

RECEIVED

NOV 22 1995

IS-T 1763

OSTI

Organic Transformations Catalyzed by Methylrhenium Trioxide

by

Zhu, Zuolin

PHD Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: October 6, 1995

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

W

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

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 peroxy 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.

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 peroxy 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

	<u>Page</u>
GENERAL INTRODUCTION	
Introduction	1
Dissertation organization	4
 CHAPTER I. REACTIONS OF ETHYLDIAZOACETATE AND ORGANIC Preprint removed AZIDES CATALYZED BY METHYLRHENIUM TRIOXIDE for separate cycling at	
Abstract	5
Introduction	5
Results	7
MTO-catalyzed decomposition of ethyl diazoacetate (EDA)	7
Ether formation	8
Formation of S-C and N-C single bonds	11
Synthesis of aziridines	11
Formation of epoxides	13
Formation of cyclopropanes	15
Decomposition of phenyl azide	16
Catalytic formation of imines	18
Discussion	19
Decomposition of EDA	19
Comparisons with traditional methods	19
The proposed intermediates	20
The suggested mechanism	21

Experimental section	25
Materials	25
General procedures	
(1) α -Alkoxy ethyl acetates	25
(2) <i>N</i> -Substituted glycine ethyl esters	26
(3) α -Thio ethyl acetates	26
(4) Aziridines	27
(5) Epoxides	29
(6) Cyclopropanes	30
(7) Imines	30
Acknowledgment	33
SUPPORTING INFORMATION	34
Appendix	44
References	45

**CHAPTER II. DEHYDRATION, AMINATION AND
DISPROPORTIONATION OF ALCOHOLS
CATALYZED BY METHYLRHENIUM TRIOXIDE**

Preprint removed for separate cycling at

Abstract	50
Introduction	51
Results	52
Formation of ethers	52
Olefins from alcohol dehydration	57
Amination of aromatic alcohols	59
Disproportionation of aromatic alcohols	60

Discussion	61
Experimental section	64
Materials	64
Symmetric ethers	64
Unsymmetric ethers	64
Amination reactions	65
Olefin formation	65
Identifications	65
Acknoeledgment	65
Supporting information	66
References	73

**CHAPTER III. METHYLRHENIUM TRIOXIDE AS A CATALYST FOR
OXIDATIONS WITH MOLECULAR OXYGEN AND
OXYGEN TRANSFER**

*Report removed
for separate cycling of*

Abstract	76
Introduction	76
Results	78
Catalyzed phosphine oxidation with molecular oxygen	78
Oxygen transfer reactions	79
Deoxygenation of epoxides	79
Deoxygenation of sulfoxides	80
Oxygen transfer from tertiary amine N-oxides	80
Deoxygenation of triphenylarsine and triphenylstibine oxides	84
Discussion	85
The oxidation of phosphines with molecular oxygen	85

Deoxygenation of epoxides	86
Deoxygenation of sulfoxides and tertiary amine oxides	87
Deoxygenation of triphenylarsine and triphenylstibine oxides	87
Experimental section	89
Materials	89
Oxidation of phosphines	89
General procedure for deoxygenation of epoxides	90
Deoxygenation of sulfoxides	91
Deoxygenation of N-oxides	92
Acknowledgment	92
References	93
 CHAPTER IV. THE OXIDATION OF ALKYNES BY HYDROGEN PEROXIDE	
<i>Preprint removed for separate cycling</i>	
Abstract	96
Introduction	96
Results	98
Internal alkynes	98
Terminal alkynes	102
Limiting peroxide	104
Discussion	106
Experimental section	110
Materials	110
Procedures for the oxidation of alkynes	111
References	117

**CHAPTER V. KINETICS AND MECHANISM OF OXIDATION OF
ANILINES BY HYDROGEN PEROXIDE CATALYZED
BY METHYL RHENIUM TRIOXIDE**

*Reprint removed
for separate cycling
at*

Abstract	121
Introduction	122
Experimental section	124
Materials	124
General procedure for synthesis of nitrosobenzenes	125
General procedure for the synthesis of <i>N</i> -oxides	125
Kinetic studies	125
Results	
Equilibrium measurements	126
Rate constants	129
<i>Para</i> -substituted <i>N,N</i> -dimethylanilines	133
The kinetics of the oxidation of 4-substituted <i>N,N</i> -dimethylanilines	134
Oxidation of <i>N</i> -phenylhydroxylamine	139
<i>N</i> -phenylhydroxylamine: Catalysis by MTO	140
Oxidation of anilines of the formula ArNH_2	140
Kinetics of the catalyzed oxidation of PhNH_2	142
Discussion	143
Acknowledgment	147
References	147

