

Bis(trimethylsilyl) Peroxide Extends the Range of Oxorhenium Catalysts for Olefin Epoxidation

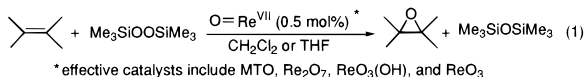
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The main goal of our research over the years has been the development of catalytic reactions for the selective oxidation of olefins. These endeavors led recently to a highly efficient olefin epoxidation process.¹ This new method is similar to the earlier Herrmann epoxidation system^{2a–d} in that both use methyltrioxorhenium (MTO) as the catalyst source and hydrogen peroxide as the oxidant. The crucial difference in the new procedure is the requirement for pyridine ligands but the solvent switch (from *tert*-butyl alcohol^{2b} to methylene chloride¹) also greatly enhances the effectiveness of the pyridine-modified rhenium catalyst. We report here on further improvements in this epoxidation catalysis, the most significant being replacement of the organometallic rhenium species (e.g., MTO) by cheaper and more stable inorganic rhenium oxides (e.g., Re₂O₇, ReO₃(OH), and ReO₃).

Among the known organometallic oxorhenium (VII) species (R–ReO₃) capable of catalyzing olefin epoxidation, MTO appears to be the most stable with respect to oxidative and/or hydrolytic removal of the alkyl group (*vide infra*).³ Hence, catalyst modification by variation of the R-substituent on the rhenium center was not rewarding despite extensive efforts in the Herrmann laboratory.^{2a–d,4} In addition, R–ReO₃ compounds, including MTO, are quite expensive.⁵ These factors provided the incentive to seek water-free epoxidation conditions which would hopefully extend the lifetime of the MTO catalyst. This goal and much more was accomplished by simply replacing aqueous H₂O₂ with bis(trimethylsilyl)peroxide (BTSP)^{6–8} as an oxygen atom source (eq 1).



In addition to MTO, readily available inorganic rhenium oxides (e.g., Re₂O₇, ReO₃(OH), and ReO₃) were also found to

(1) (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.

(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 Pat. 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) Boelwou, 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) Espenson, J. H.; Abu-Omar, M. M. *Adv. Chem. Ser.* **1997**, *253*, 99. (l) ARCO Chemical Technology; Crocco, G. L.; Shum, W. P.; Zajacek, J. G.; Kesling, H. S., Jr.; US Pat 5.166.372, 1992.

(3) (a) 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. (b) In the presence of pyridine and H₂O₂, MTO is slowly oxidized, producing pyridinium perrhenate and CH₃OH: Yudin, A. K.; Sharpless, K. B. Unpublished results.

(4) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169.

(5) (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. *et al.* In press.

exhibit high catalytic activity. Table 1 defines the scope of this new process with representative substrates including fairly unreactive olefins and/or progenitors of sensitive epoxides.^{9,10} With the present protocol, terminal olefins, problematic in the original procedure,^{1a} can be efficiently converted into the corresponding epoxides. The work-up procedure simply involves destruction of the traces of H₂O₂ with manganese dioxide and evaporation of the hexamethyldisiloxane.¹⁰

We found that when water (1 equiv with respect to the olefin) is intentionally 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 presumably due to the sensitivity of the generated epoxidizing species to excess water (*vide infra*). In addition, a 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 demonstrated that MTO is not absorbed or inactivated by the molecular sieves under these conditions. Similarly, very sluggish epoxidation is observed when Re₂O₇

(6) (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/H₂O₂ 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 (see the Supporting Information for details of a 1 mol preparation). (d) Babin, P.; Bennetau, B.; Dunoguès, J. *Synth. Commun.* **1992**, *22*, 2849.

(7) Thermal stabilities of silylated organic peroxides have been studied: Vesnovskii, B. P.; Thomadze, A. V.; Suchevskaia, 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%).

