

Reactions of Ethyl Diazoacetate Catalyzed by Methylrhenium Trioxide

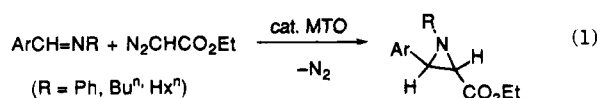
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Methylrhenium trioxide (CH_3ReO_3 or MTO)¹⁻⁴ has found wide use in catalysis, including the epoxidation⁴ and metathesis⁵ of olefins, aldehyde olefination,⁶ and oxygen transfer.⁷ Extensive reports have now appeared in the area of MTO-catalyzed substrate oxidations with hydrogen peroxide.^{4,8-15}

Certain catalytic applications of MTO for organic reactions that do not utilize peroxide have now been realized. In particular, a catalytic amount of MTO with ethyl diazoacetate (EDA) will convert aromatic imines to aziridines and convert aldehydes and ketones to epoxides. The aziridine preparation proceeds in high yields under anaerobic conditions more conveniently than with existing methods.¹⁶ Compounds with a three-membered heterocyclic ring can be obtained with the EDA/MTO catalytic system. Aromatic imines undergo cycloaddition reactions to give aziridines under mild conditions.



The reactions were carried out with several arylimines. Experiments on a 30 mmol scale, with 3% catalyst, gave isolated yields of the aziridine of 87–96%, as summarized in Table 1. The only byproduct (<5%) was diethyl maleate, the principal product when the imine was omitted. The coupling constants of the ring protons in the aziridines are in the range 2–6 Hz. For example,

Table 1. Yields of Aziridines Obtained from Arylimines (ArCH=NR) and EDA, with MTO as Catalyst^a

Ar	yield ^a (%)		
	R = <i>n</i> -hexyl	<i>n</i> -butyl	phenyl
C ₆ H ₅	93	92	87
<i>p</i> -MeOC ₆ H ₄	94	94	92
<i>p</i> -NO ₂ C ₆ H ₄	92	91	
<i>p</i> -MeC ₆ H ₄	93	93	
2-naphthyl	96	96	

^a Isolated yields, after vacuum distillation, based on EDA, which was used in small deficiency relative to the imine.

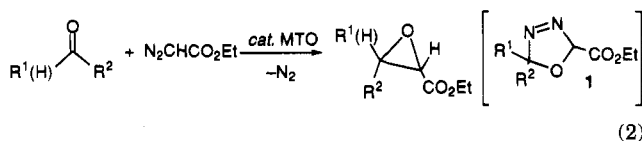
Table 2. Yields of Epoxides Obtained from Aldehydes and Ketones and EDA with MTO as Catalyst^a

R ¹	R ²	yield ^a (%)
H	C ₆ H ₅	79 (52) ^b
H	<i>n</i> -Pr	75
Me	<i>s</i> -Bu	64
Me	C ₆ H ₅	57
Me	<i>i</i> -Pr	49

^a Isolated yields, after vacuum distillation, based on EDA, taken in small deficiency relative to the imine. ^b The lower yield was obtained when the EDA was added all at once rather than dropwise.

PhCH=NPh yields a product with $J = 2.2$ Hz (CDCl₃).¹⁷ Thus, the only product is the isomer with a *trans* configuration with respect to the C–C bond. GC–MS showed that only a single stereoisomer was present. The compounds were characterized by ¹H- and ¹³C-NMR and by elemental analysis (supporting information), which in every case matched the theoretical formula.

Carbonyl compounds can also serve as substrates in cycloaddition reactions with the EDA/MTO catalytic system. Several aldehydes and ketones were employed, and in these cases they were used as the solvents, for this overall reaction:



Aldehydes gave only the *trans* epoxide, whereas ketones gave both, with the *E*-isomer predominant. (A minor product, 5–21%, was also observed with GC–MS; its formula weight was the sum of the carbonyl compound and EDA. It was identified as the Δ^3 -1,3,4-oxadiazoline, 1.) The epoxides themselves, identified by literature data,¹⁸⁻²³ were isolated in overall yields of 49–79%, Table 2.

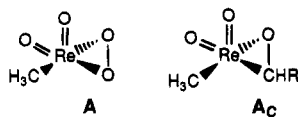
Epoxides can be obtained in higher yields and with greater convenience by other reactions, including the MTO-catalyzed reactions of alkenes and hydrogen peroxide, but they are included here to illustrate the scope of the new chemistry.

The mechanism of these transformations remains to be resolved in detail, but a metal–carbene intermediate

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analogous to many that are known^{24,25} is a distinct possibility. We were unable to write a suitable electronic structure, however, without loss of oxygen from rhenium, unlikely since the intermediate repeatedly recycles to MTO. We suggest therefore the involvement of a carbenoid intermediate, **A_C**, analogous to the well-studied peroxide **A**. Several examples of η^2 -formaldehyde and η^2 -



oxyethylidene complexes have been reported.²⁶ An electron-rich double bond may attack the $-\text{CHCO}_2\text{Et}$ group of **A_C**, just like other electron-rich centers attack the peroxide oxygen of **A**. Work is in progress to extend the scope of this chemistry and to detail the operative mechanisms.

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Supporting Information Available: The spectroscopic and analytical data for the aziridines and epoxides produced and the experimental procedures (5 pages).

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