

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

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Methylrhenium trioxide (MTO) 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 in 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. On the basis of the results of this investigation and a comparison with the interaction between MTO and water, a concerted process and a mechanism involving carbocation intermediates have been suggested.

## Introduction

Methylrhenium trioxide ( $\text{CH}_3\text{ReO}_3$  or MTO) catalyzes the epoxidation<sup>1</sup> and metathesis<sup>2</sup> of olefins, aldehyde olefination,<sup>3</sup> oxygen transfer,<sup>4</sup> and the transfer of carbene and nitrene groups from diazoalkanes and organic azides.<sup>5</sup> Many MTO-catalyzed oxidations of hydrogen peroxide have been reported, including the oxidations of alkenes,<sup>1,6,7</sup> cobalt thiolates,<sup>8</sup> organic sulfides,<sup>9</sup> anilines,<sup>10</sup> alkynes,<sup>11</sup> and phosphines.<sup>12</sup> 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  $\text{H}_2\text{O}_2$  can reasonably be used as models for them.

The dehydration of alcohols provides an important means of preparing ethers. The Williamson ether synthesis,<sup>13</sup> 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.<sup>14–18</sup> 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,<sup>19</sup> copper(II) sulfate on silica gel,<sup>20</sup> ferric chloride on silica gel,<sup>21</sup>  $\text{SOCl}_2/\text{NET}_3$ ,<sup>22</sup>  $\text{TsOH}/\text{PhH}$ ,<sup>23</sup>  $\text{BF}_3/\text{OEt}_2$ ,<sup>24</sup>  $\text{Ph}_3\text{P}/\text{CCl}_4/\text{NET}_3$ ,<sup>25</sup> or  $\text{Ph}_3\text{PBiBr}_2/\text{I}_2$ .<sup>26</sup> 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.<sup>27</sup> 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:  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ ,<sup>28</sup>  $\text{Al}(\text{O}^t\text{Bu})_3/\text{Raney Ni}$ ,<sup>29</sup>  $\text{CuO}/\text{Cr}_2\text{O}_3/\text{Na}_2\text{O}/\text{SiO}_2/\text{H}_2\text{O}$ ,<sup>27</sup>  $\text{RuCl}_2(\text{PPh}_3)_2/\text{Ph}_3\text{P}$ ,<sup>30</sup> and  $\text{Ph}_3\text{P}^+\text{-NMeC}_6\text{H}_4\text{I}^-/\text{Bu}^n\text{NHMe}/\text{DMF}$ .<sup>31</sup> We have developed a simpler procedure in which MTO is the sole catalyst.

Disproportionation of alcohols requires hydride transfer and is usually done with  $\text{Al}_2\text{O}_3$  at  $>300^\circ\text{C}$ <sup>32–34</sup> or over

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**Table 1. Yields<sup>a</sup> of Symmetric Ethers and of Other Products Formed by Alcohol Dehydration Catalyzed by Methylrhenium Trioxide**

R <sup>1</sup> R <sup>2</sup> CHOH		convn %	yield of ether, %	other products
R <sup>1</sup> =	R <sup>2</sup> =			
Ph	H	36	30	~3% PhCHO, ~3% PhMe
Ph	Me	86	80 <sup>a</sup>	~2% PhC(O)Me, ~2% PhEt
Ph	Et	89	79 <sup>b</sup>	~3% PhC(O)Et, ~3% PhCH <sub>2</sub> Et
Ph	Ph	100	100	
4-MeC <sub>6</sub> H <sub>4</sub>	Ph	100	90	~5% 4-MeC <sub>6</sub> H <sub>4</sub> C(O)Ph ~5% 4-MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Ph
4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	10	10	
4-MeC <sub>6</sub> H <sub>4</sub>	H	42	34	~4% 4-MeC <sub>6</sub> H <sub>4</sub> CHO ~4% 4-MeC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>
4-MeOC <sub>6</sub> H <sub>4</sub>	H	48	36	~6% 4-MeOC <sub>6</sub> H <sub>4</sub> CHO ~6% 4-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>
1-naphthyl	H		~4	~2% disproportionation
2-naphthyl	H		~4	~2% disproportionation
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	H		~7	
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H		~8	
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H		~8	

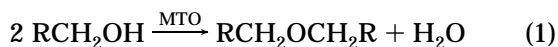
<sup>a</sup> Yields of the ethers were based on the alcohols for reactions carried out in benzene. <sup>b</sup> Two isomers, in a 1:1 ratio.

