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Atom Transfer and Rearrangement Reactions Catalyzed by Methyltrioxorhenium, MTO

by

Jacob, Josemon

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Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

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Atom transfer and rearrangement reactions catalyzed by methyltrioxorhenium, MTO

Josemon Jacob

Major Professor: James H. Espenson

Iowa State University

Methyltrioxorhenium (MTO) catalyzes the desulfurization of thiiranes by triphenylphosphine. Enormous enhancement in rate is observed when the catalyst is pretreated with hydrogen sulfide prior to the reaction. Using 2-mercaptomethylthiophenol as a ligand, we synthesized several model complexes to study the mechanism of this reaction. With suitable model systems, we were able to show that the active catalyst is a Re(V) species. The reactions are highly stereospecific and very tolerant to functional groups. As part of our studies, we synthesized and crystallographically characterized the first examples of neutral terminal and bridging Re(V)sulfidocomplexes. Some of these complexes undergo fast oxygen atom transfer reactions with organic and inorganic oxidants. Studies on these model complexes led us to the discovery that MTO catalyzes the selective oxidation of thiols to disulfides.

The utility of MTO as a Lewis acid was exploited in effecting the rearrangement of propargylic alcohols to enones and enals. This reaction works efficiently with MTO when the propargyl alcohol is benzylic. The same chemistry when extended to allylic alcohols generates the more stable isomer at equilibrium. Kinetic, ^{2}D and ^{18}O labelling and theoretical studies were carried out to establish the mechanism of this reaction and to predict the direction of equilibrium in these systems.

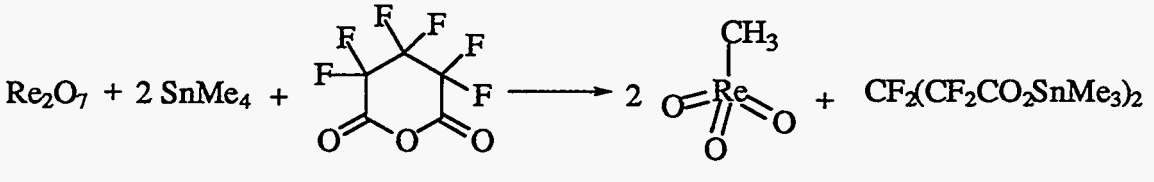
MTO activates hydrogen peroxide by forming a monoperoxo and a bisperoxocomplex both of which are efficient oxidants. Substituted arenes are selectively oxidized to *p*-quinones by the MTO/H_2O_2 system. The partially oxidized hydroquinones were detected in a few cases.

GENERAL INTRODUCTION

Introduction

Organometallic chemistry, a discipline that combines aspects of both inorganic and organic chemistry, has revolutionized research and development in the past 50 years. Homogeneous catalysis, an important application following the explosive growth in organometallic chemistry, offers higher selectivity, milder reaction conditions and high atom economy.[1] Many industrial processes are now available where stereospecific synthesis using transition metal catalysts play an indispensable role. The chemistry and reactivities of transition metal-oxo complexes have attracted extensive attention in the past decade due to their application in catalysis.[2] In my graduate research, I explored the utility of the high valent organorhenium oxide, methylrhenium trioxide (MTO) in catalytic atom transfer and rearrangement reactions.

Although MTO was first reported by Beattie and Jones in 1979,[3] its catalytic properties were not recognized till the early 90's.[4] Herrmann and coworkers who recognized the ability of MTO to activate hydrogen peroxide came up with a very facile synthesis in 1991(eqn 1).[5] The spectroscopic features of MTO are summarized in Table 1. Attractive features of MTO include its ease of synthesis and purification, stability in air, solubility in water and in most organic solvents and its effectiveness as a homogeneous catalyst.



