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Organic Reactions Catalyzed by Methylrhenium Trioxide: Reactions of Ethyl Diazoacetate and Organic Azides

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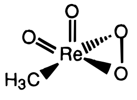
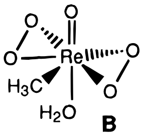
Abstract: Methylrhenium trioxide (CH_3ReO_3 or MTO) catalyzes several classes of reactions of ethyl diazoacetate, EDA. It is the first high valent oxo complex for carbene transfer. Under mild conditions and in the absence of other substrates, EDA was converted to a 9:1 mixture of diethyl maleate and diethyl fumarate. In the presence of alcohols, α-alkoxy ethyl acetates were obtained in good yield. The yields dropped for the larger and more branched alcohols, the balance of material being diethyl maleate and fumarate. An electron-donating group in the *para* position of phenols favors the formation of α-phenoxy ethyl acetates. The use of EDA to form α-thio ethyl acetates and N-substituted glycine ethyl esters, on the other hand, is hardly affected by the size or structure of the parent thiol or amine, with all of these reactions proceeding in high yield. MTO-catalyzed cycloaddition reactions occur between EDA and aromatic imines, olefins, and carbonyl compounds. Three-membered ring products are formed: aziridines, cyclopropanes, and epoxides, respectively. The reactions favor the formation of trans products, and provide a convenient route for the preparation of aziridines. Intermediate carbenoid and nitrenoid species have been proposed. In the presence of an oxygen source such as an epoxide, ethyl diazoacetate and azibenzil are converted to an oxalic acid monoethyl ester and to benzil; at the same time the epoxide was converted to an olefin. These results provide further support for the proposed intermediate, a cyclic species containing Re, O, and $CHCO_2Et$ (or, occasionally, CPhC(O)Ph) in a three-membered ring.

Introduction

Methylrhenium trioxide, during the relatively short period from the original report[1] to the more convenient preparative 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] dehydration of alcohols,[7] and oxygen transfer.[8] Extensive reports have now appeared in the area of MTO-catalyzed substrate oxidations with hydrogen peroxide. These reactions include the oxidation of alkenes,[4,9−12] cobalt thiolates,[13] alkyl and aryl sulfides,[14] anilines,[15] alkynes,[16] and phosphines.[17] 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**.

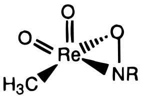


A

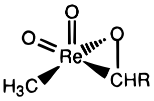


B

New applications have now been realized in which MTO catalyzes certain organic reactions that do not involve peroxide. We were led in this direction from the growing understanding of 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** and **B** transfer an oxygen.

In our initial attempts to form $\mathbf{A_N}$ we used hydroxylamines and hydrazines which are isoelectronic with hydrogen peroxide. Repeated attempts along these lines have not yet succeeded. We then found that ethyl diazoacetate[18] and organic azides will transfer "$CHCO_2Et$" and "NR" functional groups in reactions

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that are catalyzed by MTO, giving satisfactory, and often nearly quantitative, yields of pure product. Methylrhenium trioxide efficiently catalyzes the formation of (1) alkoxy ester, 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, require significant workup, and usually proceed in lower yields.

In that MTO is the first high-valent metal oxo complex reported to catalyze EDA reactions, we intend to explain these findings in terms of $\mathbf{A_N}$ and $\mathbf{A_C}$ rather than metal nitrene and carbene intermediates. The catalytic reactions are described here, but 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 these MTO-catalyzed transformations; the involvement of $\mathbf{A_C}$ and not a metal carbene was supported by experiments on azibenzil.

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 a smaller amount of ethyl glyoxalate azine. Both reactions are catalyzed by MTO, eqs 1 and 2. The reaction of EDA (10 mmol) with 10% MTO in dry benzene required 6 h to reach completion at 60 °C, or 1 week at room temperature.

