

Olefin Epoxidation with Bis(trimethylsilyl) Peroxide Catalyzed by Inorganic Oxorhenium Derivatives. Controlled Release of Hydrogen Peroxide

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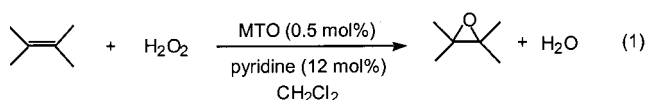
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The replacement of organometallic rhenium species (e.g., CH_3ReO_3) by less expensive and more readily available inorganic rhenium oxides (e.g., Re_2O_7 , $\text{ReO}_3(\text{OH})$, and ReO_3) can be accomplished using bis(trimethylsilyl) peroxide (BTSP) as oxidant in place of aqueous H_2O_2 . Using a catalytic amount of a proton source, controlled release of hydrogen peroxide helps preserve sensitive peroxorhenium species and enables catalytic turnover to take place. Systematic investigation of the oxorhenium catalyst precursors, substrate scope, and effects of various additives on olefin epoxidation with BTSP are reported in this contribution.

Methylrhenium trioxide (CH_3ReO_3 or MTO) was synthesized in 1979.¹ It was only recently, however, that Herrmann and others developed MTO into a well-defined catalyst for a variety of processes including olefin epoxidation with aqueous hydrogen peroxide (H_2O_2).² Regarding olefin oxidation, there is a fundamental difference between CH_3ReO_3 and OsO_4 : in contrast to OsO_4 , MTO does not react directly with olefins.³ Rather, the MTO-catalyzed epoxidation is believed to proceed through the activation of H_2O_2 by the electrophilic Re(VII) center leading to the formation of an equilibrating mixture of mono- and bisperoxorhenium complexes. The latter transfer oxygen atoms to the corresponding olefins. Notably, the $\text{OsO}_4/\text{H}_2\text{O}_2$ system has little synthetic value for olefin epoxidation. Even though epoxides are the primary products in this system, significant amounts of diols and overoxidation products are formed.⁴

The major limitation of Herrmann's original MTO/ H_2O_2 epoxidation system is acidity of the reaction medium. The protons of the water molecule coordinated to the Re(VII) center in the bisperoxo complex are highly acidic, and sensitive epoxides do not survive under these conditions.⁵ Recent efforts led to a highly efficient olefin epoxidation with 30% aqueous H_2O_2 where catalytic activity of MTO was uncoupled from acidity for the first time.^{6a} The crucial features of this new process are the requirement for a pyridine ligand and the solvent switch from *tert*-butyl alcohol^{2b} to methylene chloride^{6a} which additionally enhances effectiveness of the pyridine-modified rhenium catalyst (eq 1).

Further improvements in this epoxidation catalysis were reported, namely the use of 3-cyanopyridine as a ligand of choice for the epoxidation of terminal and *trans*-



disubstituted olefins.^{6b,c} In a more recent development, replacement of organometallic rhenium species (e.g.,

(2) For applications of MTO in organic synthesis, see: (a) Hoechst AG (Herrmann, W. A.; Marz, D. W.; Kuchler, J. G.; Weichselbaumer, G.; Fischer, R. W.) DE 3,902,357, 1989. (b) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638. (c) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243. (d) Herrmann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149. (e) Al-Ajlouni, A. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243. (f) Pestovsky, O.; van Eldik, R.; Huston, P.; Espenson, J. H. *J. Chem. Soc., Dalton Trans.* **1995**, 133. (g) Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 533. (h) Boelow, T. R.; Spilling, C. S. *Tetrahedron Lett.* **1996**, *37*, 2717. (i) Al-Ajlouni, A. M.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 3969. (j) Herrmann, W. A.; Correia, J. D. G.; Rauch, M. U.; Artus, G. R. J.; Kühn, F. E. *J. Mol. Catal.* **1997**, *118*, 33. (k) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169. (l) Espenson, J. H.; Abu-Omar, M. M. *Adv. Chem. Ser.* **1997**, *253*, 99. (m) ARCO Chemical Technology (Crocco, G. L.; Shum, W. P.; Zajacek, J. G.; Kesling, H. S., Jr.) US 5,166,372, 1992. (n) Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 877. (o) Gable, K. P. *Adv. Organomet. Chem.* **1997**, *41*, 127. (p) Wang, W. D.; Espenson, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 11335. (q) Villa de P., A.; De Vos, D. E.; Montes de C., C.; Jacobs, P. A. *Tetrahedron Lett.* **1998**, *39*, 8521. (r) Jacob, J.; Espenson, J. H. *Inorg. Chim. Acta* **1998**, *270*, 55. (s) Wu, Y. D.; Sun, J. *J. Org. Chem.* **1998**, *63*, 1752. (t) Gisdakis, P.; Antonczak, S.; Kostlmeier, S.; Herrmann, W. A.; Rosch, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2211. (u) Rudler, H.; Denise, B. *Chem. Commun.* **1998**, *19*, 2145. (v) Jacob, J.; Espenson, J. H. *Organometallics* **1998**, *17*, 1835. (w) Eager, M. D.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 2533. (x) Adam, W.; Mitchell, C. M.; Saha-Moller, C. R. *J. Org. Chem.* **1999**, *64*, 3699. (y) Huang, R. L.; Espenson, J. H. *J. Org. Chem.* **1999**, *64*, 6374. (z) Espenson, J. H. *Chem. Commun.* **1999**, *6*, 479. (aa) Adolfsson, H.; Converso, A.; Sharpless, K. B. *Tetrahedron Lett.* **1999**, *40*, 3991. (bb) Jacob, J.; Espenson, J. H. *Chem. Commun.* **1999**, *11*, 1003. (cc) Tetzlaff, H. R.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 881. (dd) Zauche, T. H.; Espenson, J. H. *Inorg. Chem.* **1999**, *37*, 6827. (ee) Wang, W. D.; Espenson, J. H. *Organometallics* **1999**, *18*, 5170. (ff) Kuhn, F. E.; Santos, A. M.; Roesky, P. W.; Herdtweck, E.; Scherer, W.; Gisdakis, P.; Yudanov, I. V.; Di Valentin, C.; Rosch, N. *Chem. Eur. J.* **1999**, *5*, 3603. (gg) Stankovic, S.; Espenson, J. H. *J. Org. Chem.* **2000**, *65*, 5528. (hh) Adam, W.; Saha-Moller, C. R.; Weichold, O. *J. Org. Chem.* **2000**, *65*, 5001. (ii) Kuhn, F. E.; Herrmann, W. A. *Struct. Bond.* **2000**, *97*, 213. (jj) Lahti, D. W.; Espenson, J. H. *Inorg. Chem.* **2000**, *39*, 2164. (kk) Jeon, H. J.; Nguyen, S. T. *Chem. Commun.* **2001**, 235.