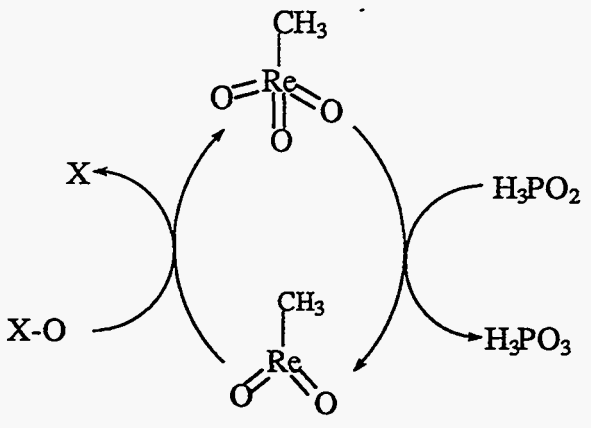
MTO (1)

Table 1. Spectroscopic features of MTO

Spectroscopy	signals
IR in CH_2Cl_2	1000(w) 967 (vs) cm^{-1}
^1H NMR in $CDCl_3$	δ 2.63 (s) ppm
^{13}C NMR in $CDCl_3$	δ 19.03 ppm
UV-Vis in H_2O	239 nm(ε 1900 L $mol^{-1}cm^{-1}$)
	270nm (ε 1300 L $mol^{-1}cm^{-1}$)

Sulfur Atom Transfer Reactions

Metal centered oxygen atom transfer reactions are interesting because of their relevance to hydroxylase enzymes in biological systems and their potential in catalytic oxidation processes.[6,7] Previous work in our lab has shown that MTO catalyzes O-atom transfer reactions from various organic and inorganic oxidants through a catalytic cycle involving a Re(V) species as shown in Scheme 1.[8,9] The mechanisms of these atom transfer reactions have been studied in detail.

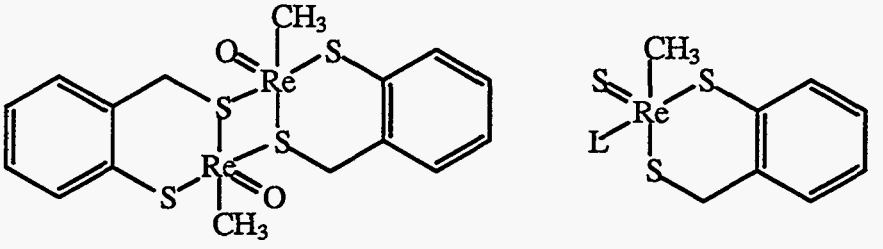


X-O = epoxides, sulfoxides, ClO_4^-, BrO_4^- etc.

Scheme 1. catalytic cycle for O atom transfer reactions with MTO

In this work, I report the extension of the chemistry to sulfur atom transfer reactions. Triphenylphosphine was used as the sulfur acceptor from episulfides in this study. The reactions were carried out in CD_3CN or C_6D_6 at room temperature with 2% MTO as the catalyst. Preliminary experiments showed that the reaction was characterized by a long induction period which could be accounted for. Mechanistic considerations suggested that the induction period could be averted by replacing the oxygen atoms on rhenium by sulfur. This was achieved by the addition of H_2S which eliminated the induction period completely.

Chart 1



D **M-L**

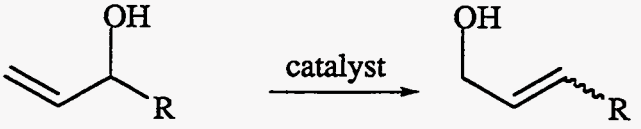
Since characterization of the catalyst obtained on reaction of MTO with hydrogen sulfide proved to be difficult, we turned to model systems. Several complexes based on 2-mercaptomethylthiophenol as a ligand were synthesized and crystallographically characterized (of general formula **D** and **M-L** in **Chart 1**). ^1H NMR or UV-Vis spectroscopy were used in the kinetic studies. A new method for the conversion of metal-oxo to sulfido compounds was developed. These results and further investigations with these complexes are discussed in chapters I, II, III and IV.

Rearrangement Reactions

Lewis acids play a vital role in catalyzing numerous organic reactions.[10] MTO, with rhenium in its highest oxidation state of +7, is a powerful Lewis acid.

