

SYNLETT

Spotlight 96

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

Methyltrioxorhenium (MTO)

Compiled by Gianluca Soldaini

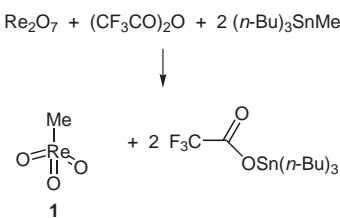


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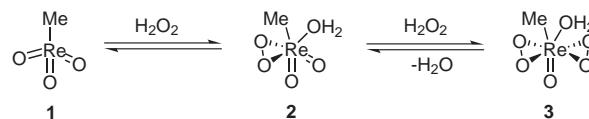
Introduction

Methyltrioxorhenium (**1**) is an important and versatile catalyst widely studied as an oxygen transfer reagent in oxidation reactions of a variety of substrates.¹ 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 1979.² Subsequently, Herrmann et al. developed a more simple and efficient synthesis based on the reaction of dirhenium heptoxide with methyltributyltin.³



MTO (**1**) reacts with H₂O₂, the usual stoichiometric oxidant, to give equilibria with formation of monoperoxo- and diperoxo-rhenium(VII) species (**2** and **3**, respectively).⁴ The latter confers a characteristic yellow color to the solution and it is the most reactive towards oxygen-accepting substrates.

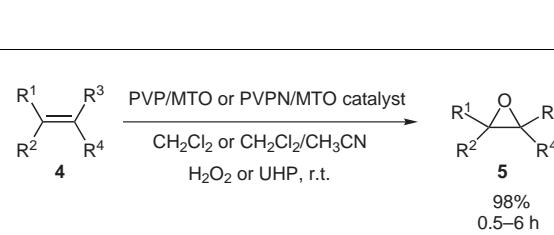
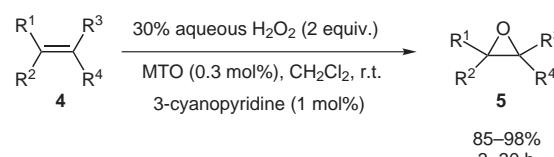
The MTO/H₂O₂ system makes use of nontoxic reagents, the oxidation and work-up procedures are very simple, water is the only byproduct, and non-aqueous solvent can be used if UHP (urea-hydrogenperoxide adduct) is used instead of H₂O₂ as the stoichiometric oxidant.



Abstracts

(A) The ability of methyltrioxorhenium to catalyze the epoxidation of alkenes **4** with hydrogen peroxide was demonstrated by Hermann in 1991.⁵ The addition of a catalytic amount of an additive, like pyridine⁶ or derivatives,⁷ 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.⁸

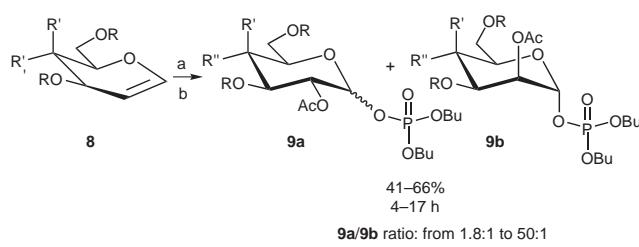
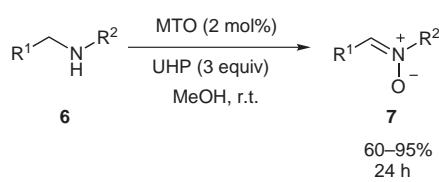
(B) The heterogenization of MTO has been achieved by using polymeric supports such as modified silica,⁹ NaY/zeolite,¹⁰ niobia,¹¹ PVP [poly(4-vinylpyridine)], PVPN [poly(4-vinylpyridine-*N*-oxide)] and polystyrene.¹² The latter systems come as interesting alternatives for the oxidation of alkenes **4**,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



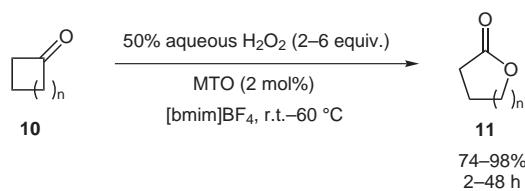
(C) The oxidation of amines is a fundamental reaction for the synthesis of oxygen-containing nitrogen compound. In this context, the system MTO/H₂O₂ is an important means to obtain nitrones **7** by oxidation of secondary amines **6**.¹⁵ With UHP as the stoichiometric oxidant, the reaction can be carried out in non-aqueous media and the products can be isolated with a simple work-up procedure in good-to-excellent yield.^{15a–b}

(D) Oxidation of glycals by MTO-hydrogen peroxide in methanol provides direct access to methyl glycosides.¹⁶ Moreover, the application of the MTO/UHP system for the oxidation of glycals **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.^{16a}

(E) The Baeyer-Villiger oxidation of cyclic ketones **10** can be performed with MTO/hydrogen peroxide system in classical solvents¹⁷ or in ionic liquids.¹⁸ 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.



a) MTO (cat.), UHP (3 equiv), DBP, ionic liquid, r.t.
b) Py, Ac₂O, r.t.



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