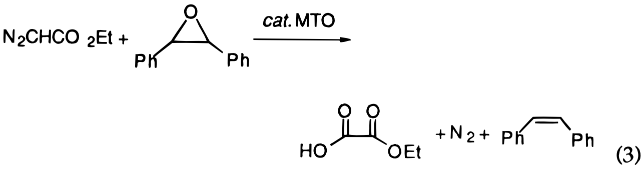
$$2N_2CHCO_2Et \xrightarrow{\text{cat. MTO}} EtO_2CCH{=}CHCO_2Et + 2N_2 \quad (1)$$

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

With MTO, the observed cis:trans ratio of the olefins from eq 1 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 cis: trans ratio of 1:0.6.

The amount of the azine obtained from eq 2 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. The mathematical analysis of this dependence is given in the Discussion Section, where the chemical model is presented.

When the MTO-catalyzed decomposition of EDA was carried out in the presence of an epoxide (for example, *cis*-stilbene oxide), the reaction yields oxalic acid monoethyl ester and the deoxygenation product, *cis*-stilbene.



Trace amounts of water led to the rapid formation of ethyl glycolate ($EtCO_2CH_2OH$); for that reason, all of the reactions reported herein were investigated in dry organic solvents.

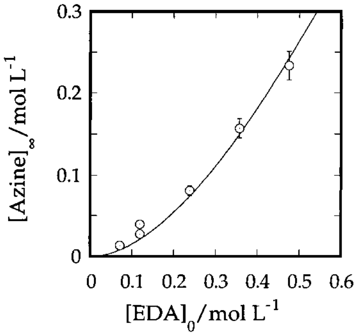


Figure 1. The MTO-catalyzed decomposition of ethyl diazoacetate (EDA) yields a mixture of an azine and diethyl maleate, as shown in Scheme 3. The final concentration of the azine product depends on the initial concentration of EDA; both quantities have the units mol L^{-1}. The smooth curve is the least-squares fit to eq A-4, which follows from the suggested reaction scheme.

Table 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] Each of the reported yields is the lowest one of 2−3 replicates, which holds for the yields in other tables as well.

Ether Formation. A series of phenols and primary, secondary, and tertiary aliphatic alcohols were used in the EDA/MTO catalytic system. The catalytic reactions resulted in alkoxy and phenoxy esters, in which a new ether linkage was realized. Ether formation from alcohols and EDA with other catalysts has been reported.[19,20] The net reaction in the present case is

$$ROH + N_2CHCO_2Et \xrightarrow{\text{cat. MTO}} ROCH_2CO_2Et + N_2 \quad (4)$$

The reactions were carried out with nearly comparable amounts of EDA and alcohol (50 mmol each), and 0.4% (0.2 mmol) of MTO. The substrate alcohols and the yields of products obtained are presented in Table 1. The phenols and the low-molecular-weight primary alcohols gave ≥87% isolated yields. Only a trace of the fumarate and maleate esters was obtained, 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.

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 5) and glycine esters (eq 6). Reactions of amines and EDA with other catalysts have been reported.[21] Only a trace of the fumarate or maleate esters was observed, and none of the azine,

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Table 2. Yields of Thioesters Obtained from the Reactions of Thiols and Ethyl Diazoacetate in Dry Benzene, 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		

Table 3. Yields of Glycine Esters Obtained from the Reactions of Amines (RNH_2, R_2NH) and Ethyl Diazoacetate in Dry Benzene 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

Table 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.

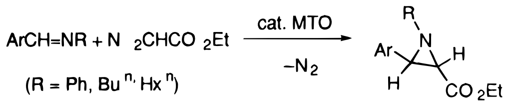
even when MTO was used at the 0.5% level. The exact starting materials, products, and yields are given in Tables 2 and 3.

$$RSH + N_2CHCO_2Et \xrightarrow{\text{cat. MTO}} RSCH_2CO_2Et + N_2 \quad (5)$$

$$RNH_2 + N_2CHCO_2Et \xrightarrow{\text{cat. MTO}} RNHCH_2CO_2Et + N_2 \quad (6)$$

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 MTO in the thiol. These reactions were complete within minutes with isolated yields exceeding 95%. For the amines, the MTO was dissolved in the amine, and the EDA added last. These reactions reached completion in 1 h and gave >85% product yield.

