Epoxidation of *trans*-Cyclooctene by Methyltrioxorhenium/H_2O_2: Reaction of *trans*-Epoxide with the Monoperoxo Complex

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The epoxidation of *trans*-cyclooctene (*trans*-**1**) with the MTO/H_2O_2, MTO/UHP, and NaY/MTO/H_2O_2 oxidants leads to a mixture of *trans*/*cis*-olefins **1**, *trans*/*cis*-epoxides **2**, and the *cis*-diol **3**. While the oxygen transfer proceeds stereoselectively, the monoperoxo rhenium complex **A**, which is generated in situ during the catalytic cycle, is responsible for the facile deoxygenation, isomerization, and hydrolysis of the *trans*-epoxide. In the case of the homogeneous MTO/H_2O_2 system, rapid decomposition of the catalytically active rhenium species into $HReO_4$ circumvents the formation of such side products. In contrast, for the heterogeneous oxidants MTO/UHP and NaY/MTO/H_2O_2, the catalytically active rhenium species are sufficiently stabilized and survive long enough to promote the observed side reactions.

Introduction

A variety of oxidation reactions with H_2O_2 are catalyzed by methyltrioxorhenium (MTO), of which the epoxidation has been investigated intensively.[1] For most olefins, this preparatively valuable catalytic oxidation proceeds cleanly in high conversion and excellent yields, with high product selectivity and diastereoselectivity. Undesirable side reactions, the most prominent is the hydrolytic opening of the epoxide ring and subsequent pinacol-type rearrangements and C−C bond cleavages, are known since the first reports on MTO/H_2O_2-mediated epoxidations.[2] Several additives, e.g., urea[2b] and pyridine,[3] have been found to circumvent these problematic side reactions, but the responsible rhenium species has to date not been defined with certainty.[2a,4]

In this context, we have observed complex oxidation chemistry in the MTO-catalyzed epoxidation of *trans*-cyclooctene as a substrate. Besides the expected ring-opening of the strained *trans*-epoxide,[5] also *cis*-epoxide and *cis*-cyclooctene were observed, which required mechanistic clarification. Herein we report our unusual results on the epoxidation of *trans*-cyclooctene **1** with the homogeneous MTO/H_2O_2 and the heterogeneous MTO/UHP and NaY/MTO/UHP oxidants. The in-situ-generated monoperoxo rhenium species has been identified as the active intermediate responsible for the complex chemistry.

Results and Discussion

trans-Cyclooctene (*trans*-**1**) was prepared from its cis isomer according to the literature.[6] The authentic reference epoxides *cis*- and *trans*-**2**[5] were obtained by DMD epoxidation of the corresponding cyclooctene diastereomers. The diols *cis*- and *trans*-**3**[7] were obtained from the cyclooctene *cis*-**1** by hydroxylation with $KMnO_4$ (*cis*-**3**) and epoxidation with HCO_2H/H_2O_2, followed by basic hydrolysis (*trans*-**3**).

The catalytic oxidation of *trans*-cyclooctene (*trans*-**1**) was conducted with the known MTO-based systems MTO/85% H_2O_2,[8] MTO/UHP,[2b] and NaY/MTO/85% H_2O_2[9] in methylene chloride at ambient temperature (ca. 20 °C). For the standard MTO/H_2O_2 oxidant, the reaction initially proceeds diastereoselectively; i.e., only the *trans*-epoxide is observed (Table 1, entries 1 and 2). However, once the substrate is completely consumed after ca. 1 h (entry 2), complex chemistry ensues on prolonged reaction time, in which the *trans*-epoxide is not only hydrolyzed to the *cis*-**3** diol, but also deoxygenated back to the olefin, as suggested by the lower extent of conversion (entry 3). Thus, for the highly diastereoselective preparation of the *trans*-**2** epoxide, the reaction must be terminated after 1 h. Mechanistically significant, some *cis*-epoxide is formed, as evidenced by the drop in the *trans*/*cis*-epoxide ratio, which signifies loss of stereoselectivity; moreover, the trans/cis ratio drops further on still longer reaction time (data not shown). The latter is even more pronounced for the heterogeneous oxidants MTO/UHP and NaY/MTO/H_2O_2, which display low *trans*/*cis*-epoxide ratios even at low conversions (compare entries 4 and 6 with 1). As for the MTO/H_2O_2 oxidant, in heterogeneous systems, the stereoselectivity deteriorates

