Aqueous Catalysis: Methylrhenium Trioxide (MTO) as a Homogeneous Catalyst for the Diels−Alder Reaction

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Abstract: The title compound proves to be an effective and efficient catalyst for the Diels−Alder reaction when the dienophile is an α,β-unsaturated ketone or aldehyde. It is especially effective in water. Equal amounts of any such dienophile and any of six representative dienes (isoprene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, 1,2,3,4,5-pentamethylcyclopentadiene, and 1,3-cyclohexadiene) were used, along with 1% MTO. The reactions gave usually >90% isolated yield of the cycloaddition product except for the larger dienophiles. Nearly exclusively, there was formed one product isomer, the same one that usually predominates. The reactions were often run in chloroform (mostly) and in other organic solvents. A select number were carried out in water, where the reactions gave a greater product yield in a considerably shorter time. Water, itself, is known to enhance the rates of Diels−Alder reactions, but MTO exerts an additional accelerating effect. Kinetics studies were carried out to show that the rate is proportional to the catalyst concentration. The products do not inhibit the reaction. The desirability of MTO as a Diels−Alder catalyst stems from a combination of favorable properties: the inertness to air/oxygen, the tolerance for many substrates, the use of an aqueous medium, and the absence of product inhibition. The initial step appears to be the (weak) coordination of the carbonyl oxygen to the electropositive rhenium center. Steric crowding around rhenium inhibits reactions of the larger dienophiles.

Introduction

The Diels−Alder (DA) reaction provides an important synthetic method for cyclization, but a catalyst is often required for the reactions carried out in this study, since the reaction is otherwise prohibitively slow.[1] The noncatalyzed reaction in water is much faster.[2−4] Transition metal complexes are known to give higher stereoselectivity than the spontaneous process. Traditional catalysts are Lewis acids, such as BCl_3, AlX_3, TiX_4, and SnX_4, but they are not without their limitations.[1] These catalysts are sensitive to water, and must often be used in nearly stoichiometric quantity. To summarize matters, it appears that the traditional Lewis acids bind to the oxygen atoms of the dienophile and product; the turnover frequency decreases during the reaction owing to product inhibition. Indeed, certain catalysts, such as BF_3, $AlCl_3$, and $TiCl_4$, can polymerize or destroy the substrate.

The ideal DA catalyst should be soluble in common solvents, capable of substantial rate accelerations, insensitive to oxygen or water, free from product inhibition, and able to bind the dienophile rapidly and reversibly.

Several nontraditional catalysts meet some of these requirements.[5−8] One example is $[CpFe(CO)P(OMe)_3(THF)]BF_4$, but it cannot tolerate oxygen and is not soluble in all of the useful solvents.[5] Catechol boron bromide or $[FeCp_2]PF_6$ can be used, although the former is a corrosive material that requires an almost stoichiometric concentration.[6] $[TiCp_2](CF_3SO_3)_2$ and $[ZrCp_2(THF)](CF_3SO_3)_2$, stable for a period of time in air, are insoluble in nonpolar solvents.[7] $[Re(salen)(NO)(H_2O)]SbF_6$, being insufficiently soluble in many solvents, requires special solvent conditions.[1] The combined catalyst $4Ph_2SnS/AgClO_4$ must be used at -78 °C.[8]

Methylrhenium trioxide (CH_3ReO_3, abbreviated as MTO), easily prepared from dirhenium heptoxide and tetramethyl tin,[9] is soluble in all common organic solvents and in water and is not sensitive to oxygen or acids. That MTO might be able to function as a catalyst was suggested by its ability to coordinate to α,β-unsaturated aldehydes, without giving the cyclic trimer of the aldehyde; this was noteworthy in light of the trimerization of other aldehydes in the presence of MTO.[10] Thus we have investigated DA reactions involving the activation of α,β-unsaturated aldehydes and ketones. The data obtained show the effectiveness of MTO in comparison with other catalysts in organic solvents.

The DA reaction in water without catalysts is now well recognized.[2,11] Recently, the catalysis of the DA reaction in water by Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions was reported; the interaction between a specifically designed dienophile and cyclopentadiene was investigated.[12] This study established the effectiveness of MTO as a catalyst for the DA reaction in water.