HY-zeolite in refluxing carbon tetrachloride.<sup>35</sup> 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 2 days: *n*-C<sub>4</sub>H<sub>9</sub>OH, ~7%; *n*-C<sub>5</sub>H<sub>11</sub>OH, ~8%; *n*-C<sub>6</sub>H<sub>13</sub>OH, ~8%. Further time did not increase the yield, as the process is limited by the buildup of water in the system, evidently implying a competition between the two hydroxylic reagents. The conversion of alcohols can be represented by this equation:



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.

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<sub>2</sub>, 4-Br, or 4-Cl, then no ether was formed, and the starting material remained unchanged. Although (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHOH 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<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH, the yields are R = H, 36%; Me, 42%; R = MeO, 48%. In these cases meso and racemic ethers were produced in nearly equal

**Table 2. Formation of Unsymmetric Ethers by Coupling Aromatic and Aliphatic Alcohols, Catalyzed by MTO**

aromatic alcohol	aliphatic alcohol	yield, % <sup>a</sup>	other product
Ph <sub>2</sub> CHOH	EtOH	89	(Ph <sub>2</sub> CH) <sub>2</sub> O, 11%
Ph <sub>2</sub> CHOH	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	91	(Ph <sub>2</sub> CH) <sub>2</sub> O, 9%
Ph <sub>2</sub> CHOH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	92	(Ph <sub>2</sub> CH) <sub>2</sub> O, 8%
Ph <sub>2</sub> CHOH	<i>n</i> -C <sub>5</sub> H <sub>11</sub> OH	95	(Ph <sub>2</sub> CH) <sub>2</sub> O, 5%
Ph <sub>2</sub> CHOH	<i>tert</i> -Me <sub>3</sub> COH	10	(Ph <sub>2</sub> CH) <sub>2</sub> O, 90%
PhCH(OH)CH <sub>3</sub>	EtOH	69	(PhMeCH) <sub>2</sub> O, 31%
PhCH(OH)CH <sub>3</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> OH	85	(PhMeCH) <sub>2</sub> O, 15%

<sup>a</sup> 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 of MTO was added.

amounts. Increasing the size of the aryl group decreased the conversion; with 1-naphthyl and 2-naphthyl groups, only 6% conversion was found. Table 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 substituents, 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*-butyl alcohol, 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.

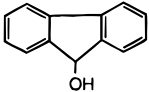
The successful strategy for unsymmetric aromatic ethers is based on using the more reactive aromatic alcohol at a much lower concentration than the aliphatic alcohol. Even then, some of the symmetric ether from the aromatic alcohol was formed. If the two alcohols used had similar reactivities, such as PhCH(OH)Me and PhCH(OH)Et, then three ethers were formed, (PhCHMe)<sub>2</sub>O, (PhCHEt)<sub>2</sub>O, 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 3.

**Olefins from Alcohol Dehydration.** The process in eq 2 was observed for the aliphatic alcohols, but the yields were quite low. With aromatic alcohols, however, the

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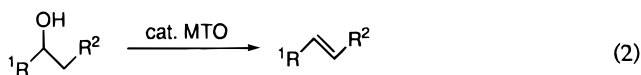
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**Table 3. Yields of Unsymmetric Ethers from Pairs of Aromatic Alcohols, Catalyzed by MTO**