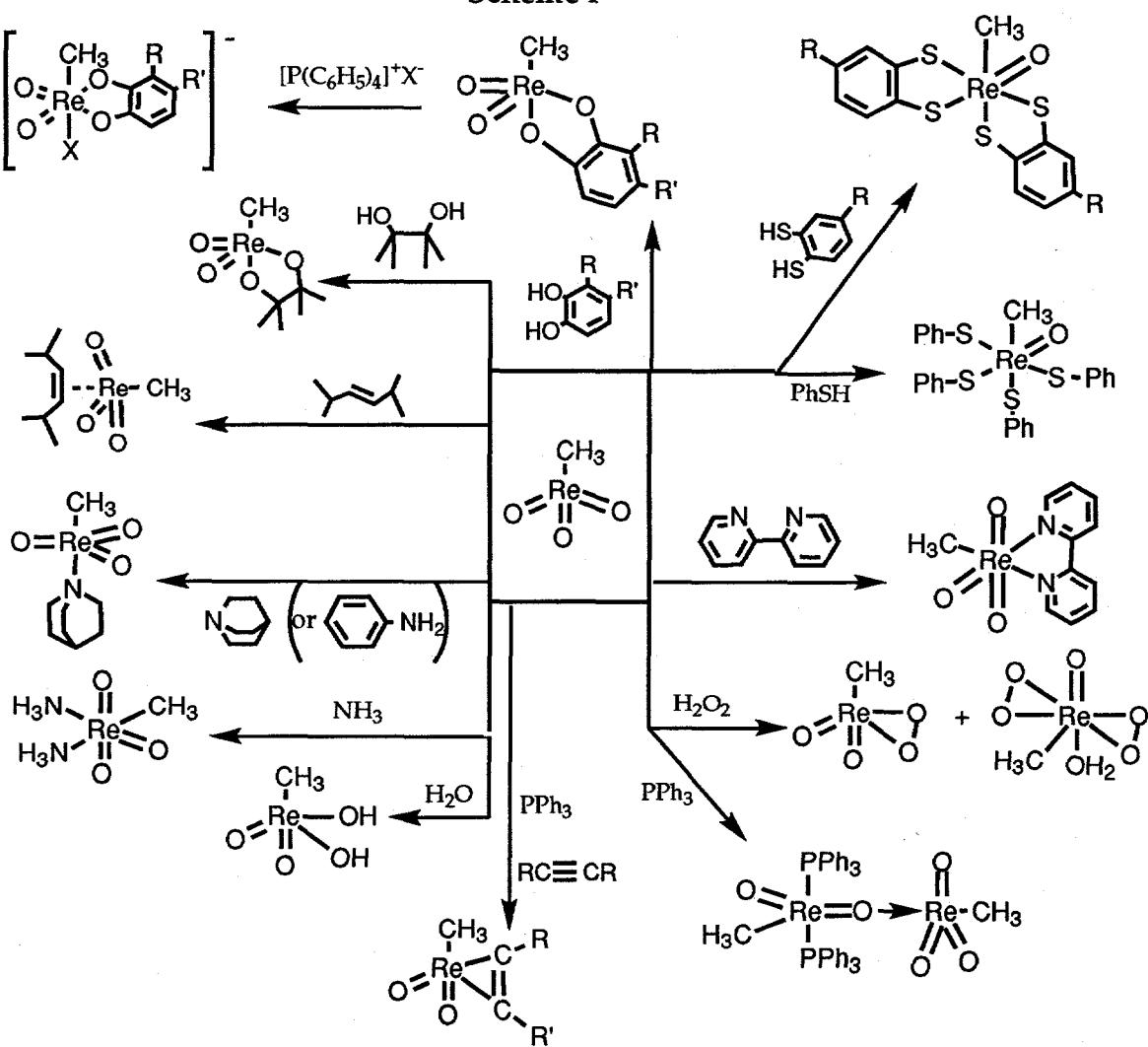
**CHAPTER VI. A CONVENIENT SYNTHESIS OF
BIS (ALKOXY) RHENIUM (VII) COMPLEXES**

*Reprint removed
for separate cycling
at*

Abstract	151
Introduction	151
Results and discussion	152
Experimental section	157
<i>Synthetic procedure</i>	157
<i>Spectroscopic data</i>	157
Acknowledgment	158
References	158
GENERAL SUMMARY	160
ACKNOWLEDGMENTS	162

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?

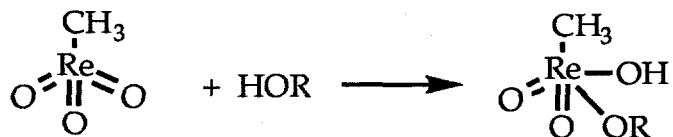
Scheme I



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 needed 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.

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 peroxy 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.