In this study, the utility of MTO in effecting a 1,3-transposition of hydroxyl groups in allylic and propargylic alcohols were investigated (eqns 2 and 3).

(2)



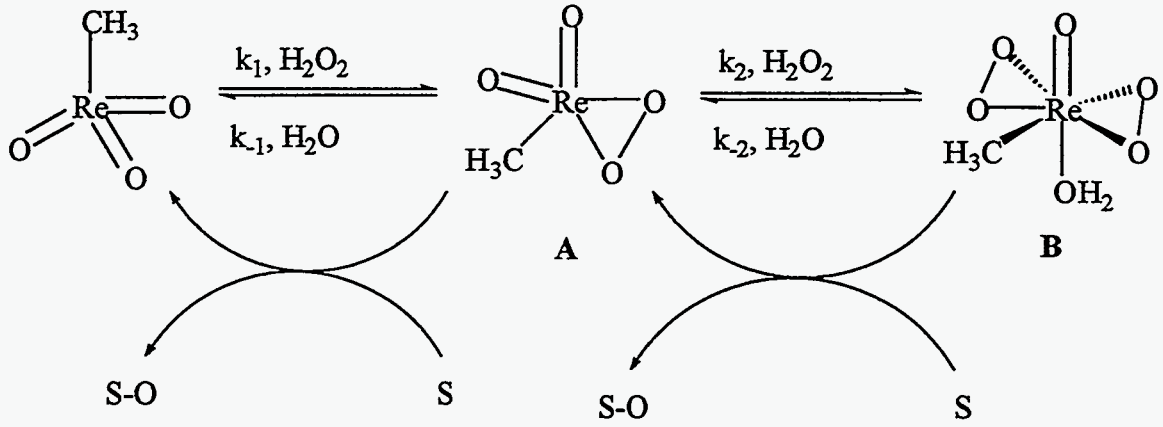
(3)

Propargylic alcohols on rearrangement give α,β-unsaturated aldehydes or ketones which are valuable as Michael acceptors in synthesis. In this study, the rearrangement of a variety of aliphatic and aromatic propargylic alcohols were studied in the presence of catalytic amounts of MTO. The reactions are characterized by a long induction period which was poorly understood. The same chemistry was extended to allylic alcohols and the more stable product predominates at equilibrium. Kinetic, equilibrium and labeling studies (deuterium and ^{18}O) were carried out to determine the mechanism of isomerization. In collaboration with Prof. Mark Gordon's group at ISU, we carried out theoretical studies on model systems to predict the direction of equilibrium in these systems. The results of these investigations are summarized in chapters V and VI.

Oxidation of Arenes to *p*-Quinones

Selective C-H bond activation of readily available chemical feedstocks poses a great scientific challenge in that the first formed products are generally more reactive than the starting materials. Hence selectivity is a major challenge to anyone working in this field. In fact, great advances have been made in the

selective functionalization of CH_4 to CH_3OH in recent years. Hydrogen peroxide is considered one of the best sources of oxygen atom in oxidation reactions since the product after oxidation is water and hence no problems arise in terms of



Scheme 2. Catalytic cycle for oxidations with MTO and H_2O_2

waste disposal. Although hydrogen peroxide reactions by themselves are slow, MTO activates hydrogen peroxide to form a monoperoxocomplex, A and a bisperoxo complex, B. Both these complexes are capable of transferring oxygen atoms to various oxidants in a catalytic cycle as shown in Scheme 2. Previous work in our lab has shown that the MTO/H_2O_2 system can oxidize a range of substrates and the kinetics and mechanisms of these reactions have been studied in detail.[11-15] In this study, the direct oxidation of substituted arenes to p-quinones by hydrogen peroxide catalyzed by MTO was investigated. The reactions were studied in acetic acid at 60°C with 8 mol% catalyst and was monitored by GC-MS. The results of this investigation are summarized in Chapter VI.