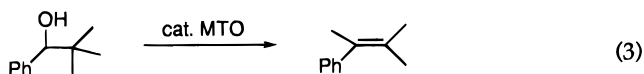
Alcohol A	Alcohol B	Ratio, A/B	Yield, % <sup>a</sup>
	(4-MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHOH	3:1	93
PhCH(OH)Et	(4-MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHOH	5:1	85
PhCH(OH)Me	(4-MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHOH	10:1	90
PhCH(OH)Et	(4-ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHOH	1:15	83
Ph <sub>2</sub> CHOH	(4-ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHOH	1:5	89
PhCH <sub>2</sub> OH	Ph <sub>2</sub> CHOH	10:1	100
PhCH(OH)Me	Ph <sub>2</sub> CHOH	10:1	99
PhCH(OH)Et	Ph <sub>2</sub> CHOH	10:1	96
PhCH(OH)Me	PhCH(OH)Et	1:1	34

<sup>a</sup> 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 of dry benzene.

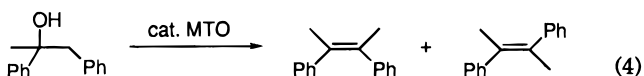
olefin yields were satisfactory, although accompanying amounts of ether and disproportionation products were formed. The data are given in Table 4. For the aliphatic alcohols, the solvent as well as the reagent, the data are given in terms of catalytic turnovers, rather than yields. As the yield of olefins formed is low for some of these alcohols, the term "turnover" was used to describe reaction. For example, dehydration of 15 mL (124 mmol) of PhCH(OH)Me by 0.2 mmol of MTO in 3 days yields 20 mmol of styrene; no solvent was used.



Some polymer formation, also MTO-catalyzed, accompanied these reactions. A solution of 0.2 mmol of MTO in 25 mL of the alcohol was sealed in a 30-mL glass vial for 1 month, at which time 11% of the alcohol had been 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:

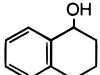

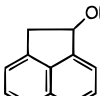

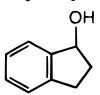



The tertiary aromatic alcohol, 1,2-diphenyl-2-propanol, yielded two olefins, (*Z*)- and (*E*)-methylstilbenes, in a 1:5 ratio:



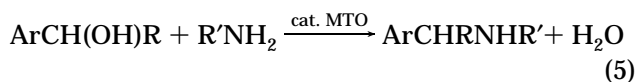
By way of comparison, dehydration with sulfuric acid, which occurs through a pure E<sub>1</sub> mechanism, gave a *Z*:*E* ratio of 1:18.<sup>36</sup>

**Table 4. MTO-Catalyzed Dehydration of Alcohols To Form Olefins**

Part A. Reactions with the alcohol as the solvent <sup>a</sup>		
Alcohol	Product	Turnovers <sup>b</sup>
3-octanol	3-octene	40
1-dodecanol	1-dodecene	43
cyclo-octanol	cyclo-octene	76
c-C <sub>6</sub> H <sub>13</sub> CH <sub>2</sub> OH	methylenecyclohexane	12
PhCH(OH)Me	PhCH=CH <sub>2</sub>	100
PhCH(OH)Et	PhCH=CHMe	108
2-methyl-2-hexanol	Pr <sup>n</sup> CH=CMe <sub>2</sub> , Bu <sup>n</sup> CMe=CH <sub>2</sub>	66
Part B: Reactions in benzene <sup>c</sup>		
Alcohol	Product	Yield, % <sup>d</sup>
PhCH(OH)Bu <sup>t</sup>	PhCMe=CMe <sub>2</sub>	11
PhCMe <sub>2</sub> OH	(Ph,Me)C=CH <sub>2</sub>	46
		71
		89
		64
PhCH(OH)CHMe <sub>2</sub>	PhCH=CMe <sub>2</sub>	33

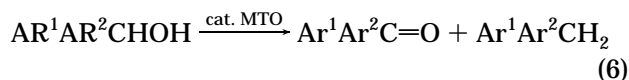
<sup>a</sup> MTO (0.2 mmol) was dissolved in 15 mL of alcohol and allowed to stand for 3 days. <sup>b</sup> Turnovers = mol of product/mol of catalyst, after 3 days. <sup>c</sup> The alcohol (20 mmol) and MTO (0.2 mmol) were dissolved in 100 mL of dry benzene and allowed to stand for 3 days. <sup>d</sup> Isolated yield.