(3) This is true regarding olefin epoxidation. However, MTO is known to exhibit metathesis activity (see ref 2k).

(4) Milas, N. A.; Sussman, S. *J. Am. Chem. Soc.* **1936**, *58*, 1302.

(5) The water molecule coordinated to the rhenium center of the bisperoxo complex of MTO is highly acidic: Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1991.

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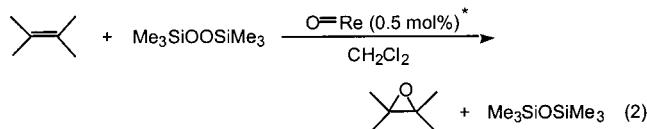
[§] Present address: Senomyx, 11099 N. Torrey Pines Road, La Jolla, CA 92037.

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(1) Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.

MTO) by cheaper and more readily available inorganic rhenium oxides (e.g., Re_2O_7 , $\text{ReO}_3(\text{OH})$, and ReO_3) was accomplished with bis(trimethylsilyl) peroxide (BTSP) as oxidant in place of aqueous H_2O_2 (eq 2).⁷ Systematic investigation of the oxorhenium catalyst precursors and various additives in olefin epoxidation with BTSP are reported in the present paper.



*effective catalysts include MTO, Re_2O_7 , $\text{ReO}_3(\text{OH})$, and ReO_3

Results and Discussion

Discovery of the beneficial effect of pyridine in the MTO-catalyzed epoxidation prompted detailed study of this phenomenon with the goal of further improving the system.⁸ From the very beginning, salient features of the pyridine-modified protocol seemed counterintuitive. For example, base-mediated decomposition pathways of MTO in aqueous H_2O_2 have been established.⁹ The hydroperoxide (HOO^-) species is known to induce decomposition of MTO into methanol and catalytically inactive perrhenate (ReO_4^-). Pyridine would be expected to facilitate this detrimental process by increasing the pH of the medium. Indeed, pyridinium perrhenate is formed during MTO-catalyzed epoxidations mediated by pyridine, but this does not adversely affect the epoxidations of most olefins, since full conversion is reached well before significant levels of catalyst decomposition are reached. Another important role attributed to pyridine in these systems is that of a buffer for the Lewis acidic $\text{Re}(\text{VII})$ species, thereby enabling even sensitive epoxides to survive.

Despite overall efficiency of the original pyridine-modified system, lower conversions were observed for less reactive substrates such as terminal olefins, due to premature destruction of the catalyst. Although 3-cyanopyridine provided a remedy for this class of olefins, a more general way of extending catalyst lifetime became a challenge. Among the known organometallic oxorhenium(VII) species ($\text{R}-\text{ReO}_3$) capable of catalyzing olefin epoxidation, MTO is most stable with respect to oxidative and/or hydrolytic removal of the alkyl group (vide infra). Hence, catalyst modification by variation of the R-substituent on the rhenium center was not rewarding

despite extensive efforts in the Herrmann laboratory.^{2,10} Elimination of water from the reaction could become an alternate path toward increased turnovers because catalyst decomposition should be largely suppressed. At the same time, the presence of pyridine should prevent the epoxide ring opening and allow one to observe ligand effects on the selectivity features of the oxygen atom transfer event. A water-free environment should also eliminate possible complications from phase transfer effects. Obviously, any process that involves H_2O_2 as the oxygen atom source produces at least 1 equiv of water as byproduct, which will defeat an anhydrous system unless an efficient water removal can be incorporated in the process design. A possible solution to the problem could be an oxidant that acts as an "anhydrous" analogue of H_2O_2 . Readily accessible bis(trimethylsilyl) peroxide (BTSP)^{11,12} has been previously used in this capacity.¹³ To our surprise, however, MTO showed little to no reactivity toward BTSP in CDCl_3 (eq 3) under stoichiometric conditions,^{14a} in marked contrast to the reaction between MTO and aqueous H_2O_2 that instantaneously generates a mixture of mono- and bisperoxorhenium

(10) (a) Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R.; Romao, C. C. *Inorg. Chem.* **1992**, *31*, 4431. (b) For the most recent, and best, procedure, see: Herrmann, W. A.; Kratzer, R. M.; Fischer, R. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2652.