Dissertation Organization

The dissertation consists of seven chapters. Chapter I corresponds to a manuscript submitted to *Chemical Communications*. Chapter II corresponds to a manuscript published in *Inorganic Chemistry*. Chapters III and IV have been submitted as communications to *Inorganic Chemistry*. Chapter V has been published in *Organometallics* and Chapter VII in *Inorganica Chimica Acta*. We

decided not to publish the work described in Chapter VI. Each chapter is self-contained with its own equations, figures, tables and references. Following the last manuscript is general conclusions. Except for the theoretical studies described in Chapter V and the X-ray structural analysis, all the work in this dissertation was performed by the author of this thesis, Josemon Jacob.

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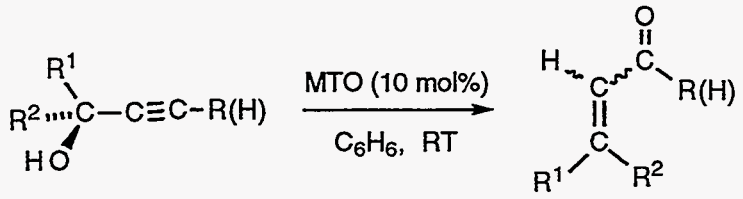
CHAPTER VI. ISOMERIZATION OF PROPARGYLIC ALCOHOLS TO ENONES AND ENALS CATALYZED BY METHYLRHENIUM TRIOXIDE

Introduction

The oxophilicity of rhenium in the highly electrophilic and organic-soluble compound methylrhenium trioxide (CH_3ReO_3, abbreviated as MTO) affords any number of possibilities for organic transformations. The potential of MTO as a catalyst for selective oxidations was considerably advanced by a synthesis of MTO[1] more convenient than the original.[2]

Selective oxidations comprise one major area first recognized for MTO.[3-12] Other, non-oxidative transformations have also been discovered: alcohols are catalytically dehydrated to ethers,[13] aldehydes oligomerized to 1,3,5-trioxanes,[14] epoxides and carbonyl compounds converted 1,3-dioxolanes;[14] also, epoxides and sulfoxides are deoxygenated with triphenyl phosphine as the oxygen acceptor and MTO as the catalyst,[15,16] etc. Epoxides are catalytically converted to 1,2-diols with MTO, and much more rapidly with MTO/H_2O_2.[17,18]

With these points in mind, the possibility of using easily-synthesized propargylic alcohols as synthetic precursors in catalytic reactions was examined. These alcohols afford rearrangement products, α,β-unsaturated carbonyl compounds.[19] They are valuable intermediates in organic synthesis, finding application for fragrances, carotenoids, etc.[20] Certain transition metal complexes are known to mediate the isomerization of propargylic alcohols by a 1,3 transposition of oxygen, as given in eq 1, referred to as a Meyer-Schuster rearrangement,[21-25] or by hydride migration, a Rupe rearrangement.[21,26-29]



(1)

Owing to the potential synthetic economy of such isomerizations, both of these rearrangements have been the focus of prior effort, as cited previously. During our studies of the catalytic functionalization of alcohols and related oxygen-containing substances[13,16] we found that MTO could catalyze several rearrangement reactions of oxygenates. Consequently we examined its effect on propargylic alcohols, and report here MTO catalyzes the rearrangement of propargylic alcohols into α,β-unsaturated aldehydes and ketones with a 1,3- shift of OH group.

Results and Discussion

A considerable number and variety of secondary and tertiary α-acetylenic alcohols were examined. The findings are summarized in **Table 1**. Most of the catalytic reactions with MTO produced good yields of the rearranged enals and enones. Those propargylic alcohols that are benzylic (R^1 = arene, eq 1) gave the rearranged carbonyl compounds in good yield. Both internal and terminal alkynes underwent efficient catalytic conversion to the rearranged product.