Results

Reactions in Chloroform. The reactions in chloroform were carried out with 10 mmol each of the diene and the dienophile in 20 mL of chloroform at room temperature. The MTO catalyst

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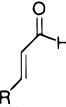(8) Mukaiyama, T.; Watanabe, K.; Shiina, I. *Chem. Lett.* **1995**, 1.
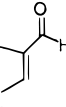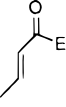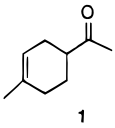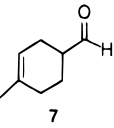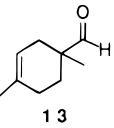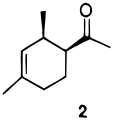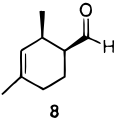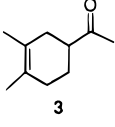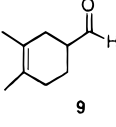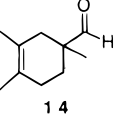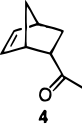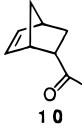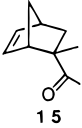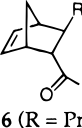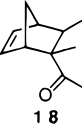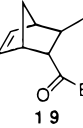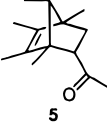
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Table 1. Diels−Alder Reactions Catalyzed by MTO in Chloroform at Room Temperature[a]

[a] Reaction time, yield, isomer ratio (by ^{1}H NMR). **1**: 18 h, 90%, >99:1. **2**: 12 h, 94%, 98:2. **3**: 1 h, 92%; **4**: 1 h, 95%, >99:1. **5**: 1 h, 92%, 90:10. **6**: 4 d, 94%, ≫99:1. **7**: 18 h, 90%, >99:1. **8**: 12 h, 93%, 97:3. **9**: 1 h, 98%. **10**: 1 h, 90%, >99:1. **11**: 1 h, 94%; 90:10. **12**: 4 d, 94%, ≫99:1. **13**: 4 h, 91%, ≫99:1. **14**: 2 h, 89%. **15**: 1 h, 88%, 90:10. **16**: 2 d, 40%, 82:18. **17**: 2 d, 58%, 85:15. **18**: 2 d, 36%, 80:20. **19**: 2 d, 80%, ≫99:1.

was present at the 1% level. The results from these DA reactions are collected in Table 1, which displays the reaction times, yields, and stereoselectivities for reaction products **1**−**19**. The data show that MTO efficiently catalyzes DA cycloaddition reactions compared with the situation in its absence; the times required without catalyst have been tabulated.[1] Many of the same reactions, conducted without a catalyst, require thousands of hours.[1] Accelerations by MTO of the order 10^5 were observed in many cases. Most of the MTO-catalyzed reactions were quantitative or nearly so, and they proceeded with high stereoselectivity. Indeed, some of the reactions gave but a single isomer, such as that between methyl vinyl ketone and 1,3-cyclohexadiene.

Much less satisfactory yields (36−56%, see Table 2) were obtained for dienophiles with β-substituents, such as *trans*-2-hexenal, *trans*-2-pentenal, and *trans*-4-hexen-3-one. A long reaction time, 4 weeks, was required, but isomer ratios >96:4 were realized.

Effect of Solvents. The effect of solvents on the reaction of *trans*-2-methyl-1,3-pentadiene with methyl vinyl ketone was determined. The selectivity of this reaction remained high, and it gave almost the same yield of product, independent of solvent, after 12 h. The yields were as follows: benzene (90%), acetone (91%), acetonitrile (91%), THF (93%), and chloroform (94%). Specially purified[13] chloroform was used instead, but the results were the same. The other solvents were used as received, and the results obtained show that this is a satisfactory procedure.
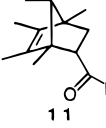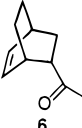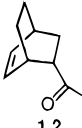
Reactions in Aqueous Solution. Water is the one solvent that made a substantial difference. It sped up the reaction and resulted in higher selectivity than the others. For example, the MTO-catalyzed reaction between *trans*-2-methyl-1,3-pentadiene and methyl vinyl ketone in water gave a 90% yield of **2** in 4 h with the two isomers being formed in a ratio >99:1. Data from some other reactions carried out in water are collected in Table 3, with the corresponding data in chloroform given for comparison.