(11) (a) Cookson, P. G.; Davies, A.; Fazal, N. *J. Organomet. Chem.* **1975**, *99*, C31. (b) Taddei, M.; Ricci, A. *Synthesis* **1986**, 633. (c) For a convenient, large-scale (0.5 mol) preparation of BTSP from bis(trimethylsilyl)urea and urea/ H_2O_2 complex in dichloromethane, see: Jackson, W. P. *Synlett* **1990**, 536. The product obtained according to this method is virtually free of hexamethyldisiloxane, a common, albeit harmless, byproduct in cognate BTSP preparations. (d) Babin, P.; Bennetau, B.; Dunoguès, J. *Synth. Commun.* **1992**, *22*, 2849. (e) BTSP is now commercially available from Gelest.

(12) **WARNING:** Thermal stabilities of silylated organic peroxides have been studied: Vesnovskii, B. P.; Thomadze, A. V.; Suchevskaya, N. P.; Aleksandrov, Yu. A. *Zh. Prikl. Khim.* **1982**, *55*, 1005. Pure BTSP has an active oxygen content of only 9% (cf. *tert*-butyl hydroperoxide 17.8%; di-*tert*-butyl peroxide 10.9%; hydrogen peroxide 47%). We would like to stress, however, that despite its great thermal stability, BTSP is subject to facile hydrolysis in the presence of water and acids which results in formation of hazardous 100% H_2O_2 . Additionally, Professors Henri Kagan and Dieter Seebach recently brought to our attention two reports that document explosions upon contact between BTSP and metal needles: (a) Riant, O.; Samuel, O.; Flessner, T.; Taudien, S.; Kagan, H. B. *J. Org. Chem.* **1997**, *62*, 6733. (b) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. Thus, only plastic or glass pipets should be used in handling BTSP.

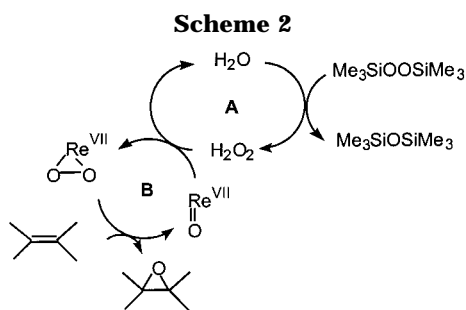
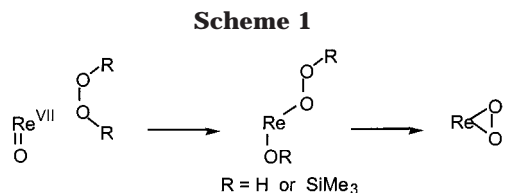
(13) For applications of BTSP in organic synthesis, see: (a) Brandes, D.; Blaschette, A. *J. Organomet. Chem.* **1973**, *49*, C6. (b) Brandes, D.; Blaschette, A. *Ibid.* **1974**, *73*, 217. (c) Tamao, K.; Kumada, M.; Takahashi, T. *Ibid.* **1975**, *94*, 367. (d) Salomon, M. F.; Salomon, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4290. (e) Adam, W.; Rodriguez, A. *J. Org. Chem.* **1979**, *44*, 4969. (f) Suzuki, M.; Takada, H.; Noyori, R. *Ibid.* **1982**, *47*, 902. (g) Weber, W. P. *Silicon Reagents in Organic Synthesis*; Springer-Verlag: New York, 1983. (h) Kanemoto, S.; Oshima, K.; Matsubara, S.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2185. (i) Matsubara, S.; Takai, K.; Nozaki, H. *Ibid.* **1983**, *24*, 3741. (j) Matsubara, S.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2029. (k) See ref 6b. (l) Hayakawa, Y.; Uchiyama, M.; Noyori, R. *Tetrahedron Lett.* **1986**, *27*, 4195. (m) Curci, R.; Mello, R.; Troisi, L. *Tetrahedron* **1986**, *42*, 877. (n) Kanemoto, S.; Matsubara, S.; Takai, K.; Oshima, K.; Utimoto, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3607. (o) Davis, F. A.; Lal, S. G.; Wei, J. *Tetrahedron Lett.* **1988**, *29*, 4269. (p) Olah, G. A.; Ernst, T. D. *J. Org. Chem.* **1989**, *54*, 1204. (q) Camporeale, M.; Fiorani, T.; Troisi, L.; Adam, W.; Curci, R.; Edwards, J. O. *Ibid.* **1990**, *55*, 93. (r) Shibata, K.; Itoh, Y.; Tokitoh, N.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3749. (s) Chémia, F.; Julia, M.; Uguen, D. *Bull. Soc. Chim. Fr.* **1993**, *130*, 547. (t) Irie, R.; Hosoya, N.; Katsuki, T. *Synlett* **1994**, 255. (u) Prouilhac-Cros, S.; Babin, P.; Bennetau, B.; Dunoguès, J. *Bull. Soc. Chim. Fr.* **1995**, *132*, 513. (v) Adam, W.; Korb, M. N. *Tetrahedron* **1996**, *52*, 5487. (w) Adam, W.; Golsch, D.; Sundermeyer, J.; Wahl, G. *Chem. Ber.* **1996**, *129*, 1177. (x) Barton, D. H. R.; Chabot, B. M. *Tetrahedron* **1997**, *53*, 487. (y) Barton, D. H. R.; Chabot, B. M. *Ibid.* **1997**, *53*, 511. (z) see ref 12. (aa) Sakurada, I.; Yamasaki, S.; Gottlich, R.; Iida, T.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 1245. (bb) Cox, P. B.; Loh, V. M.; Monteils, C.; Baxter, A. D.; Boyd, E. A. *Tetrahedron Lett.* **2001**, *42*, 125.