**Amination of Aromatic Alcohols.** Secondary amines were obtained from primary aromatic alcohols and aliphatic or aromatic amines as in eq 5. These preparations were carried out by using the alcohol in excess in dry benzene. 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 5.

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



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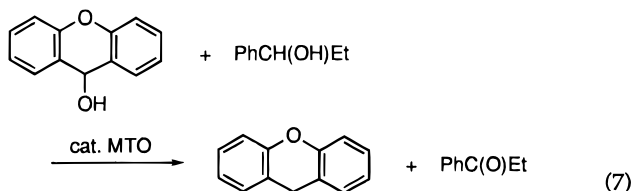
**Table 5. Yields of Secondary Amines from MTO-Catalyzed Aminations of Alcohols, eq 5**

alcohol	amine	yield, % <sup>a</sup>	other products
Ph <sub>2</sub> CHOH	PhNH <sub>2</sub>	91 (26) <sup>b</sup>	(Ph <sub>2</sub> CH) <sub>2</sub> O
9-xanthenol	PhNH <sub>2</sub>	96	disproportionation
(MeOC <sub>6</sub> H <sub>4</sub> )CHOH	PhNH <sub>2</sub>	>95	disproportionation
(MeC <sub>6</sub> H <sub>4</sub> )PhCHOH	PhNH <sub>2</sub>	>95	MeC <sub>6</sub> H <sub>4</sub> CHOPh
(MeOC <sub>6</sub> H <sub>4</sub> )CHOH	<i>n</i> -C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	94	disproportionation
Ph <sub>2</sub> CHOH	<i>n</i> -C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	92	(Ph <sub>2</sub> CH) <sub>2</sub> O

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

4-Methoxybenzhydrol gave both disproportionation (60% of the starting alcohol) and ether formation (40%). Monoaryl alcohols, ArCH<sub>2</sub>OH, underwent disproportionation to a much smaller extent: Ar = Ph, 6%; 4-MeC<sub>6</sub>H<sub>4</sub>, 8%; 4-MeOC<sub>6</sub>H<sub>4</sub>, 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%.

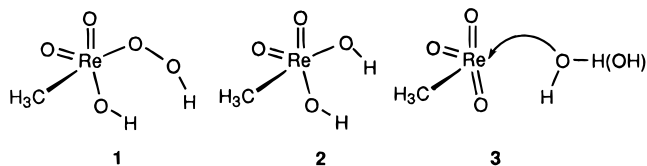
Disproportionation was also observed between two different alcohols, 9-hydroxyxanthene and excess PhCH(OH)Et, which yielded only one set of products when the reaction was carried out in dry benzene, eq 7. No mixed ether was formed.



It should also be noted that no EPR signal was observed during the course of the disproportionation of 4,4'-dimethoxybenzhydrol, even when the spectrum was recorded at 110 K in frozen C<sub>6</sub>H<sub>6</sub>.

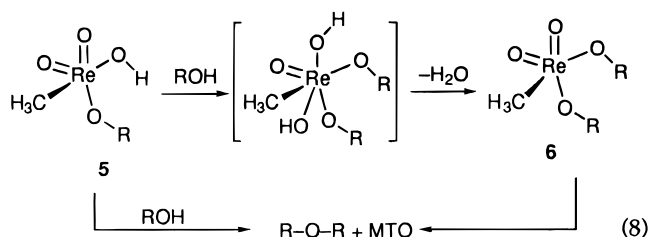
### Discussion

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<sub>3</sub>Re(O)<sub>2</sub>(η<sup>2</sup>-O<sub>2</sub>), **A**, and CH<sub>3</sub>Re(O)(η<sup>2</sup>-O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O), **B**, may be pertinent to the present work. Intermediate **1** has been characterized as a precursor to **A**,<sup>37</sup> 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<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O on the highly electropositive Re(VII) center, as shown in **3**, will generate the intermediates **1** and **2**.