Synthesis of Aziridines. Aziridines resulted from the reaction of EDA/MTO with imines. Aromatic imines, prepared with MTO catalysis as reported in a subsequent section, were used as substrates. The C=N double bond of the imines was converted to an aziridine under mild conditions; this cycloaddition reaction (eq 7) was catalyzed by MTO.



(7)

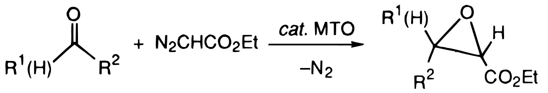
The yields of the aziridines were ≥87%, as specified in Table 4. As to byproducts, only a trace amount of the fumarate and maleate esters could be detected, and none of the azine. Only a single isomer of the aziridine was obtained, as determined by GC-MS. The coupling constants for the ring protons for these products are in the range 2−4 Hz, which verifies that the trans (*E*) isomer is obtained. For example, the product from PhCH=NPh has J_{HH} = 2.5 Hz in $CDCl_3$, which agrees with an earlier report.[22]

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

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

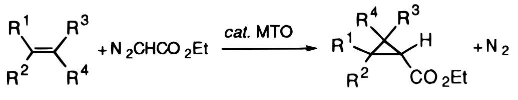


(8)

The rates decrease in the order aliphatic aldehydes > aromatic aldehydes > ketones. The aldehyde reactions form largely the isomer 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 detectable amounts of both geometric isomers as described in the Experimental Section. In addition to the epoxides, which are formed in yields of 49−79% (see Table 5), a minor product was also seen in the GC−MS data. Although this method is not reliable for quantitation, 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.

The reactions of aldehydes or ketones with EDA are clearly not the most useful epoxide synthesis that one might devise. More practical epoxide-forming reactions include alkene−hydrogen peroxide reactions catalyzed by MTO.[4,9,23,24] Nonetheless, epoxide formation in these cases proved informative as to the breadth of MTO catalytic chemistry and is instructive as to the mechanisms employed by these systems.

Formation of Cyclopropanes. As the formation of cyclopropanecarboxylic esters is one of the most studied reactions of EDA[25] and given 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,



(9)

The olefin itself was used as the solvent; reactions do occur but very slowly in dry benzene and methylene chloride. Isolated yields of 57−87% were obtained, Table 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 the Experimental Section. For example, α-methylstyrene yields the

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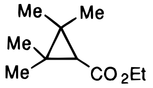
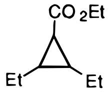
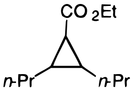
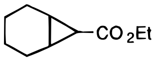
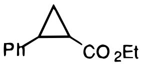
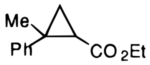
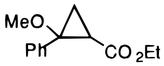
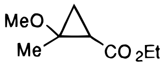
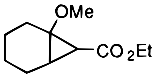
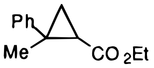
Table 6. Yields[a] of Cyclopropanes Formed from Olefins and Ethyl Diazoacetate, Catalyzed by MTO

Alkene	Product	Yield (%)
2,3-Dimethyl-2-butene		57
cis-3-Hexene		63
trans-4-Octene		59
Cyclohexene		71
Styrene		81
α-Methylstyrene		60[b]
α-Methoxystyrene		87
2-Methoxypropene		69
1-Methoxycyclohexene		74

[a] For isolated product. [b] EDA was present from the outset, not added dropwise as in the other reactions.

cyclopropanes **3** and **4** in a 3:2 ratio. They were characterized by ^{1}H- and ^{13}C-NMR,[26] as detailed in the supporting information.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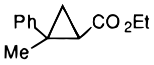
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Phenyl azide is catalytically decomposed under mild conditions by a trace of MTO in dry benzene (eq 10). The product is diphenyldiazene (azobenzene), whose ^{13}C-NMR spectrum in $CDCl_3$ (δ 122.69, 128.80, 130.71, and 152.52 ppm) agrees with the literature.[27]

$$2PhN_3 \xrightarrow{\text{cat. MTO}} Ph{-}N{=}N{-}Ph + 2N_2 \qquad (10)$$

Catalytic Formation of Imines. The reactions of aromatic aldehydes with alkyl and aryl azides produced imines in good yields (Table 7) when a stoichiometric quantity of triphenylphosphine was added along with a catalytic amount of MTO (eq 11). These reaction occur even in the absence of MTO, but more slowly.