(6) (a) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189. (b) Copéret, C.; Adolffson, H.; Sharpless, K. B. *Chem. Commun.* **1997**, *16*, 1565. (c) Adolffson, H.; Copéret, C.; Chiang, J. P.; Yudin, A. K. *J. Org. Chem.* **2000**, *65*, 8651.

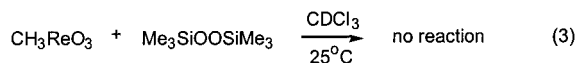
(7) Yudin, A. K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 11536.

(8) For a recent mechanistic investigation of the MTO-catalyzed olefin epoxidation, see ref 2p.

(9) (a) Herrmann et al. used *N*-bases in order to suppress epoxide ring opening (see ref 5) albeit at the expense of detrimental effect on catalytic activity. For the most recent study of the MTO/Lewis base catalysts in olefin epoxidation, see: Herrmann, W. A.; Ding, H.; Kratzer, R. M.; Kühn, F. E.; Haider, J. J.; Fischer, R. W. *J. Organomet. Chem.* **1997**, *549*, 319. (b) For a comprehensive study on the base-induced decomposition of MTO, see: Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966. (c) In the presence of pyridine and H_2O_2 , MTO is slowly oxidized, producing pyridinium perrhenate and CH_3OH : Yudin, A. K.; Sharpless, K. B., unpublished results. (d) Herrmann, W. A.; Kratzer, R. M.; Ding, H.; Thiel, W. R.; Glas, H. *J. Organomet. Chem.* **1998**, *555*, 293. (e) Adolffson, H.; Converso, A.; Sharpless, K. B. *Tetrahedron Lett.* **1999**, *40*, 3991.



complexes.² As previously reported by Curci et al.,^{14b} BTSP is at least 50 times more reactive than H₂O₂ in stoichiometric oxidation of sulfides to sulfoxides which may account for the observed lack of *nucleophilic* reactivity of BTSP toward Re(VII) in our system.



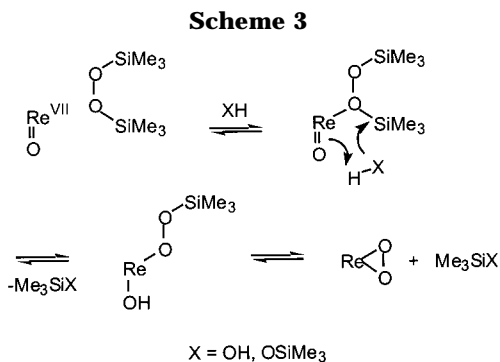
The expected formation of the peroxo complexes in the BTSP/Re(VII) system must be accompanied by silylation of the rhenium-bound oxo ligand (Scheme 1, R = SiMe₃). This process is apparently much slower than its protic counterpart (Scheme 1, R = H). Formation of the peroxo complexes in the MTO/BTSP system does occur, *but only upon addition of 1 equiv amount of water*. Hydrolytic generation of H₂O₂ from BTSP accounts for this result, and we subsequently established that a *catalytic* amount of MTO is sufficient to generate H₂O₂ in the BTSP/H₂O system.¹⁵ Other proton sources (e.g., CH₃OH) are equally effective in promoting hydrolysis.

In accord with the aforementioned observations, no olefin epoxidation takes place in the MTO/BTSP system under water-free conditions. A *trace* of a protic species (e.g., water) is essential to enable rapid turnover of the catalytic cycle.¹⁶ The scenario shown in Scheme 2 involves hydrolytic generation of free H₂O₂ from BTSP. Thus, intrinsic “slow addition” of hydrogen peroxide to the oxorhenium species is managed by the “proton dependent” cycle A (Scheme 2) which accomplishes transfer of the peroxo group from silicon to rhenium (cycle B). This represents a novel “controlled release” mode for the H₂O₂

(14) (a) We felt that the substantial Lewis acidity of MeReO₃ would enable it to react with BTSP. (b) Curci et al. has demonstrated that silylated peroxides are 50 to 100 times more effective than the corresponding hydrido analogues in *electrophilic* oxygen atom transfer to sulfides. Simple rate laws that do not require acid catalysis were deduced for these processes (see ref 2m).