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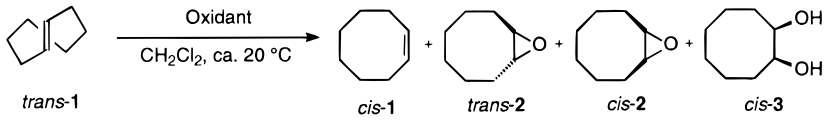
Table 1. Mass Balances, Conversions, and Trans/Cis Ratios for MTO-Catalyzed Epoxidations of the *trans*-Cyclooctene (*trans*-1)



					product distribution	
entry	oxidant[b]	time (h)	convn[a] (%)	mb[a] (%)	**1** (trans/cis)[a]	**2** (trans/cis)[a]
1	MTO/85% H_2O_2	0.5	89	82	14 (>95:5)	86 (>95:5)
2		1	>95	91	2 (>95:5)	98 (>95:5)
3		2	85	88	17 (>95:5)	77[c] (89:11)
4	MTO/UHP	0.5	42	91	64 (>95:5)	36 (79:21)
5		2	60	85	47 (>95:5)	53 (77:23)
6	NaY/MTO/85% H_2O_2	0.5	23	87	89 (>95:5)	11 (61:39)
7		2	43	74	76 (>95:5)	24 (45:55)

[a] Determined by ^{1}H NMR spectroscopy on the reaction mixture against naphthalene as internal standard, reproducible within the experimental error (±5% of the given value). [b] Methyltrioxorhenium (MTO), urea/hydrogen peroxide adduct (UHP), zeolite (NaY); reaction performed with 330 μmol *trans*-**1** in 0.6 mL $CDCl_3$, 1:100:100 MTO/H_2O_2/*trans*-**1**. [c] Also 6% of the *cis*-diol (*cis*-**3**) was formed.

Table 2. Mass Balances (mb) and Trans/Cis Ratios of the Control Experiments for the Isomerization of *trans*-Cyclooctene (*trans*-1) and *trans*-Cyclooctene Epoxide (*trans*-2)

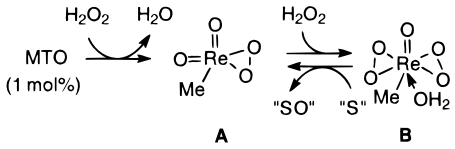
entry	substrate	catalyst	mb[a] [%]	*trans*/*cis*[a]	
1	(*trans*-**1**)	MTO (1 mol%)	95	92 : 8	(**1**)
2		$HReO_4$ (1 mol%)	93	>95 : 5	
3	(*trans*-**2**)	MTO (1.0 mol%)	>95	>95 : 5[b]	(**2**)
4		$CH_3ReO_2(O_2)$ (10 mol%)	50	-[c]	
5		$CH_3ReO(O_2)_2$ (1 mol%)	48	>95 : 5	

[a] Determined by ^{1}H NMR spectroscopy directly on the reaction mixture against naphthalene as internal standard, error ±5% of the given value. [b] Besides ca. 70−75% epoxide, also *trans*/*cis*-cyclooctene (10−15%) and *cis*-diol (15%) were observed. [c] All epoxide was consumed, and a 1:1 mixture of *trans*/*cis*-cyclooctene (20%) and *cis*-diol (29%) was observed.

on prolonged reaction times (compare entries 4, 5 and 6, 7). Although the expected initial order of reactivity; i.e., MTO/H_2O_2 > MTO/UHP > NaY/MTO/H_2O_2 is obeyed, the highest *trans*/*cis*-epoxide ratio was found for the most Lewis-acidic of all catalytic oxidants used here, namely the MTO/H_2O_2.

The question arises as to the origin of the *cis*-**2** epoxide. To assess whether the observed decrease of the *trans*/*cis*-epoxide ratio stems from *trans*-olefin isomerization and subsequent epoxidation of the *cis*-cyclooctene or from subsequent isomerization of the *trans*-epoxide, the persistence of the authentic *trans*-**1** cyclooctene and *trans*-**2** epoxide was checked under various conditions as control experiments (Table 2). Only marginal olefin isomerization took place with MTO alone (entry 1) and none with its decomposition product $HReO_4$ (entry 2). The control experiments with the authentic *trans*-epoxide were more instructive. Although no isomerization of the *trans*-epoxide was observed with MTO alone (entry 3), or with the diperoxo complex **B** (entry 5), under conditions at which mainly the monoperoxo complex **A** is generated (i.e., with 10 mol % of MTO and 8 mol % of 30% H_2O_2, entry 4), no epoxide was recovered after 24 h. Instead, in a poor mass balance (entry 4), 29% of the cis diol and 20% of trans/cis-**1** were found. Also in the case of MTO