Although the reaction between dienes and dienophiles may not be homogeneous, our study of the reaction between cyclopentadiene and methyl vinyl ketone suggested that much of the reaction occurs in the water phase, because the isomer ratios are so different. These are the data for four equimolar mixtures of cyclopentadiene and methyl vinyl ketone (neat reaction) at room temperature run under different conditions

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CH₃ReO₃ as a Catalyst for Diels—Alder Reaction

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Table 2. MTO-Catalyzed Diels—Alder Reactions[a] between Dienes and Larger Dienophiles

Dienophile →	Pr^n / / CHO	(O) Et	Et / CHO
Diene ↓			
(isoprene)		**23**[b]	
(dimethylbutadiene)	**20**	**24**	**25**
(tetramethylcyclopentadiene)	**21**		
(cyclohexadiene)	**22**		

[a] Reaction time, yield, isomer ratio (by ^{1}H NMR). **20**: 4 wk, 26%, >99:1. **21**: 4 wk, 56%, 96:4. **22**: 4 wk, 26%, >99:1. **23**, 4 wk, 38% (but ~100% conversion). **24**: 4 wk, 49%. **25**: 4 wk, 41%. [b] Unlike the other reactions, this reaction occurred with 100% conversion. Most of the diene underwent a "self-DA" reaction, eq 4.

Table 3. MTO-Catalyzed Diels—Alder Reactions[a] in Water As Compared to Chloroform

Dienophile →	(MVK)	(acrolein)	(diene)
Diene↓			
(isoprene)	**1**	**7**	
	A: 2.5 h, 90%, >99:1	2.5 h, 91%, >99:1	
	C: 18 h, 90%, >99:1	18 h, 90%, >99:1	
(cyclohexadiene)	**6**	**12**	
	A: 16 h, 91%, >99:1	16 h, 90%, >>99:1	
	C: 4 d, 94%, >>99:1	4 d, 94%, 98:2	
(dimethylbutadiene)	**2**	**8**	**26**
	A: 4h, 90%, >99:1	16 h, 90%, >>99:1	10 h, 90%, 95:5
	C: 12 h, 94%, 98:2	4 d, 94% >>99:1	1 wk, 90%, 80:20

[a] Entries for each product (identified by number) are the reaction time, yield, and isomer ratio (by ^{1}H NMR), with aqueous solution (**A**) first, then chloroform (**C**).

that establish this point. The reaction times to 50% conversion are also given, but cannot readily be intercompared.

conditions	endo/exo	t_{50}/min
neat	3.15:1	45
1% MTO	15.4:1	20
aqueous	20:1	25
aqueous, 1% MTO	>99:1	14

Reactions of those dienophiles with β-substituents, such as *trans*-2-hexenal, *trans*-2-pentenal, and *trans*-4-hexen-3-one, were not improved by running the reactions in an aqueous medium, unlike the ones listed in Table 3.

Kinetics. The kinetics of the reaction between cyclopentadiene and methyl vinyl ketone in water was monitored at 250 nm ($\epsilon_{diene} = 2 \times 10^4$ L mol^{-1} cm^{-1}) and 25 °C with and without MTO. The pseudo-first-order rate constants, k_{obs}, were obtained
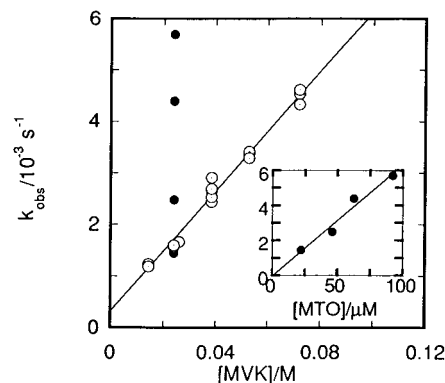

Figure 1. Kinetic data for the reaction between cyclopentadiene and methyl vinyl ketone (MVK) in the absence (open circles) and presence (filled circles) of MTO in aqueous solution. The pseudo-first-order rate constants (with [CpH] = 0.42 mM) vary linearly with [MVK], the excess reagent; the small intercept can be attributed to the self-Diels—Alder reaction of CpH. The rate constants at various concentrations of MTO (to 92 μM) at constant [MVK] = 0.024 M are shown in the inset as a function of [MTO].
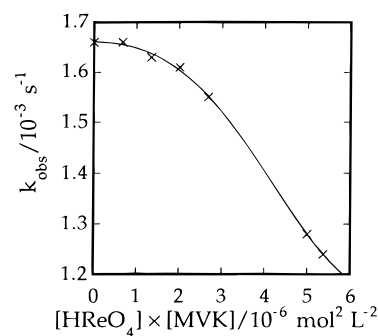