(15) BTSP is hydrolyzed to H₂O₂ within 2 h in the presence of 1 equiv of H₂O and 0.5 mol % MTO (Yudin, A. K.; Sharpless, K. B., unpublished results).

(16) An induction period can be attributed to the necessity of “acidity build-up”. Adventitious moisture can trigger an autocatalytic decomposition of acid-sensitive BTSP into H₂O₂ and hexamethyldisiloxane. Alternatively, *partial* hydrolysis of BTSP could afford Me₃SiOOH which could act as an oxidant in the present system. For the use of silyl hydroperoxides in epoxidation, see: (a) Dannley, R. L.; Jalics, G. J. *J. Org. Chem.* **1965**, *30*, 2417. (b) Rebek, J.; McCready, R. *Tetrahedron Lett.* **1979**, *20*, 4337.



addition in rhenium-catalyzed epoxidation processes.¹⁷ In contrast, it is impossible to exercise such control in H₂O₂ (aqueous or anhydrous) protocols.¹⁸ Slow addition of H₂O₂ does not help in achieving higher conversions due to faster MTO decomposition at lower H₂O₂ concentrations.⁷

The most significant outcome of the limited water content in the present system is high catalytic epoxidation activity of *inorganic* high valent oxorhenium species. Thus, simple inorganic derivatives (e.g., Re₂O₇, ReO₃⁻(OH), and ReO₃) efficiently catalyze epoxidations with BTSP despite the hydrolytic instability of inorganic rhenium peroxides.¹⁹

Although we have established that MTO catalyzes generation of H₂O₂ from BTSP, the requirement for protic species in epoxidation can be explained by other closely related scenarios. In a more general way, the need for a proton source is accommodated in Scheme 3 where a regenerable XH species helps in ferrying the peroxo group from silicon to rhenium.

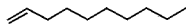
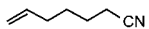
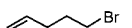
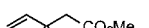


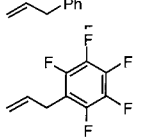
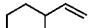

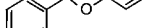

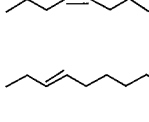

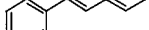

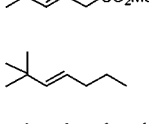


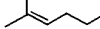
Having established the requirement for a proton source, we examined how the amount of such additive affects the reaction. For instance, reactivity was found to be a function of water concentration, and beyond a certain range (5–10 mol %) catalysis became inefficient, either due to the limited number of turnovers (cycle A) or due to the sensitivity of the catalytically active species to water. In fact, we noted that when excess water (1 equiv relative to the olefin) is added at the beginning of the MTO-catalyzed epoxidation of *cis*-4-octene, BTSP is hydrolyzed within 10 min (as determined by GC), and poor conversions are observed. In addition, significant amount of the diol, resulting from hydrolytic ring opening of the epoxide, is formed. At the other extreme, efforts to remove all traces of water by running the process in the presence of 4 Å molecular sieves almost stopped the epoxidation catalysis. Control experiments demonstrate that MTO is not absorbed or inactivated by the molecular sieves under these conditions, ruling out catalyst removal as the origin of lost activity. Similarly, very sluggish reaction takes place when Re₂O₇ is used as a catalyst for the epoxidation of 1-decene under anhydrous conditions (ca. 7% conversion after 2.5 h). The reaction is dramatically accelerated upon addition of 5 mol % water and reaches 70% completion within 1 h. It appears that the

(17) For recent use of HReO₄/BTSP system for pyridine *N*-oxidation, see Copéret, C.; Adolffson, H.; Chiang, J. P.; Yudin, A. K.; Sharpless, K. B. *Tetrahedron Lett.* **1998**, *39*, 761.

(18) Ironically, MTO is stabilized at higher H₂O₂ concentrations: Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157.

(19) Peroxo perrhenic acid (H₄Re₂O₁₃) was isolated in the Re₂O₇/H₂O₂ system as a highly hydrolytically labile, explosive compound: Herrmann, W. A.; Correia, J. D. G.; Kuhn, F. E.; Artus, G. R. J. *Chemistry – A Eur. J.* **1996**, *2*, 168.

Table 1. Epoxidation of Olefins with Bis(trimethylsilyl) Peroxide (BTSP) Catalyzed by High-Valent Oxorhenium Derivatives^{a,b}

Entry	Alkene	Catalyst Precursor/ ^c Solvent	Yield, %	Time, h
1		A / CH ₂ Cl ₂	94	14
2		A / CH ₂ Cl ₂	92	18
3		B / CH ₂ Cl ₂	82	9
4		B / CH ₂ Cl ₂	77	15
5		B / CH ₂ Cl ₂	82	3
6		B / CH ₂ Cl ₂	88	9
7		C / CH ₂ Cl ₂	90	15
8		A / CH ₂ Cl ₂	95	7
9		B / CH ₂ Cl ₂	95	8
10		D / CH ₂ Cl ₂	88	12
11		E / CH ₂ Cl ₂	80	18
		F / CH ₂ Cl ₂	90	9
12		A / THF	96	10
		B / CH ₂ Cl ₂	90	3
13		B / CH ₂ Cl ₂	90	3
14		B / CH ₂ Cl ₂	70	4
15		G / CH ₂ Cl ₂	96	4
16		G / CH ₂ Cl ₂	81	14
17		G / CH ₂ Cl ₂	82	14
18		A / CH ₂ Cl ₂	82	10
19		A / CH ₂ Cl ₂	78	13