Scheme 1. Catalytic Cycle in MTO-Mediated Oxidations

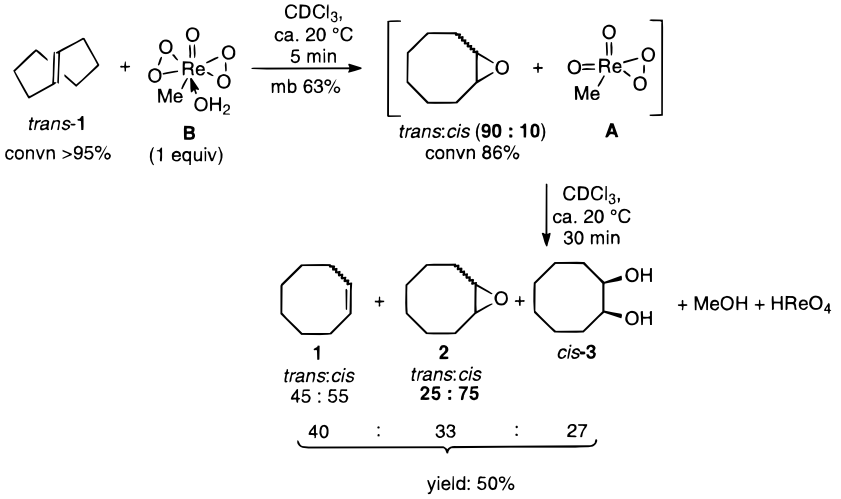


alone, significant amounts of cyclooctene (10−15%) and *cis*-diol **3** (15%) were formed.

It is generally accepted[1e,8] that under normal oxidation conditions, i.e., with a 100-fold excess of the oxygen donor H_2O_2 relative to the rhenium catalyst, no MTO is present in solution, but rather the oxygen-transferring agent diperoxo complex **B**. Thus, the MTO may hardly be the culprit for the observed loss of diastereoselectivity during the epoxidation of cyclooctene *trans*-**1**, but maybe the monoperoxo complex **A**. This becomes evident from inspection of the catalytic oxidation cycle in the MTO-catalyzed epoxidation (Scheme 1): For every oxidized olefin molecule, one molecule of the monoperoxo complex **A** is formed, which subsequently regenerates the diperoxo complex **B** with hydrogen peroxide.

To gain further mechanistic insight into the complex MTO-catalyzed oxidation process of *trans*-cyclooctene, the formation and disappearance of the epoxides by NMR spectroscopy was monitored with time. For this purpose, *trans*-cyclooctene was treated with 1 equiv of in-situ-generated diperoxo complex **B** (Scheme 2). Within the first 5 min (convn >95%), a 90:10 trans/cis mixture of the epoxides and the monoperoxo complex **A** is obtained. Subsequently, after an additional 30 min, most of the *trans*-epoxide is selectively consumed. At this point, not only are the *trans*/*cis*-cyclooctenes **1** (45:55) and the *cis*-**3** diol formed, but more *cis*-**2** epoxide is observed after the second step than produced in the first step. To substantiate this result, the monoperoxo complex **A** was generated in-situ by treating the diperoxo complex **B** with 1 equiv. of cyclopentene (data not shown), whose epoxide is not deoxygenated. To this reaction mixture was then added an equimolar amount (based on rhenium complex) of *trans*/*cis*-epoxides (1:1) and the time profile for epoxide consumption was assessed (Figure 1). As anticipated, the *trans*-epoxide was consumed within minutes after addition and 10−15% of the *trans*/*cis*-**1** cyclooctenes were

Scheme 2. Stoichiometric Oxidation of *trans*-Cyclooctene (*trans*-1) to the *trans*/*cis*-Epoxycyclooctanes (90:10) by the Diperoxo Complex B (1 equiv) for the In Situ Generation of the Monoperoxo Complex A and Further Reaction