Several aliphatic propargylic alcohols (R = alkyl) were also investigated. They gave low yields; two examples are presented in entries 10 and 12; seven others, not tabulated, were equally unsatisfactory. Two silyl-substituted acetylenes, entries 6 and 11, underwent a previously-reported[13] condensation reaction to an ether (eq 2) rather than rearrangement, and a third bearing a strongly electron-attracting group, entry 5, underwent neither reaction.

$$2\ R^1R^2C(OH)C{\equiv}CSiMe_3 \rightarrow [Me_3SiC{\equiv}CCR^1R^2]_2O + H_2O \qquad (2)$$

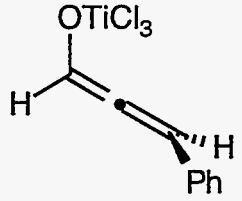
Water has been shown to inhibit ether formation.[13] When 1 eq of water was also added was added at the start of one of the reactions (repeating entry 11 in table 1), no ether formed within 3 days. This is probably due to the preferential coordination of water to the catalyst. The starting material remain unchanged during this period.

Several days were required for these reactions to reach completion. This delay is the result of a long induction period, often 2-4 days, more than an inherently slow process. Once that time had elapsed, product buildup occurred usually within 10-24 hours and could be observed in the ^1H NMR spectra.

Our attempts to use ^1H NMR to determine the origin of the induction period were not successful. Neither MTO alone nor the reaction mixture gave signals for species other than those for the separate species themselves. Variation of the catalyst to substrate ratio doesn't seem to have any significant effect on the induction period. The phenomenon of an induction period is not unique to this one MTO catalytic system, as it has been observed elsewhere. The reactions between alcohols and ethyl diazoacetate[30,31] experienced long and unaccountable delays before the onset of reaction. Neither exceptionally dry materials nor deliberately moist ones altered the situation.[32] When 1 eq of water and propargyl alcohol were added, only 30% conversion was found; otherwise it was 98% (entry 1).

Further NMR studies were carried out for 1-phenyl-2-propyne-1-ol, entry 1. After 18 h, the ^1H spectrum showed two new olefinic doublets at δ 5.80 and 5.35 ppm with a coupling constant of 2.1 Hz, probably indicating an allene type intermediate. This intermediate was detected in no more than 10% yield. The

concentration of the intermediate was too low for a reliable ^{13}C NMR signal. When $TiCl_4$ was added, its concentration was considerably enhanced and the ^{13}C spectrum showed a new signal at 202.17 ppm, which comes in the region expected for the central carbon of an allene. The carbonyl carbons of the products have chemical shifts of δ 189 (Z) and 190 (E) ppm.[33]The effect of titanium(IV) is to stabilize the intermediate; we suggest the species formed in this interaction is:



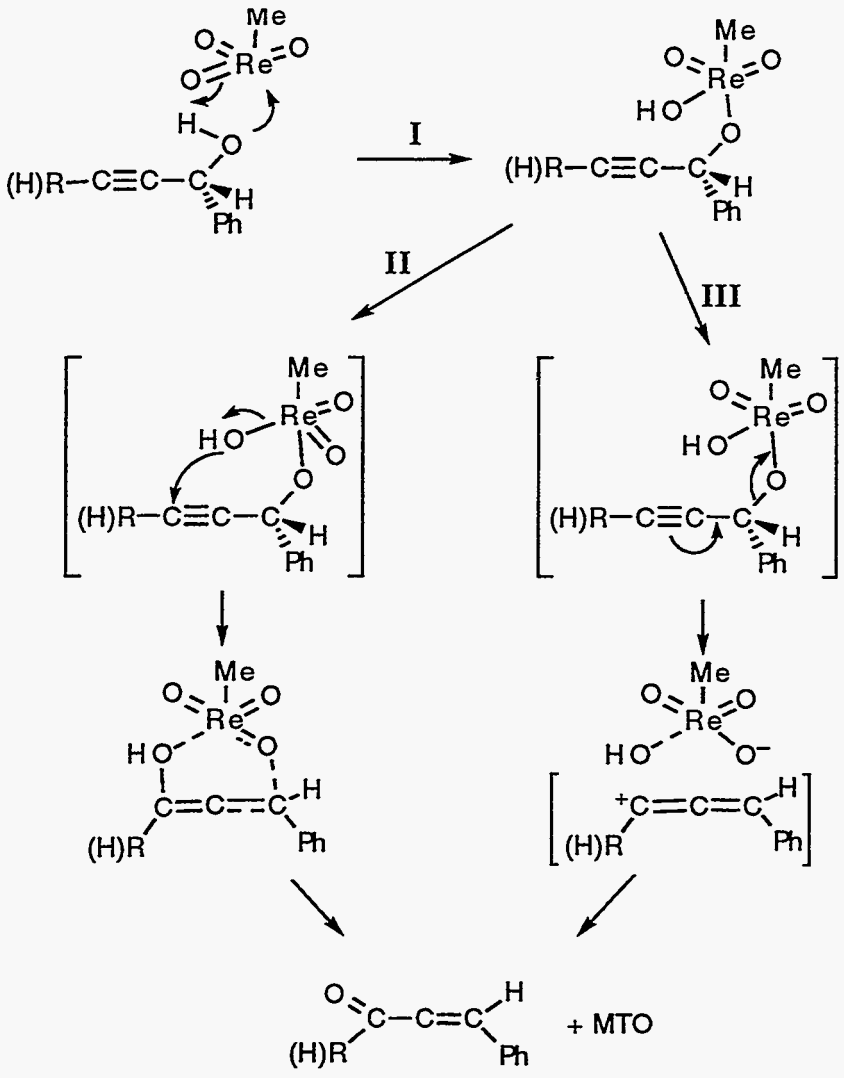
In our efforts to find a co-catalyst to accelerate the rearrangement, we tried both $TiCl_4$ and $Sn(OTf)_2$, but neither were effective. Instead, each of them led to the formation of a more intense NMR signal for the intermediate, increasing its concentration as depicted.