Figure 2. Kinetic data for the reaction between cyclopentadiene (0.42 mM) and methyl vinyl ketone (MVK, 24 mM) in the presence of HReO$_4$ (28−224 mM) in aqueous solution. The fitting is a general polynomial curve.

at varying concentrations of methyl vinyl ketone (14.4−72 mM) and at a constant concentration of cyclopentadiene (0.42 mM). The plot of k_{obs} versus the concentration of methyl vinyl ketone is a linear plot through the origin, as shown in Figure 1. The slope of the straight line gives a second-order rate constant of $5.88 \pm 0.06 \times 10^{-2}$ L mol^{-1} s^{-1}. In the presence of MTO, the kinetic study was carried out with both concentrations held constant ([cyclopentadiene] = 0.42 mM and [methyl vinyl ketone] = 24 mM), MTO being varied in the range of 0.022−0.092 mM. The acceleration by MTO is apparent, as shown in the inset in Figure 1.

The effect of the perrhenic acid (HReO$_4$) on the reaction between cyclopentadiene and methyl vinyl ketone was also investigated, as it is the decomposition product of MTO. This effect was explored, even though it was shown by ^{1}H NMR that only a very small portion of MTO had decomposed[14] within the normal reaction time. The study was carried out in water at 25 °C with constant concentrations of both cyclopentadiene (0.42 mM) and methyl vinyl ketone (24 mM) and varying concentrations of HReO$_4$ (28−224 mM). The reaction was markedly slower in the presence of the acid, as shown in Figure 2. Two conclusions can be drawn: (1) under these conditions specific acid catalysis is absent and (2) the accelerating effect of MTO is unrelated to an acid effect.

Mixed solvents such as 1:1 acetonitrile−water and 1:1 acetone−water were used to enhance the solubility of the dienes,

(14) Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966.

eliminating the need for stirring. Compared to water, the reaction in CH₃CN−H₂O gave a decreased yield in a given time. Presumably this is the result of a reduced reaction rate. In both of these solvent pairs, the reaction between *trans*-2-methyl-1,3-pentadiene and methyl vinyl ketone gave an 80% yield in 12 h, compared to 90% in 4 h in water alone.

**Stability of MTO.** The stability of MTO in the presence of dienophiles and dienes (separately) was studied by two methods. A solution of MTO and either of these reagents was prepared in the desired solvent. The solutions were monitored by GC-MS or by ¹H NMR. According to these techniques, MTO did not decompose in any of the deuterated organic solvents in a month's time. In water, however, MTO was stable for only a week, doubtless a result of this decomposition reaction:[14]

$$CH_3ReO_3 + H_2O \rightarrow CH_4 + ReO_4^- + H^+ \quad (1)$$
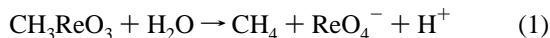
When a diene or dienophile was added, the MTO resonance shifted upfield by ca. 0.06 ppm, indicating some interaction. We were unable, however, to obtain a stable MTO−dienophile complex.

Self [2 + 4] Cycloaddition Reactions. Some unexpected findings came to light during the studies of the stability of MTO in the presence of dienes and dienophiles. It turns out that certain of the dienes undergo a "self-DA" reaction. As an example, *trans*-2-methyl-1,3-pentadiene undergoes such a reaction in the absence of any α,β-unsaturated carbonyl dienophile provided 1% MTO is present. This compound acts as its own dienophile. The reaction is
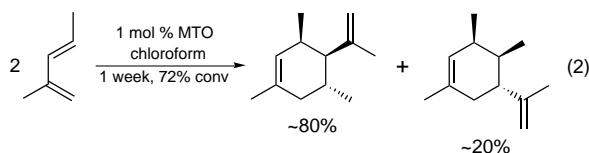
Similar "self-DA" reactions took place for isoprene and pentamethylcyclopentadiene, but for them a small amount of a dienophile was necessary for the self-coupling. Such self-coupling provides the reason that compounds **1** and **7** were formed in only 90% yield (Table 1). The portion of the diene that had not been converted to the DA product had reacted with itself, catalyzed by MTO, thus leaving a small amount of unconverted dienophile. The data obtained under these conditions can be represented by a composite of two separate chemical equations:
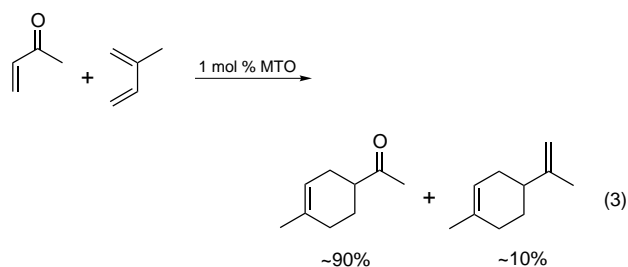
The same explanation accounts for the reduced yields for compounds **16−19**. In each of these cases a minor amount of the self-DA byproduct was detected.