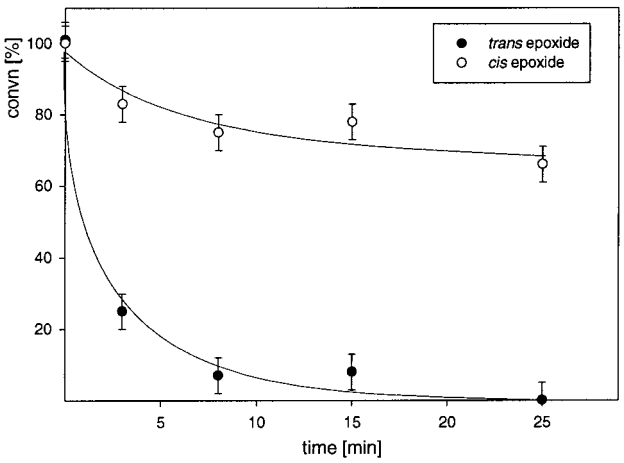


Figure 1. Time profile for the decomposition of *trans*/*cis*-epoxycyclooctanes **2** (1:1 mixture) by the monoperoxo complex **A** (1 equiv), generated in situ through stoichiometric epoxidation of cyclopentene by the diperoxo complex **B**.

formed, while the amount of *cis*-epoxide remained essentially unchanged (Figure 1). Low mass balances were obtained in these stoichiometric reactions, which accounts for the appreciable amount of unidentified decomposition products compared to the catalytic runs (Table 1, entries 1−3), for which such complex chemistry is essentially negligible.

These results unequivocally establish that the monoperoxo complex **A** selectively reacts with the *trans*-epoxide. As products thereof, the *trans*/*cis*-**1** cyclooctenes are formed, along with some *cis*-epoxide, which implicates selective deoxygenation of the *trans*-epoxide. In this context it is relevant to mention that the deoxygenation of epoxides by MTO has been observed before in the absence of H_2O_2,[10] but required PPh_3 as oxygen acceptor and large amounts of the rhenium catalyst (10 mol %); thus, the monoperoxo complex **A** cannot be the deoxygenating agent in this process. Rather, a mechanism was proposed, in which the PPh_3 generates the methyldioxorhenium (MDO) species from MTO, and MDO is reactive enough to deoxygenate epoxides, *N*-oxides, and sulfoxides. In our case, however, no phosphine is present and the reactions are performed with hydrogen peroxide. As stated above (cf. Scheme 1), under these conditions the monoperoxo complex **A** is formed and serves as the deoxygenating species. The mechanistic details are as yet obscure for this deoxygenation of the *trans*-cyclooctene epoxide.

Now that the rhenium species responsible for the unprecedented epoxide deoxygenation and loss of diastereoselectivity has been identified, namely the monoperoxo complex **A**, the question remains, why the various MTO-based oxidants examined herein (Table 1) display such differences in their trans/*cis* selectivity for the epoxidation of *trans*-cyclooctene **1**. In the case of MTO/H_2O_2 (entry 1), the *trans*-**1** cyclooctene is oxidized cleanly trans-selectively by the catalytically *in-situ*-generated diperoxo complex **B**. Rapid decomposition of the rhenium species to catalytically inactive products[11] such as $HReO_4$ circumvents the deoxygenation of the *trans*-epoxide, as evidenced by the fact that the decomposition products do not subsequently alter the *trans*/*cis*-epoxide ratio (Table 2, entry 2). For the MTO/UHP[2b] and NaY/MTO/85% H_2O_2[9] oxidants, we have recently demonstrated that the oxidizing rhenium species are stabilized and persist longer in the host interior. Therefore, in the heterogeneous oxidation systems the interaction between the sensitive *trans*-epoxide and the monoperoxo complex **A** is more pronounced than in the MTO/H_2O_2 case, and more epoxide decomposition occurs (lower *trans*/*cis*-epoxide ratios, entries 4−7, Table 1). An alternative explanation may be that in the heterogeneous oxidations, MTO faces a lower effective concentration of H_2O_2, which favors the formation of the monoperoxo complex **A** and, consequently, the degradation of the *trans*-epoxide is more facile. However, no significant difference in the amounts of the monoperoxo complex **A** was observed by NMR and UV analyses in the heterogeneous versus homogeneous systems.

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Conclusion

We have demonstrated that the MTO-catalyzed oxygen transfer to *trans*-cyclooctene proceeds initially stereoselectively, but the *trans*-epoxide does not persist under the reaction conditions and is in part deoxygenated, isomerized and hydrolyzed. The monoperoxo complex **A**, which is generated during the oxygen transfer from the diperoxo complex **B**, is responsible for the facile transformation of the *trans*-epoxide to the cyclooctenes **1**.

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Supporting Information Available: The experimental procedures for the MTO-catalyzed oxidations of *trans*-cyclooctene as well as control experiments are reported. This material is available free of charge on the Internet at http://pubs.acs.org.

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