The reaction was also carried out by adding PhCH(OH)C≡CH (cf. entry 1) in three successive portions to a given MTO-solvent mixture. The first portion (0.072 mmol) was, after 3.5 d, converted to product in 82% yield. The second portiom (0.06 mmol) gave 83% conversion (overall) after 1.5 days, and the third (0.06 mmol) 73% conversion in 1.5 d. The fact that the second two increments cut the reaction time more than two-fold suggests that a more active form of MTO is produced during the induction period. Clearly the catalyst is not deactivated as a result of having participated in a large number of turnovers.

Mechanism

Scheme 1 presents a plausible mechanism. We were guided in our thinking by the results obtained for MTO-catalyzed reactions of alcohols, where it was shown that the initial step is an association between MTO and the alcohol;

actually, addition of RO–H across Re=O, reaction I.[13] Within the alkoxyrhenium complex so formed, it appears the bonds reorganize either as in Reactions II or III, which represent polar and ionic alternatives. Reaction II would give rise to an allenol-type intermediate that goes on to give the α,β-unsaturated aldehyde or ketone. Evidence for such came from the NMR data for the detected intermediate, presented in the preceding section. **Scheme 1. Scheme 1. Suggested Mechanism**



The intermediate amounts to, at most, 10% of the substrate taken; the MTO catalyst was used at the 10% level. This coincidence hints that the allenol intermediate may be bound to rhenium.

That fact that the *p*-nitro compound did not rearrange at all is indicative of a powerful electronic effect. An ionic mechanism, Reaction III of Scheme 1, can be considered. On this basis a higher rate would have been expected for entries 7 and 9, whereas they take a longer time, perhaps owing to steric factors. Changing the solvent to the more polar solvent acetonitrile did not increase the rate, but this is very likely just another manifestation of the long induction period. The catalyst is very stable in benzene.

Conclusions. The Meyer-Schuster rearrangement of propargylic alcohols to α,β-unsaturated ketones and aldehydes proceeds in good-to-excellent yields with the MTO catalyst. The rearranged products are valuable Michael acceptors widely used in organic synthesis. The variable induction period which is poorly understood poses a serious limitation to this otherwise interesting reaction.

EXPERIMENTAL SECTION

Materials. The propargylic alcohols were prepared according to literature procedures.[34,35] Their purities were checked by ^{1}H and ^{13}C NMR and by GC-MS. Methylrhenium trioxide was synthesized according to a literature procedure.[1] Anhydrous benzene was obtained commercially, and used as such, avoiding exposure to atmospheric moisture. The NMR spectra were measured at 300 MHz for protons with Me_4Si as an internal standard.