In all these studies, polymerization was observed only for *trans*-2-methyl-1,3-pentadiene. In water, some polymeric material was obtained after 2 days.

Dienophiles also can undergo "self-DA" coupling in the presence of MTO, but less readily than the dienes. Methacrolein

Table 4. MTO-Catalyzed Diels−Alder Reactions[a] of Some Active Dienophiles at Room Temperature[b]

[a] Reaction time, yield, isomer ratio (by ¹H NMR). **27**: 6 h, 96%. **28**: 6 h 95%. **29**: 6 h, 95%. **30**: 40 min, >99%; ≫99:1. **31**: 3 h; 95%. **32**: 4 h, >99%. **33**: 1 h, >99%. **34**: 1 h; >99%. **35**: 40 h, >99%. **36**: 20 min, 95%. **37**: 15 min, >95%. **38**: 15 min, 96%. **39**: 45 min, 98%, ≫99:1. [b] Products **37−39** were obtained in chloroform, the others in acetone, where the quinones have better solubility.

forms such a product in the absence of dienes, as in the following equation:
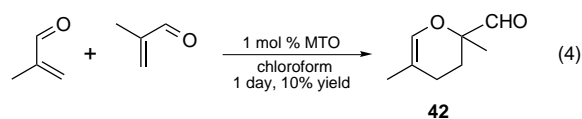
The dimer of methyl vinyl ketone was also observed with MTO in water, but its formation required the presence of a diene. In these cases the yield of the dimer was very low, and it was detected only by GC-MS. Thus it is not entirely clear that the low-yield compound is the result of a [2 + 4] DA reaction.

Product Inhibition. Product inhibition was investigated by the following procedure. A solution of methyl vinyl ketone and *trans*-2-methyl-1,3-pentadiene (5 mmol each in 50 mL of chloroform) with 1% MTO was monitored by GC-MS. After 15 h, when the reaction was complete, 5 mmol of each of the reagents again was added to the same solution. This second reaction also took 15 h to reach completion. Thus, the products did not inhibit the MTO-catalyzed reaction, a fact that along with others must be kept in mind in formulating the mechanism.

Other DA Reactions. Other DA reactions catalyzed by MTO were examined. MTO is an effective catalyst for reactive dienophiles that have substituents at the β-position. Thus 1,4-benzoquinone and maleic anhydride reacted rapidly with dienes in the presence of MTO. Such dienophiles and dienes (5 mmol each with 1 mol % MTO in 40 mL of solvent) were employed in this study. The results are listed in Table 4.

Although a "double" DA reaction is often encountered under ultra-high pressure or in concentrated solutions of lithium
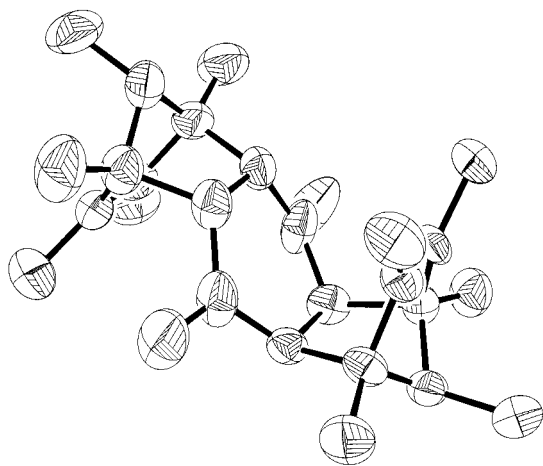
Figure 3. An ORTEP diagram of the structure of **40**, determined by single-crystal X-ray analysis.