$$RN_3 + ArCHO + PPh_3 \xrightarrow{\text{cat. MTO}} ArCH{=}N{-}R + N_2 + Ph_3PO \qquad (11)$$

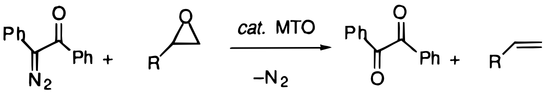
Table 7. Yields[a] of Imines Formed from Organic Azides and Aryl Aldehydes, Catalyzed by MTO, in the Presence of Triphenylphosphine

	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-naphthylCHO	88	85	86

[a] Yields refer to isolated product.

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

The Intermediate A$_C$. Further evidence in support of the mechanistic information was obtained from experiments involving azibenzil, **5**, prepared from benzil monohydrazone by oxidation with HgO.[28] The MTO-catalyzed conversion of **5** into benzil proceeded at more than 90% yield; **6** was verified by ^{1}H- and ^{13}C-NMR. The reaction occurs in the presence of an epoxide; in this work styrene oxide and propylene oxide were used successfully. The epoxide was converted to the olefin according to the net reaction depicted in eq 12.



(12)

5 R = Ph, Me **6**

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.[29] In contrast, reactions with ceric ammonium nitrate,[30] lithium bromide,[31] and copper(II) salts[32] yield predominantly the fumarate.

Very few methods have been reported for the catalytic preparation of aziridines from aromatic imines and EDA. Metallic copper[33] and copper complexes have been reported as the catalysts.[34,35] Except for epoxide formation, the new reactions with EDA/MTO gave higher yields.

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.[12−17,24,36−38] 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 catalyst from **A** to MTO and from **B** to **A**.

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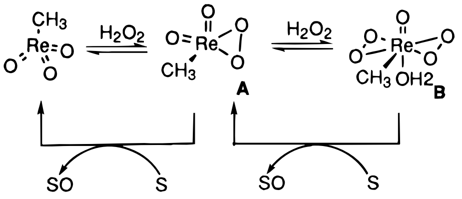
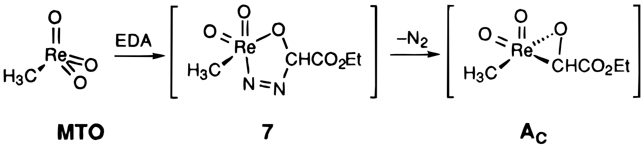
Scheme 1



Scheme 2



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 the participation of $\mathbf{A_C}$. Furthermore, another intermediate, **7**, may intervene between MTO and $\mathbf{A_C}$. The suggested structures are shown in Scheme 2.

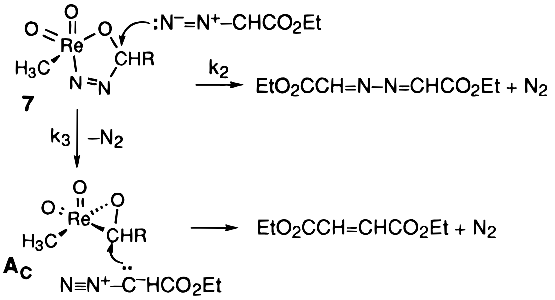
The Suggested Mechanism. The mechanism of these transformations remains to be resolved in detail, although we prefer to explain the reactions by invoking $\mathbf{A_C}$ rather than by metal–carbene intermediates. Many known metal carbenes contain the metal in a low oxidation state, 0–II.[39] Some of these materials are capable of carbene transfer. High-oxidation-state carbenes are also known,[40–43] but none has been reported to transfer the carbene. We propose that the key steps in the EDA/MTO system are these. First is the formation of the $\mathbf{A_C}$ or $\mathbf{A_N}$ intermediate. 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.[39,44,45] Indeed, were there neither these nor other examples, the conversion of the normally nucleophilic peroxide ion into an electrophilic center upon coordination to MTO would provide a convincing illustration. 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 13.