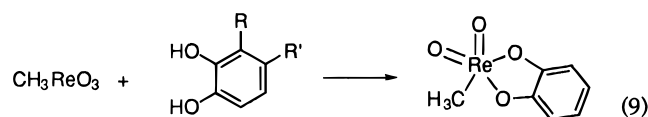


From these comparisons, and since the rhenium diperoxide **B** is yellow, like the peroxorhenium complex, it is logical to infer that the reaction between MTO and

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**.



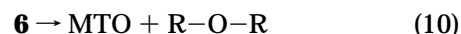
Attempts to isolate **5** and **6** were not successful; this is not unduly discouraging, however, since the OH analogues have not been directly seen. As an independent precedent, we note the condensation reaction between MTO and 1,2-dihydroxybenzene.<sup>38</sup>



Certain Lewis acids, such as zinc chloride,<sup>18</sup> catalyze the formation of ethers from alcohols, but these are really stoichiometric reactions that are critically dependent on the solvent; the zinc chloride reaction, for example, is successful only in dichloroethane. 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 occurred with alcohols containing an electron-withdrawing group at the para position such as NO<sub>2</sub>, 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 reactions occur through a carbocation intermediate (**7**).

Two possible mechanisms can be suggested on the basis of 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 10:

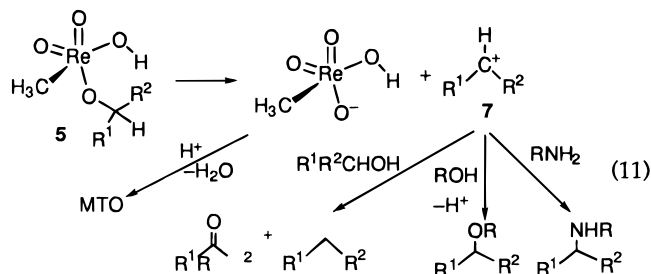


This mechanism also explains why the smaller primary alcohols can form ethers, whereas the larger ones cannot: 1-dodecanol and 1-undecanol yield only the alkene by dehydration. This is due to the limited space in the coordination sphere of MTO. The dehydration reaction of 1,2-diphenyl-2-propanol should 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**.

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

(38) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organometallics* **1990**, *9*, 782-787.



Those alcohols that can generate a stable carbocation allow a second alcohol to react with it; this yields a ketone 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 11 is the dominant one for the primary aliphatic alcohols, whereas a carbocation intermediate provides the major pathway for the aromatic alcohols. Because an aromatic alcohol can form a more stable carbocation intermediate than an aliphatic alcohol, higher conversions were observed for the aromatic alcohols.

### Experimental 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.<sup>39</sup>

**Symmetric Ethers. General Procedure.** The alcohol (40 mmol) and MTO (0.2 mmol) were dissolved in 100 mL of dry benzene, and the solution was allowed to stand at room temperature for 2 days. Much of the solvent was removed by rotary evaporation. Separation and purification of the ether was realized by vacuum distillation, recrystallization, or column chromatography using hexane/ethyl acetate (10:1 to

1:1) as the eluant. Alternatively, toluene, dichloromethane, chloroform, acetone, and the alcohols themselves can be used as solvent.

**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 2 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 to 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 of MTO.

**Amination Reactants.** The alcohol (3 mmol), amine (1 mmol), and MTO (0.2 mmol) were dissolved in 20 mL of dry benzene and allowed to stand for 2 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 3 days. The olefins were isolated by distillation. For some of the aromatic alcohols, dry benzene with 20 mmol of alcohol and 0.2 mmol of MTO was used.

**Identifications.** The products were identified by their NMR spectra, Tables S-1 and S-2, in comparison with literature data.<sup>39,40</sup>

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**Supporting Information Available:** Tables of NMR data for all of the reaction products (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO951613A

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

(40) Pouchert, C. J.; Behnke, J. *The Aldrich Library of <sup>13</sup>C and <sup>1</sup>H FT-NMR Spectra*; 1993.