^a 10 mmol scale. ^b 1.5 equiv of BTSP per double bond was used. ^c A: Re₂O₇ (0.5 mol %), H₂O (5 mol %); B: ReO₃ (0.5 mol %), H₂O (5 mol %); C: ReO₃ (0.5 mol %), H₂O (1 mol %); D: Re₂O₇ (0.5 mol %), pyridine (1 mol %), H₂O (5 mol %); E: 2py/HReO₄ (0.5 mol %), H₂O (5 mol %); F: MTO (0.5 mol %), H₂O (5 mol %); G: ReO₃ (0.5 mol %), pyridinium trifluoroacetate (5 mol %).

optimal water concentration is in the 5–10 mol % range depending on the substrate (vide supra).

The Role of Pyridine Derivatives and Other Additives. In accord with previous observations,^{6a} additives such as pyridines serve to prevent sensitive epoxide ring opening by buffering the highly acidic rhenium species. Moreover, under present homogeneous conditions, the modulation of reactivity at the rhenium center is uncoupled from the phase transfer effects. Participation of water as a potential ligand is also minimized.²⁰ Compared to the original process, the

amount of the pyridine ligand which is necessary for the desired epoxide protection, is now decreased from 12 to 0.5–1 mol %. In the case of aqueous H₂O₂/MTO system, pyridine induces formation of the catalytically inactive perhenic acid which results in lower turnovers for less reactive substrates. In principle, inorganic oxorhenium catalysts should easily tolerate pH increase since no labile R–Re bond is present in the catalytically active species. At the same time, catalytic turnover in the present system crucially depends on efficient hydrolysis of BTSP and excess pyridine (10–12 mol %) dramatically slows down the reaction for all substrates. The optimal amount of the pyridine additive sufficient to maintain the epoxide protection is 0.5–1 mol % with minimal detrimental effect on the rate.⁷ We have also found that progenitors of highly sensitive epoxides do not tolerate even relatively low water concentrations. The preferred proton sources in such instances should contain conjugate bases of low nucleophilicity which do not participate in epoxide ring opening. In this regard, pyridinium trifluoroacetate was found to be particularly effective as a supplier of protons (Table 1, entries 15–17).

Catalyst Precursors. Comparable reactivity is observed among all inorganic oxorhenium derivatives (see Table 1). However, ReO₃ is preferred (at least for laboratory scale epoxidations) due to its non-hydroscopic nature relative to Re₂O₇. Unlike the rest of the precatalysts, ReO₃ does not dissolve in the reaction milieu at the start. As the reaction proceeds, Re(VI) is rapidly oxidized to Re(VII), so that the solution acquires bright yellow color, characteristic of the peroxorhenium(VII) species.

One of the most significant implications of the present controlled H₂O₂ release version of epoxidation is overall increase in the lifetime of oxorhenium catalysts. Indeed, hydrolytic removal of the methyl group from the rhenium center of the catalyst is no longer the origin of lost activity. Thus, the catalytically active species are preserved throughout the process and can be reused after evaporative removal of the solvent and the epoxide.

Substrate Scope. Table 1 defines the scope of this new process with representative substrates including fairly unreactive olefins and/or precursors to sensitive epoxides. The optimal substrate concentration is in the 0.5–2 M range with dichloromethane as solvent.²¹ No special precautions to exclude moisture during the reaction need to be taken. We stress, however, that because the catalytic turnover depends on the presence of protic additives and is inhibited at high water concentrations, it is good practice to account for any water beyond the deliberately added amount. With this in mind we recommend anhydrous dichloromethane. Upon completion of the reaction, the workup procedure simply involves

(20) Variable temperature NMR experiments indicate lability of the rhenium-bound pyridine ligands. Thus, ¹H NMR spectra of MTO in the presence of 2 equiv of pyridine are identical at –65 °C and at 25 °C and show one kind of pyridine species (Yudin, A. K.; Sharpless, K. B., unpublished results).

(21) Such species had long been known to exhibit weak activity as epoxidation catalysts: (a) For the epoxidation of C_{2–20} olefins with stoichiometric Re₂O₇ in the presence of pyridine, see: Union Oil Co. of California (Fenton, D. M.) US 3,316,279. (c) For early applications of Re₂O₇ in olefin/H₂O₂ oxidation catalysis, see: duPont de Nemours and Co. (Parshall, G. W.) US 3, 657, 292 and 3,646,130, 1972. (d) Warwel and co-workers found that Re₂O₇ is a more effective epoxidation catalyst if the right solvent is chosen. Their system employs 60% aqueous H₂O₂ in 1,4-dioxane at 90 °C and 1,2-diols are isolated in good yields, the initially formed epoxides being unstable in this system: Warwel, S.; Rüschen Klaas, M.; Sojka, M. *Chem. Commun.* **1991**, 1578. (e) See ref 17.

destruction of the traces of H_2O_2 with manganese dioxide and evaporation of dichloromethane and hexamethyldisiloxane ($\text{Me}_3\text{SiOSiMe}_3$, bp 100 °C).