perchlorate in ether (e.g., 5 M LiClO₄ in Et₂O),[15] a low level of MTO (1 mol%) in organic solvents such as chloroform, acetone, or benzene promotes a "double" DA reaction. 1,2,3,4,5-Pentamethylcyclopentadiene is quite reactive compared with other dienes. Its ordinary reaction with 1,4-benzoquinone gave compound **30** rapidly and quantitatively (see Table 4). Moreover, when this diene and benzoquinone were taken in a 2.4:1 ratio, then two molecules of 1,2,3,4,5-pentamethylcyclopentadiene combined with the benzoquinone in a reaction catalyzed by MTO in chloroform. Four different products were found by GC-MS with 100% conversion of 1,4-benzoquinone after 1 h at room temperature. Two of these four, comprising more than 95% of the total, are the major products of a "double" DA reaction:
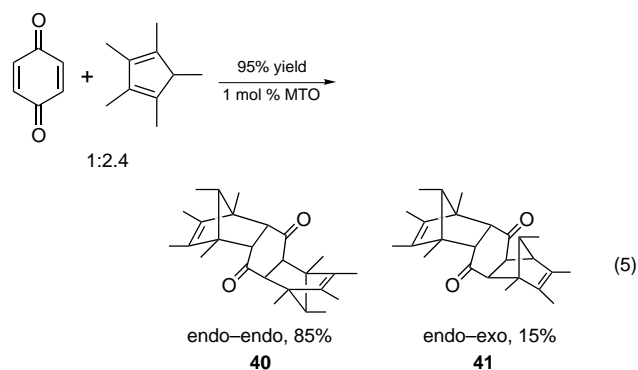
The double DA product has not been identified before, and it could not be characterized unambiguously with the usual spectroscopic methods. Thus we undertook a single-crystal X-ray study of the major product. The details of the structure and its solution are given in the Supporting Information. An ORTEP diagram of the structure is presented in Figure 3, confirming the identity of the compound and its endo−endo arrangement. The bond lengths are in acceptable ranges: av. C=O, 121.4 pm; average C=C, 132.1 pm; average C−C, 152.6 pm (range 148.4−157.9 pm).

Limitations of MTO. MTO catalysis did not give satisfactory yields for certain dienophiles with substituents at the β-position, such as *trans*-2-hexenal, *trans*-2-pentenal, and *trans*-4-hexen-3-one. No reaction was observed for 2-cyclohexen-1-one or 2-cyclopenten-1-one, and a less than 20% product yield was observed for methyl methacrylate with more reactive dienes

such as *trans*-2-methyl-1,3-pentadiene under the same conditions as used in this study for other ketone and aldehyde dienophiles.

Discussion

Catalytic Reactions. Easily-prepared and air-stable MTO catalyzes DA reactions under mild conditions. It accelerates the reactions of α,β-unsaturated aldehydes and ketones, other than those with β-substituents, compared with the corresponding thermal reactions. MTO is convenient to use since it is soluble in most solvents; indeed, its high solubility in water gives it potential application for aqueous media.

The substrates were not decomposed by MTO, and only in one case, that of *trans*-2-methyl-1,3-pentadiene with dienophiles in water, did the diene polymerize. MTO is generally an excellent catalyst for α,β-unsaturated aldehydes and ketones, dienophiles lacking β-substituents, but not for α,β-unsaturated esters or for α,β-unsaturated aldehydes and ketones with β-substituents.

Mechanistic Considerations. We suggest a rapid and reversible interaction between MTO and the oxygen atom of the dienophiles (and, presumably, that of the products). These are labile equilibria that lie toward the separate components. The reasons are these. First, there is no product inhibition, which rules out strong binding. Second, the ¹H NMR of the methyl group of MTO shifts upfield about only 0.06 ppm when a dienophile is added to the MTO solution. Third, no stable complexes were observed between MTO and dienophiles. MTO meets all criteria for a desirable DA catalyst.

