

# SYNLETT Spotlight 96

## Methyltrioxorhenium (MTO)

Compiled by Gianluca Soldaini



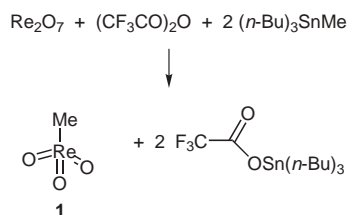
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Gianluca Soldaini studied chemistry at the University of Florence where he received his Graduated Diplome in 2001. He is currently working on his Ph.D. thesis under the supervision of Prof. A. Goti at the University of Florence. His research focuses on metal-catalyzed oxidation reactions.

Dipartimento di Chimica Organica "Ugo Schiff", Università degli Studi di Firenze, Polo Scientifico, via della Lastruccia 13, I-50019 Sesto Fiorentino (FI), Italy  
E-mail: gsoldaini@unifi.it

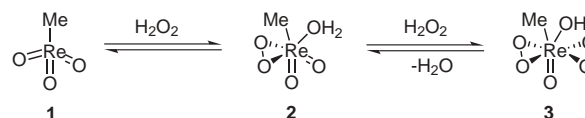
### Introduction

Methyltrioxorhenium (**1**) is an important and versatile catalyst widely studied as an oxygen transfer reagent in oxidation reactions of a variety of substrates.<sup>1</sup> The important features of MTO as a catalyst are its ease of synthesis, commercial availability and stability to air. MTO was firstly synthesized by Beattie and Jones in 1979.<sup>2</sup> Subsequently, Herrmann et al. developed a more simple and efficient synthesis based on the reaction of dirhenium heptoxide with methyltributyltin.<sup>3</sup>



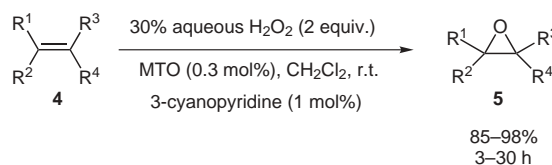
MTO (**1**) reacts with  $\text{H}_2\text{O}_2$ , the usual stoichiometric oxidant, to give equilibria with formation of monoperoxo- and dperoxo-rhenium(VII) species (**2** and **3**, respectively).<sup>4</sup> The latter confers a characteristic yellow color to the solution and it is the most reactive towards oxygen-accepting substrates.

The MTO/ $\text{H}_2\text{O}_2$  system makes use of nontoxic reagents, the oxidation and work-up procedures are very simple, water is the only byproduct, and non-aqueous solvent can be used if UHP (urea-hydrogenperoxide adduct) is used instead of  $\text{H}_2\text{O}_2$  as the stoichiometric oxidant.

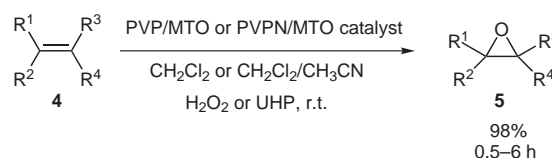


### Abstracts

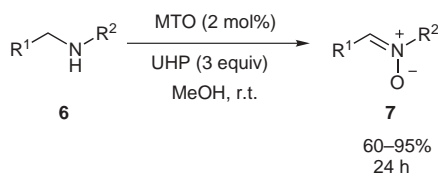
(A) The ability of methyltrioxorhenium to catalyze the epoxidation of alkenes **4** with hydrogen peroxide was demonstrated by Herrmann in 1991.<sup>5</sup> The addition of a catalytic amount of an additive, like pyridine<sup>6</sup> or derivatives,<sup>7</sup> leads to rate enhancement of the reaction, increases catalyst lifetime and, especially, prevents epoxide **5** from being hydrolyzed to the corresponding diol. Interesting results in terms of enhancement of reactivity have been obtained by using hexafluoro-2-propanol as solvent.<sup>8</sup>



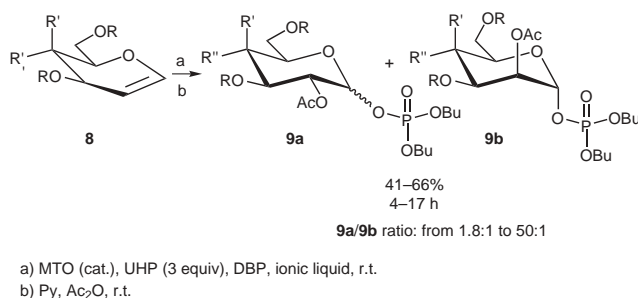
(B) The heterogenization of MTO has been achieved by using polymeric supports such as modified silica,<sup>9</sup> NaY/zeolite,<sup>10</sup> niobia,<sup>11</sup> PVP [poly(4-vinylpyridine)], PVPN [poly(4-vinylpyridine-*N*-oxide)] and polystyrene.<sup>12</sup> The latter systems come as interesting alternatives for the oxidation of alkenes **4**, phenols,<sup>13</sup> and for the Baeyer-Villiger oxidation.<sup>14</sup> These methods are more environmentally friendly, allowing an easy recovery and reuse of the catalyst.