With the present system, terminal olefins, problematic in the original procedure,^{6a} are efficiently converted into the corresponding epoxides within short reaction times. Disubstituted olefins (both cis and trans) present little problem as do the tri- and tetrasubstituted olefins. However, in the latter two cases water has to be replaced by pyridinium trifluoroacetate as an external proton source (vide supra). Thereby, a conjugate base of lower nucleophilicity is involved which reduces the undesired epoxide ring opening. Notably, the original H_2O_2 /pyridine system remains superior for the preparation of certain extremely acid-sensitive epoxides such as styrene oxide and indene oxide. Easily oxidizable substrates such as phenyl ethers are also beyond the scope of this new protocol due to the competitive oxidation of the aromatic ring.

Conclusions. Conditions were found under which simple inorganic oxorhenium compounds act, for the first time, as efficient olefin epoxidation catalysts.^{21,22} The crucial factor enabling these inorganic oxorhenium species to exhibit high activity for epoxidation catalysis is thought to be the nearly anhydrous conditions which are achieved and maintained by using BTSP as the oxygen atom source, along with only a trace of a protic agent (e.g., H_2O) to catalyze slow transfer of the peroxide moiety from silicon to rhenium. If, as seems probable, BTSP becomes available on a large scale, this new "anhydrous" rhenium-catalyzed process could become one of the most convenient methods available for epoxidation of olefins at either laboratory or fine chemical production scales. In addition to the fact that the inexpensive inorganic rhenium catalyst precursors are as effective as MTO, an especially attractive feature of these "anhydrous" systems is the simple workup which entails only rotary evaporation of the dichloromethane and hexamethyldisiloxane from the reaction mixture.

Experimental Section

General. Anhydrous hexanes and dichloromethane were obtained using the method described by Grubbs.²³ BTSP was obtained using literature procedure.¹¹ All olefins and rhenium derivatives were purchased from Aldrich Chemical Co.

Standard Procedure for Epoxidation with Re_2O_7 /BTSP Using Water as a Proton Source (exemplified for 1-decene, Table 1, entry 1). In a 25 mL scintillation vial equipped with a magnetic stirrer was placed 1-decene (1.41 g, 10 mmol) followed by addition of 4 mL of dichloromethane. To this solution was added BTSP¹² (2.8 g, 15 mmol). The vial was immersed into ice/water bath. After 5 min Re_2O_7 (24 mg, 0.05 mmol) was added followed by 10 μL of water. The reaction turned bright yellow and was allowed to warm to room temperature and stirred for 14 h. Disappearance of BTSP in the course of the reaction was monitored by gas chromatography. Upon completion, water (3 drops) was added followed by manganese dioxide (ca. 5 mg) in order to decompose the remaining H_2O_2 . The destruction of H_2O_2 was evident by the disappearance of yellow color. The mixture was then dried over Na_2SO_4 . Concentration afforded 1-decene oxide (1.48 g, 94%

yield) of a colorless oil. Analytically pure sample was obtained by distillation.

Standard Procedure for Epoxidation with ReO_3 /BTSP Using Water as a Proton Source (exemplified for *trans*-3-decene, Table 1, entry 11). In a 25 mL scintillation vial equipped with a magnetic stirrer was placed *trans*-3-decene (1.41 g, 10 mmol) followed by addition of 4 mL of dichloromethane. To this solution was added BTSP¹² (2.8 g, 15 mmol). The vial was immersed into ice/water bath. After 5 min ReO_3 (11.7 mg, 0.05 mmol) was added followed by 10 μL of water. The reaction turned bright yellow and was allowed to warm to room temperature and stirred for 9 h. Disappearance of BTSP in the course of the reaction was monitored by gas chromatography. Upon completion, water (3 drops) was added followed by manganese dioxide (ca. 5 mg) in order to decompose the remaining H_2O_2 . The destruction of H_2O_2 was evident by the disappearance of yellow color. The mixture was then dried over Na_2SO_4 . Concentration afforded *trans*-3-decene oxide (1.41 g, 90% yield) of a colorless oil. Analytically pure sample was obtained by distillation.

Standard Procedure for Epoxidation with ReO_3 /BTSP Using Pyridinium Trifluoroacetate as a Proton Source (exemplified for 2-methyl-2,3-tetradecene, Table 1, entry 16). In a 25 mL scintillation vial equipped with a magnetic stirrer was placed 2-methyl-2-tetradecene (1.96 g, 10 mmol) followed by addition of 4 mL of dichloromethane. To this solution was added BTSP¹² (2.8 g, 15 mmol). The vial was immersed into ice/water bath. After 5 min ReO_3 (11.7 mg, 0.05 mmol) was added followed by pyridinium trifluoroacetate (97 mg, 5 mol %). The reaction turned bright yellow and was allowed to warm to room temperature and stirred for 14 h. Disappearance of BTSP in the course of the reaction was monitored by gas chromatography. Upon completion, water (3 drops) was added followed by manganese dioxide (ca. 5 mg) in order to decompose the remaining H_2O_2 . The destruction of H_2O_2 was evident by the disappearance of yellow color. The mixture was then dried over Na_2SO_4 . Concentration afforded 2-methyl-2,3-epoxytetradecane (1.71 g, 81% yield) of a colorless oil. Analytically pure sample was obtained by distillation.