The catalytic activity of MTO lies in its ability to reversibly and weakly to bind a dienophile or a diene. This interaction lowers the net energy of the HOMO and the LUMO relative to the starting materials and influences the orbital coefficients.[16]
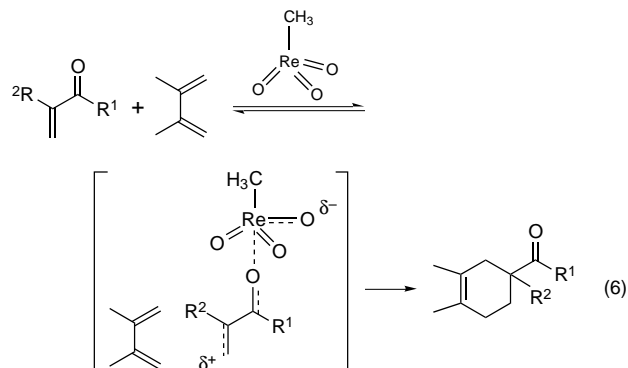
DA products were not formed when 2-cyclohexen-1-one and 2-cyclopenten-1-one were used as dienophiles. These two α,β-unsaturated ketones have larger equilibrium constants for enol formation than the others do.[17] An enol will form a more stable complex with MTO than an enone will,[12,18,19] eliminating the opportunity for the catalytic activation of enones.

The accelerations by aqueous media, we believe, are due to two effects suggested in the literature:[12] enforced hydrophobic interactions and hydrogen bonding to the activating group of the dienophiles.
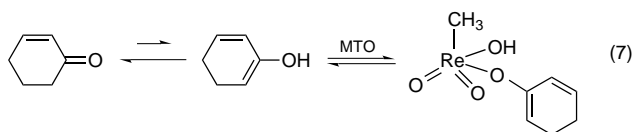
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It is not entirely clear why MTO is not effective for the reactions of the α,β-unsaturated aldehyde and ketone dienophiles that have β-substituents, and why using water as a solvent does not speed up these reactions. The limited coordination space around MTO may pose one problem; also, water may compete with dienophiles for MTO.[10,18,19]

Experimental Section

General. Methylrhenium trioxide was either prepared from dirhenium heptoxide and tetramethyl tin[20] or purchased (Aldrich). The dienes and dienophiles are commercially available and were purified by simple distillation under argon or by recrystallization.[13] Cyclopentadiene was prepared by cracking the dimer.[21] The solvents were used as received, save for the use of purified chloroform[13] in one instance. All the reactions were carried out in chloroform and monitored by GC-MS unless otherwise noted.

Reaction Procedures. Both dienophiles and dienes, 10 mmol of each, were dissolved in 20 mL of the solvent. MTO was added at the 1% level, and the bottle capped to prevent evaporation. The reactions were conducted at room temperature. The progress was monitored intermittently by GC-MS. When the reaction had been completed, the products were obtained by distillation and identified by MS and NMR data.[22–26] These are known materials, and the results are presented in the Supporting Information.

The reactions in water followed the same general procedure, but they required vigorous stirring. The products were extracted with diethyl ether.

The reactions of quinones and maleic anhydride followed the same procedure, except that 5 mmol of the reagents in 40 mL of solvent were used. The reaction was allowed to stand, tightly capped, and was then monitored by GC-MS before the separation.

Product **40** was obtained as colorless crystals after recrystallization from acetone. It was identified by its NMR and IR spectra, by elemental analysis, and by X-ray crystal analysis. ^{1}H NMR (δ/ppm, referenced to SiMe$_4$): 2.48 (s, 4H), 1.50 (s, 12H), 1.26 (s, 12H), 0.48 (d, 6H). ^{13}C NMR (δ/ppm, referenced to solvent): 211.74, 134.88, 63.18, 60.42, 59.93, 14.87, 12.15, 7.14. IR (NaBr plate, ν/cm^{-1}): 2957 (s), 2848 (s), 1679 (s), 1377 (s), 1227 (s), 1002 (s), 910 (s). Anal. Found: C, 81.97; H, 9.62. C$_{26}$H$_{36}$O$_2$ requires: C, 82.05; H, 9.53. Mp 148−149 °C. The X-ray structure is given in Figure 3. A summary of data collection procedures, the method of structural solution, and the details of its refinement are given in the Supporting Information.

Supporting Information Available: The spectroscopic data for previously-known products and the crystallographic parameters for **40** (24 pages). See any current masthead page for ordering and Internet access instructions.

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