General procedure. In a typical experiment, the propargylic alcohol (1.25 mmol) and MTO (0.125 mmol) were added to 10 mL anhydrous benzene in a round-bottomed flask and stirred at room temperature. The reaction was

monitored intermittently by TLC. After the reaction was complete, the solvent was evaporated under vacuum and the products isolated by column chromatography, if necesssary. The products were characterized by ^{1}H and ^{13}C NMR and by GC-MS. The spectral data are in good agreement with accepted values.[36,37]

Table 1. Products and yields of catalytic rearrangement of propargylic alcohols to ketones and aldehydes

	Substrate			Product		
Entry	R	R^1	R^2	yield	Time/d	E/Z
1	H	Ph	H	98%	4	9:1
2	H	Ph	Me	95	7	2:1
3	Ph	*p*-$MeOC_6H_4$	H	>99	2	1:4
4	H	*p*-$MeOC_6H_4$	H	83	4	5:2
5	$SiMe_3$	*p*-$O_2NC_6H_4$	H	nr		
6[a]	$SiMe_3$	*p*-$MeOC_6H_4$	H	98	3	
7	H	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	96	7	
8	*n*-C_6H_{13}	Ph	H	43	5	2:1
9	*n*-C_6H_{13}	Ph	Ph	95	7	
10	H	*n*-C_5H_{11}	H	5	4	

11[a]	$SiMe_3$	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	98	3	
12	Me	Me	Et	30	5	2:1

[a] The ether formed by condensation of two substrate molecules, as shown in eq 2, was the major product.

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SUPPORTING INFORMATION

Table 2: NMR data in $CDCl_3$ (rel to Me_4Si) for the less common products

Product	^1H NMR	^{13}C NMR
Ph(Me)C=CH-CHO (Z-isomer)	9.46 (d, 1H, J 8.1 Hz), 7.67-7.32 (m, 5H), 6.13(dq, 1H, J 8.1,1.5 Hz), 2.3 (d, 3H, J 1.5 Hz)	193.40, 162.12, 138.37, 129.68, 128.28, 127.21, 125.92, 26.38
Ph(Me)C=CH-CHO (E-isomer)	10.17 (d, 1H, J 7.8 Hz), 7.67-7.32 (m, 5H), 6.4 (dq, 1H, J 1.2, 7.8 Hz) 2.56 (d, 3H, J 1.2Hz)	191.21, 157.60, 136.56, 129.11, 128.35, 126.21, 122.17, 16.32
Ph-CO-CH=CH-Ar (Z-isomer)	7.99 (dd, 2H, J 8.4,1.5 Hz), 7.79-7.48 (m, 5H), 7.42 (d, 1H, J 11.4 Hz), 7.34 (d, 1H, J 11.4 Hz), 6.9 (dd, 2H, J 8.4, 1.5 Hz), 3.79 (s, 3H)	190.34, 161.55, 144.54, 138.34, 132.43, 130.11, 128.43, 128.27, 127.43, 119.55, 114.28, 55.22
Ph-CH=CH-CO-$(CH_2)_5$-CH_3 (E-isomer)	7.63 (d, 2H), 7.56 (d, 1H, J 16 Hz), 7.15 (m, 3H), 6.65 (d, 1H, J 16 Hz), 2.38 (t, 3H), 1.73-1.68 (m, 2H), 1.45-1.14 (m, 8H), 0.94 (3H, t, J 7.2 Hz)	201.82, 135.91, 130.14, 130.09, 129.11, 128.40, 126.70, 41.08, 32.02, 31.54, 29.32, 24.21, 22.80, 14.25