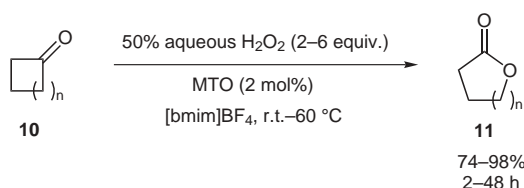
(C) The oxidation of amines is a fundamental reaction for the synthesis of oxygen-containing nitrogen compound. In this context, the system MTO/H<sub>2</sub>O<sub>2</sub> is an important means to obtain nitrones **7** by oxidation of secondary amines **6**.<sup>15</sup> With UHP as the stoichiometric oxidant, the reaction can be carried out in non-aqueous media and the products can be isolated with a simple work-up procedure in good-to-excellent yield.<sup>15a–b</sup>



(D) Oxidation of glycols by MTO-hydrogen peroxide in methanol provides direct access to methyl glycosides.<sup>16</sup> Moreover, the application of the MTO/UHP system for the oxidation of glycols **8** in the presence of dibutylphosphate as activating protector of the anomeric position afforded glycosyl phosphates **9**, powerful glycosyl donors and useful tools for the construction of various glycoconjugates. The reaction, carried out in ionic liquid, leads to complete conversion and good diastereoselectivities for the epoxidation reaction.<sup>16a</sup>



(E) The Baeyer-Villiger oxidation of cyclic ketones **10** can be performed with MTO/hydrogen peroxide system in classical solvents<sup>17</sup> or in ionic liquids.<sup>18</sup> The latter procedure allows recovery of the lactone **11** by simple extraction and the catalyst can be repeatedly recycled and reused for the lactonization process in the same reaction medium.



## References

- (1) For reviews, see: (a) Romao, C. C.; Kuhn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197. (b) Owens, S.; Arias, J.; Abu-Omar, M. M. *Catal. Today* **2000**, *55*, 317. (c) Kuhn, F. E.; Herrmann, W. A. *Chemtracts* **2001**, *14*, 59.
- (2) Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.
- (3) (a) Herrmann, W. A.; Kuhn, F. E.; Fischer, R. W.; Thiel, W. R.; Romo, C. C. *Inorg. Chem.* **1992**, *31*, 4431. (b) Herrmann, W. A.; Kratzer, R. M.; Espenson, J. H.; Wang, W. *Inorg. Synth.* **2002**, *33*, 110.
- (4) (a) Yamazaki, S.; Espenson, J. H.; Huston, P. *Inorg. Chem.* **1993**, *32*, 4683. (b) Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966.
- (5) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638.
- (6) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189.
- (7) Adolfsson, H.; Coperet, C.; Chiang, J. P.; Yudin, A. K. *J. Org. Chem.* **2000**, *65*, 8651.
- (8) Iskra, J.; Bonnet-Delbon, D.; Bégué, J.-P. *Tetrahedron Lett.* **2002**, *43*, 1001.
- (9) Wang, T.-J.; Li, D.-C.; Bai, J.-H.; Huang, M.-Y.; Jiang, Y.-Y. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 531.
- (10) Adam, W.; Saha-Möller, C. R.; Weichold, O. *J. Org. Chem.* **2000**, *65*, 2897.
- (11) Bouh, A. B.; Espenson, J. H. *J. Mol. Catal. A: Chem.* **2003**, *206*, 37.
- (12) Saladino, R.; Neri, V.; Pelliccia, A. R.; Caminiti, R.; Sadun, C. *J. Org. Chem.* **2002**, *67*, 1323.
- (13) Saladino, R.; Neri, V.; Mincione, E.; Filippone, P. *Tetrahedron* **2002**, *58*, 8493.
- (14) Bernini, R.; Mincione, E.; Cortese, M.; Saladino, R.; Gualandi, G.; Belfiore, M. C. *Tetrahedron Lett.* **2003**, *44*, 4823.
- (15) (a) Goti, A.; Nannelli, L. *Tetrahedron Lett.* **1996**, *37*, 6025. (b) Soldaini, G.; Cardona, F.; Goti, A. *Org. Synth.* **2004**, *81*, in press. (c) Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 877. (d) Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *J. Org. Chem.* **1996**, *61*, 8099. (e) Zauche, T. H.; Espenson, J. H. *Inorg. Chem.* **1997**, *36*, 5257.
- (16) (a) Soldaini, G.; Cardona, F.; Goti, A. *Tetrahedron Lett.* **2003**, *44*, 5589. (b) Boyd, E. C.; Jones, R. V. H.; Quayle, P.; Waring, A. J. *Green Chem.* **2003**, *5*, 679.
- (17) Herrmann, W. A.; Fischer, R. W.; Correia, J. D. G. *J. Mol. Catal.* **1994**, *94*, 213.
- (18) Bernini, R.; Coratti, A.; Fabrizi, G.; Goggiamani, A. *Tetrahedron Lett.* **2003**, *44*, 8991.