.43 (10H); ^{13}C–NMR: δ=134.69; δ=127.52, δ=126.03, δ=125.88, δ=98.76 and δ=42.72.

Acknowledgments

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.

References

(1) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326.

(2) Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491.

(3) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272.

(4) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1636.

(5) Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organomet.* **1994**, *13*, 4531.

(6) Zhu, Z.; Espenson, J. H. In *290th annual meeting of ACS*; Anaheim, CA, 1995; Div. Org. Chem.

(7) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157.

(8) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638.

(9) Al-Ajlouni, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243.

(10) Herrmann, W. A.; Watzlowik, P.; Kiprof, P. *Chem. Ber.* **1991**, *124*, 1101-1106.

(11) Herrmann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Kusthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165-1182.

(12) Gable, K. P. *Organomet.* **1994**, *13*, 2486-2488.

(13) Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *submitted for publication*

(14) Gable, K. P.; Juliette, J. J. *J. Am. Chem. Soc.* **1995**, *117*, 955-962.

(15) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946-948.

(16) Herrmann, W. A.; Wang, M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1641.

(17) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1994**, *116*, 833-839.

(18) Gable, K. P.; Juliette, J. J. J. *American Chemical Society, 209th annual meeting*; Anaheim, CA, 1995.

(19) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Cat.* **1994**, *86*, 243.

(20) Camps, F.; Coll, J.; Messeguer, A.; Pericas, M. A. *Tet. Lett.* **1981**, *22*, 3859.

(21) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals;* 3d ed.; Butterworth-Heinemann: Oxford, 1988.

GENERAL SUMMARY

Methylrhenium trioxide, CH_3ReO_3 (MTO), catalyzes the decomposition of ethyl diazoacetate to yield diethyl 2-butenedioic acid esters or azine depend on the ratio of MTO and diazo chemicals used. In the presence of substrates which contain double bonds, such as olefins, imines or organic carbonyl compounds, cyclopropanes, aziridines or epoxides were formed by cycloaddition. These reactions may occur through a [2+3] process. Catalytic reactions between ethyl diazoacetate and alcohols, phenols, thiols, thiophenols or amines yield α-alkoxy ethyl acetates, α-thio ethyl acetates or ethyl glycine esters. Organic azides was converted azo compounds mediated by MTO. In the presence of triphenylphosphine, MTO catalyzed the reactions between organic azides and aromatic aldehydes that yielded organic imines in high yields.

The interaction between MTO and alcohols gives dehydration products, such as ether or olefins, depending on the alcohols used. The electron-donor groups of aromatic alcohols cause the disproportionation of alcohols to occur, leading to carbonyl compounds and alkanes. The amination of alcohols with amines was also catalyzed by MTO. Besides these reactions, oxygen transfer occurs from epoxides, sulfoxides, tertiary amine *N*-oxides and some metal oxides to triphenyl phosphine in the presence of catalytic amount of MTO.

Several oxidations with molecular oxygen and hydrogen peroxide were found to be catalyzed by MTO. With molecular oxygen, tertiary phosphines were converted to corresponding oxides; using hydrogen peroxide, anilines were

converted to nitroso benzene and tertiary aromatic amines were transferred to *N*-oxides. The fact that electron withdrawing groups decrease this reaction rate constants suggest peroxo group of A and B is electrophilic under these conditions.

Coordination of epoxides with MTO yields corresponding bis(alkoxy)rhenium (VII) complexes which are water sensitive and react with triphenyl phosphine to form triphenyl phosphine oxide, olefins and MTO.

ACKNOWLEDGMENTS

I would like to thank Professor James Espenson for his guidance and encouragement during my graduate career. I am also thankful to the members of my research group for their friendship and for sharing with me their own ideas and useful discussions. I am pleased to acknowledge informative discussion with Professor Glen A. Russell.

I would like to acknowledge my wife Meng for her support and love which give me direction, hope, encouragement and help.

I would like to thank Methylrhenium trioxide which, by using its amazing character, have make me enjoy research and allowed me to obtain a Ph.D. degree.

The work was supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences under contract W-7405-Eng-82. The United States government has assigned the DOE Report number IS-T 1763 to this thesis.