1,2-Epoxy-5-bromopentane: ^1H NMR (400 MHz, CDCl_3) δ 1.45–1.65 (m, 1 H), 1.68–1.85 (m, 1 H), 1.85–2.10 (m, 2 H), 2.40–2.50 (m, 1 H), 2.60–2.8 (m, 1 H), 2.80–3.00 (m, 1H), 3.30–3.50 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.12, 30.84, 33.07, 46.75, 51.26.

3,4-Epoxy-2,2-dimethylpentanoic acid methyl ester: ^1H NMR (400 MHz, CDCl_3) δ 0.92 (s, 3 H), 0.94 (s, 3 H), 2.21 (d, $J = 14$ Hz, 1 H), 2.28 (d, $J = 14$ Hz, 1 H), 2.56–2.62 (m, 2 H), 2.83–2.85 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.25, 23.47, 33.31, 43.65, 44.00, 51.26, 58.59, 171.84; High-resolution MS calcd for $\text{C}_8\text{H}_{15}\text{O}_3$ ($M + 1$) 159.1021, found 157.1026.

1,2-Epoxy-5-acetoxypentane: ^1H NMR (400 MHz, CDCl_3) δ 1.40–1.90 (m, 4 H), 1.99 (s, 3 H), 2.40–2.44 (m, 1 H), 2.60–2.75 (m, 1 H), 2.80–2.90 (m, 1 H), 3.90–4.10 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.08, 25.09, 28.97, 46.91, 51.65, 63.86, 171.02.

1,2-Epoxy-3-phenylpropane: ^1H NMR (400 MHz, CDCl_3) δ 2.56 (d, $J = 2.68$ Hz, 1 H), 2.57 (d, $J = 2.68$ Hz, 1 H), 2.79–2.97 (m, 3 H), 3.15–3.19 (m, 1 H), 7.25–7.37 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.61, 46.68, 52.28, 126.51, 128.44, 128.93, 137.05.

1,2-Epoxy-3-ol benzyl ether: ^1H NMR (400 MHz, CDCl_3) δ 2.61 (m, 1 H), 2.78 (m, 1 H), 3.19 (m, 1H), 3.44 δ (m, 1 H), 3.78 (m, 1H), 4.56 (d, $J = 18.34$ Hz, 1 H), 4.70 (d, $J = 18.34$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 44.24, 50.82, 70.73, 73.32, 127.61, 128.30, 128.37, 137.79.

***trans*-2,3-Epoxyheptanoic acid methyl ester:** ^1H NMR (400 MHz, CDCl_3) δ 0.80–1.00 (t, $J = 2.68$ Hz, 3 H), 1.10–1.25 (t, $J = 7.08$ Hz, 3 H), 1.45–1.60 (m, 2 H), 2.40–2.60 (m, 2 H), 2.60–2.70 (m, 1 H), 2.90–3.00 (m, 1 H), 4.00–4.15 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 9.57, 14.00, 24.66, 37.63, 53.55, 59.43, 60.61, 170.32.

***trans*-2,3-Epoxy-2-ethyloctane:** ^1H NMR (400 MHz, CDCl_3) δ 0.85–0.91 (t, $J = 7.44$ Hz, 6 H), 0.91–1.00 (t, $J = 7.56$ Hz, 3 H), 1.30–1.70 (m, 10 H), 2.68–2.71 (t, $J = 6.00$ Hz,

(22) MTO and Re_2O_7 were purchased from Strem Chemicals, Inc. ReO_3 and HOReO_3 were purchased from Aldrich Chemical Co. For industrial sources of rhenium, see: Peacock, R. D. *The Chemistry of Technetium and Rhenium*; Elsevier: Amsterdam, 1966.

(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.08, 25.09, 28.97, 46.91, 51.65, 63.86, 171.02.

trans-3,4-Epoxy-2,2-dimethylheptane: ^1H NMR (400 MHz, CDCl_3) δ 0.84 (s, 9 H), 0.87–0.90 (t, $J = 7.12$ Hz, 3 H), 1.30–1.55 (m, 4 H), 2.38 (d, $J = 2.44$ Hz, 1 H), 2.69–2.72 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.84, 19.37, 25.72, 30.56, 34.23, 55.19, 66.77.

2,3-Epoxy-2-methyltetradecane: ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, $J = 6.8$ Hz, 3 H), 1.20–1.55 (m, 26 H), 2.69 (t, $J = 5.9$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.06, 18.69, 22.66, 24.89, 26.49, 28.82, 29.32, 29.48, 29.54, 29.56, 29.61, 31.90, 58.19, 64.56.

2,3-Dimethyl-2,3-epoxyheptane: ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, $J = 6.8$ Hz, 3 H), 1.20–1.50 (m, 4 H), 1.28 (s, 3H), 1.29 (s, 3H), 1.30 (s, 3H), 1.52–1.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.03, 18.56, 20.85, 21.39, 22.94, 27.81, 34.91, 62.22, 64.84.

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