(8) 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.; Bennetau, B.; Dunoguès, J. *Bull. Chem. 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) We recently became aware that Sundermeyer and co-workers used BTSP for the oxidation of olefins and aromatic hydrocarbons catalyzed by the d⁰-oxo- and -peroxo metal complexes: Kleinhenz, D.; Jost, C.; Wahl, G.; Sundermeyer, J. Submitted for publication.

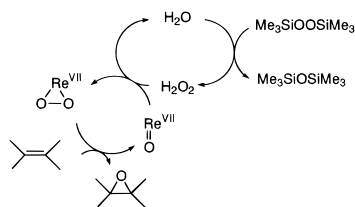
(9) The original MTO-based procedure (ref 1a) remains superior for the preparation of highly acid-sensitive epoxides (e.g., indene oxide).

(10) Standard procedure for epoxidation on a 10 mmol scale in dichloromethane exemplified for 1-decene (Table 1, entry 3). In a 25 mL scintillation vial equipped with a magnetic stirring bar, 1-decene (1.41 g, 10 mmol) was placed followed by addition of 4 mL of dichloromethane. To this solution was added BTSP (2.8 g, 15 mmol). The vial was immersed into ice/water bath. After 5 min Re₂O₇ (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 H₂O₂. The destruction of H₂O₂ was evident by the disappearance of yellow color. The mixture was then dried over Na₂SO₄. Concentration afforded 1-decene oxide (1.48 g, 94% yield) of a colorless oil. Analytically pure sample was obtained by distillation.

Table 1. Epoxidation of Olefins with Bis(trimethylsilyl) Peroxide (BTSP) Catalyzed by High-Valent Oxorhenium Derivatives

Entry ^{a,b}	Olefin	Catalyst Precursor ^{c,f} Solvent	Time (h)	Isolated Yield (%)
1		A / CH ₂ Cl ₂	15	92
		B / CH ₂ Cl ₂	20	90
		C / CH ₂ Cl ₂	12	88
2		A / CH ₂ Cl ₂	9	90
		D / CH ₂ Cl ₂	16	85
		F / CH ₂ Cl ₂	11	79
3		D / CH ₂ Cl ₂	14	94
		D / neat	8	83
4		D / CH ₂ Cl ₂	18	92
5		D / CH ₂ Cl ₂	7	95
6		D / THF	10	96
7 ^d		E / THF	12	68
		G / THF	10	82
8 ^e		G / THF	13	78

(a) 10 mmol scale; (b) 1.5 eq BTSP per double bond was used; (c) A: CH₃ReO₃ (0.5 mol%), pyridine (1 mol%); B: CH₃ReO₃ (0.25 mol%), pyridine (0.5 mol%); C: Re₂O₇ (0.5 mol%), pyridine (1 mol%); D: Re₂O₇ (0.5 mol%); E: HReO₄ (0.5 mol%); F: ReO₃ (0.5 mol%); G: Re₂O₇ (1 mol%); (d) *syn*-diepoxide was obtained (>99:1); (e) *anti*-diepoxide was obtained (>99:1)

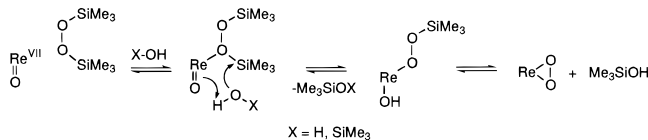
Scheme 1

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. On the basis of these observations, there appears to be a role for a *trace* of water or similar protic species (e.g., CH₃OH is also effective) to enable rapid turnover of the catalytic cycle.¹¹ The scenario shown in Scheme 1 indicates the hydrolytic generation of free H₂O₂ from BTSP.