(13)

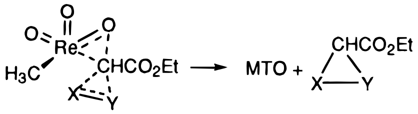
The products (slowly) obtained when $\mathbf{A_C}$ is allowed to form in the absence of a substrate can be rationalized on a similar basis. Attack of the nucleophilic EDA upon $\mathbf{A_C}$ will afford the ester products. On the other hand, attack of EDA on **7** prior to loss of N_2 will afford the azine, as in 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 $k_2/k_3 = (1.89 \pm 0.03)$ L mol^{-1}.

Scheme 3

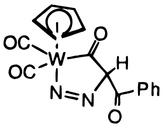


Scheme 4

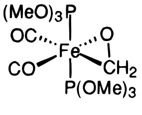


Those substrates that contain C═N and C═C double bonds yield three-membered-ring products; that with the C═O group we presume does the same, except that the phosphine disrupts the oxaziridine structure to excise the oxygen atom. In general, the reaction appears to proceed as shown in Scheme 4.

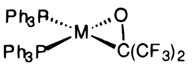
The first intermediate in Scheme 3, **7**, represents the product of a [3 + 2] cycloaddition reaction of EDA to a rhenium–oxygen double bond. The second intermediate, $\mathbf{A_C}$, is formed by the elimination of molecular nitrogen. Neither has been isolated to this point. Structure **8**[46] represents a tungsten analog of the first intermediate **7**. Several compounds (**9a–e**)[47–54] are stable analogs of the proposed intermediate $\mathbf{A_C}$.



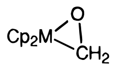
8



9a



9b (M=Ni); **9c** (M=Pt)



9d (M=V); **9e** (M=Mo)

Further evidence for the intermediate $\mathbf{A_C}$ comes from the MTO-catalyzed decomposition of EDA in the presence of

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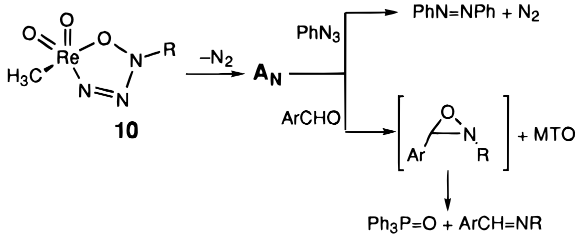
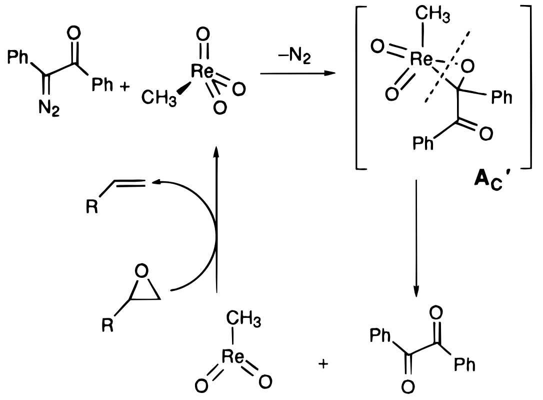
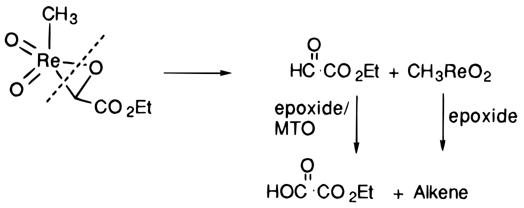
Scheme 5



Scheme 6



epoxides. This reaction yields the oxalic acid monoethyl ester, and may occur as follows:

 (14)

As written, this reaction produces an aldehyde. We have shown in independent experiments that with *cis*-stilbene oxide benzaldehyde forms the carboxylic acid in an MTO-catalyzed reaction. For example, the reaction of *cis*-stilbene oxide, benzaldehyde, and MTO (in 20:2:1 ratio with 14 mg of MTO in 1 mL of $CDCl_3$) gave 90% benzoic acid and stilbene in 20 h.

