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

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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 H_2O_2 , 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/ H_2O_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 H_2O_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 1991.⁵ 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.

References

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