Thus, intrinsic “slow addition” of hydrogen peroxide to the oxorhenium precursor is managed by the “proton dependent” cycle (Scheme 1) which accomplishes transfer of the peroxy group from Si to Re. In contrast, it is very difficult to exercise such control in the H₂O₂ (aqueous or anhydrous) MTO-catalyzed epoxidation processes; for example, slow addition of H₂O₂ does not help in achieving higher conversions due to faster MTO decomposition at lower H₂O₂ concentrations.¹²

Worthy of note, hydrolysis of BTSP to H₂O₂ (Scheme 1) is the simplest of many scenarios which could explain the requirement for protic species. In a more general way, the need for a proton source is accommodated in Scheme 2. Here, a

(11) In contrast to epoxidation with aqueous H₂O₂ where equilibrating bis- and monoperoxy complexes are produced instantaneously upon exposure of the catalyst to the oxidant, the reaction between equimolar amounts of MTO and BTSP has a considerable induction period under anhydrous conditions. We attribute this phenomenon to the necessity of “acidity build-up” (the water molecule coordinated to the rhenium center of the bisperoxy complex of MTO is highly acidic: Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem. Int. Ed. Engl.* **1993**, *103*, 1991). Adventitious moisture can trigger an autocatalytic decomposition of an 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. *Org. Chem.* **1965**, *30*, 2417. (b) Rebek, J.; McCready, R. *Tetrahedron Lett.* **1979**, *20*, 4337.

Scheme 2

regenerable XOH species helps in ferrying the peroxy group from silicon to rhenium.¹¹

In accord with the previous observations, additives such as pyridines serve to prevent sensitive epoxide ring-opening by buffering the highly acidic rhenium species.¹ Notably, compared to the original system, the amount of ligand necessary to achieve the desired protection is now decreased from 12 to 0.5–1 mol % in both MTO and Re₂O₇-catalyzed epoxidations.¹³ In some instances MTO loadings can be lowered to 0.25 mol % without affecting conversions—a manifestation of prolonged catalyst lifetime under the present conditions.

The use of Re₂O₇, ReO₃(OH), and ReO₃ as catalyst precursors is a particularly important feature of the present protocol. Catalytic activities of these inorganic rhenium species for epoxidation with H₂O₂ were known to be very poor.¹⁴ Generally, the high acidity of these systems does not allow epoxides to be isolated except in special cases such as *cis*-cyclooctene (which yields an epoxide which is particularly resistant to acid-catalyzed ring opening).^{14e} In the present system, Re oxides are comparable and in some cases superior to MTO especially for the epoxidation of terminal olefins and dienes. The cost of the process can be significantly reduced by using these less-expensive oxorhenium catalysts in combination with BTSP which is now more available through improved preparations.^{6,15} We 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% H₂O₂.⁸

In summary, conditions were found under which simple inorganic oxorhenium species act, for the first time, as efficient olefin epoxidation catalysts. It appears that the hydrolytic stability of MTO has been the sole reason for its superiority over other rhenium oxides for epoxidation catalysis. In addition, use of BTSP, which can be easily and economically prepared on a large scale, leads to one of the simplest epoxidation processes imaginable.

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Supporting Information Available: Experimental details (2 pages). See any current masthead for ordering and Internet access instructions.

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(12) 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.

(13) The use of 12 mol % of pyridine completely arrested the reaction, presumably due to base-mediated decomposition of MTO (see also ref 3).

(14) (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 Pat. 3,316, 279. (b) For early applications of Re₂O₇ in olefin/H₂O₂ oxidation catalysis see: duPont de Nemours and Co.; Parshall, G. W.; US Pat. 3,657,292 and 3,646,130, 1972. (c) 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.; Rüsche gen Klaas, M.; Sojka, M. *Chem. Commun.* **1991**, 1578. (d) Herrmann, W. A.; Correia, J. D. G.; Kuhn, F. E.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 168.

(15) MTO and Re₂O₇ were purchased from Strem Chemicals, Inc. ReO₃ and HOREO₃ were purchased from Aldrich Chemical Co. For industrial sources of rhenium, see: Peacock, R. D. *The Chemistry of Technetium and Rhenium*; Elsevier: Amsterdam, 1966.