The reactions of the organic azides may also be explained in terms of the proposed intermediate $\mathbf{A_N}$. Species **10** would presumably be formed from MTO by the analogous process, and would be subject to nucleophilic attack, leading to the products observed, Scheme 5.

The conversion of azibenzil to benzil by MTO-catalyzed oxygen transfer from an epoxide provides further proof for the suggested intermediate $\mathbf{A_C}$, because no metal carbenes have been reported to react with epoxides to form carbonyl compounds. Thus we propose a sequence in which $\mathbf{A_C}'$, analogous to $\mathbf{A_C}$ from ethyl diazoacetate, is formed first from MTO and azibenzil. It then reacts further to form benzil and methylrhenium dioxide. The latter species abstracts oxygen from an epoxide; this is a known reaction reported in our earlier work.[8] The sequence of steps is diagrammed in Scheme 6.

Experimental Section

Materials. Butyl, hexyl,[55] and phenyl[56] 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[57] 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.

For these and other previously-known materials, the spectroscopic parameters and other analytical data are given in the Supporting Information.

General Procedures: (1) α-Alkoxy Ethyl Esters. The alcohol (54 mmol) and MTO (50 mg, 0.2 mmol) were dissolved in 100 mL of dry benzene (usually) or methylene chloride in a three-necked round-bottom flask. Ethyl diazoacetate (50 mmol) was added dropwise at room temperature. 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.[27,58−60]

(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. The ethyl diazoacetate (50 mmol) was added dropwise at room temperature; with this method the reactions were complete within 1 h, it being much faster here where no solvent diluent was used. The products were identified, in comparison with literature data.[21,27,58,59,61,62]

(3) α-Thio Ethyl Esters. The first method under (1) was used, except that the reaction was allowed to proceed for 3 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.[27,59,63−65]

(4) Aziridines. The imine (35 mmol, prepared as in (7)) and MTO (250 mg, 1 mmol) were dissolved in 100 mL of 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 h, 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 microanalytical data,[30,64−66] as presented in the supporting information.

(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 3 days, during which time the reaction was monitored with GC-MS, the product was isolated by vacuum distillation. The products were identified spectroscopically in comparison with data from the literature.[66−71]

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(6) Cyclopropanes. The method was the same as that used for the epoxides, and the products (see the supporting information) were similarly identified.[72−75] Some of these substrates (e.g., styrene), but not all (e.g., α-methylstyrene), led to small yields of compounds believed from MS and NMR data 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 of 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 h of stirring, the solvent was removed by rotary evaporation. The imines were obtained by vacuum distillation or by recrystallization from ethanol.

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 for his help with the derivation given in the Appendix.

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

$$\frac{\mathrm{d}A}{\mathrm{d}M} = \frac{k_2 E}{k_3} = \kappa E = \kappa\{a - 2A - 2M\} \qquad \text{(A-1)}$$

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

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

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

$$a = \frac{1}{\kappa}(e^{2\kappa M_\infty} - 1) = \frac{1}{\kappa}(\exp^{2\kappa((a/2) - \mathrm{A}_\infty)} - 1) \qquad \text{(A-3)}$$

From this we find

$$A_\infty = \frac{a\kappa - \ln(a\kappa + 1)}{2\kappa} \qquad \text{(A-4)}$$

which is the form used to fit A_∞ as a function of a (=$[\mathrm{EDA}]_0$), as shown in Figure 1.

Supporting Information Available: The spectroscopic data for the products, including microanalytical data for the new compounds (15 pages). See any current masthead page for ordering and Internet access instructions.

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