Ph-CH=CH-CO-$(CH_2)_5$-CH_3 (Z-isomer)	7.63 (d, 2H), 7.15 (m, 3H), 6.48 (1H, d, J 12 Hz), 5.94 (d, 1H, J 12 Hz), 2.24 (t, 2H), 1.62 (m, 2H), 1.45-1.14 (m, 8H), 0.89 (3H, t, J 7.2 Hz)	198.80, 142.43, 138.93, 135.16, 129.22, 128.97, 128.13, 43.63, 31.89, 29.08, 24.36, 22.80, 14.25
Ar_2C=CH-CHO	9.77 (d, 1H, J 8.4Hz), 7.19 (d, 2H, J 8.8 Hz), 6.95 (d, 2H, J 8.8 Hz), 6.64-6.60 (overlapping doublets, 5H, J= 8.4, 8.8 Hz)	192.21, 161.85, 160.95, 160.83, 132.59, 130.66, 129.58, 127.92, 126.23, 114.29, 113.19, 54.83, 54.74
Ph_2C=CH-CO-$(CH_2)_5$-CH_3	7.18-6.99 (m, 10H), 6.53 (s, 1H), 2.06 (t, 2H, J 6.6 Hz), 1.58-1.48 (m, 2H), 1.24-1.06 (m, 6H), 0.82 (t, 3H, J 7.2 Hz)	200.73, 152.02, 141.70, 139.65, 130.05, 129.17, 128.65, 128.57, 128.50, 128.39, 127.82, 43.16, 31.89, 29.19, 24.57, 22.82, 14.22

Ar = *p*-methoxyphenyl

GENERAL CONCLUSIONS

MTO catalyzes the desulfurization of thiiranes by triphenylphosphine. Enormous enhancement in rate is observed when MTO is pretreated with hydrogen sulfide prior to the reaction. The reaction is stereospecific and very tolerant to functional groups. Using 2-mercaptomethylthiophenyl as a ligand in model systems based on MTO, it was shown that the active form of the catalyst is a Re(V) species. Seven new complexes were synthesized and crystallographically characterized. The synthesis of the first examples of neutral terminal and bridging Re(V)sulfido complexes is particularly noteworthy. A new approach using P_4S_{10} for the conversion of M=O to M=S was developed. Some of these complexes undergo fast oxygen atom transfer reactions with organic and inorganic oxidants. We were able to trap the first formed complex in these reactions when DMSO is used as the ligand. These studies led us to the discovery that MTO catalyzes the selective oxidation of thiols to disulfides.

1,3-transposition of the hydroxyl group in a propargyl alcohol leads to an enone or an enal. MTO was shown to catalyze this reaction in good to excellent yields when the propargyl alcohol is benzylic. The same chemistry was extended to allylic systems where the more stable isomer at equilibrium is generated. The direction of the equilibrium is largely decided by the nature of the OH group, i.e., whether it is primary, secondary or tertiary. In the case of aliphatic allylic alcohols, 3° is preferred to 2° to 1°. For aromatic allyl alcohols, the more conjugated isomer predominates largely at equilibrium. Oxygen-18 labelling showed that the OH groups of parent and product are the same. The reaction is first order with respect to allyl alcohol and MTO, but strongly inhibited by traces of water. Theoretical calculations suggest the same in the case of aliphatic allyl alcohols though aromatic allyl alcohols do not follow the predictions. Studies of

deuterium labelled substrates show a large *equilibrium isotope* effect (K= 1.20 ± 0.02). For isomeric allyl alcohols differing in the position of deuterium only, the isomer with the deuterium at sp^3 centre predominates at equilibrium. The effect of conjugation from a phenyl group appears to be less important since calculations suggest that the phenyl group is forced out of plane of the allylic π system.

Arenes are oxidized to *p*-quinone by hydrogen peroxide in presence of catalytic amounts of MTO. In some cases, the intermediate hydroquinones were detected in small amounts. The active catalyst species are the previously-characterized η^2–peroxorhenium complexes, $CH_3Re(O)_2(\eta^2\text{–}O_2)$ and $CH_3Re(O)(\eta^2\text{–}O_2)_2(H_2O)$. Separate tests showed that hydroquinones and phenols are oxidized by H_2O_2–MTO more rapidly than the simple arenes; in the proposed mechanism they are intermediate products.

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