

# SYNLETT Spotlight 96

## Methyltrioxorhenium (MTO)

Compiled by Gianluca Soldaini



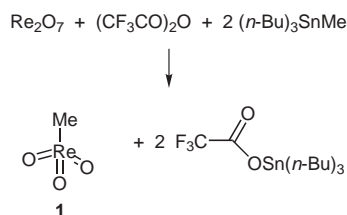
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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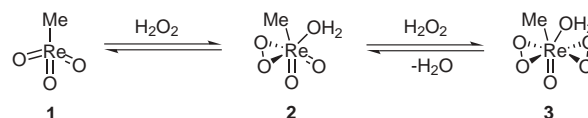
### Introduction

Methyltrioxorhenium (**1**) is an important and versatile catalyst widely studied as an oxygen transfer reagent in oxidation reactions of a variety of substrates.<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>



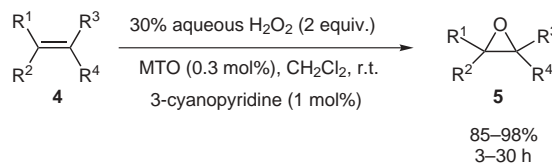
MTO (**1**) reacts with  $\text{H}_2\text{O}_2$ , the usual stoichiometric oxidant, to give equilibria with formation of monoperoxo- and dperoxo-rhenium(VII) species (**2** and **3**, respectively).<sup>4</sup> The latter confers a characteristic yellow color to the solution and it is the most reactive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

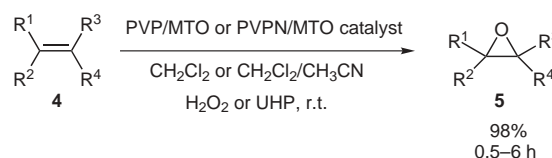


### Abstracts

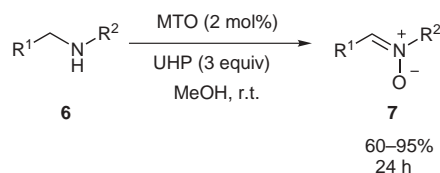
(A) The ability of methyltrioxorhenium to catalyze the epoxidation of alkenes **4** with hydrogen peroxide was demonstrated by Herrmann in 1991.<sup>5</sup> The addition of a catalytic amount of an additive, like pyridine<sup>6</sup> or derivatives,<sup>7</sup> leads to rate enhancement of the reaction, 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>



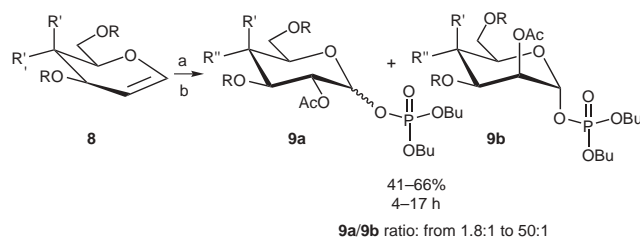
(B) The heterogenization of MTO has been achieved by using polymeric supports such as modified silica,<sup>9</sup> NaY/zeolite,<sup>10</sup> niobia,<sup>11</sup> PVP [poly(4-vinylpyridine)], PVPN [poly(4-vinylpyridine-N-oxide)] and polystyrene.<sup>12</sup> The latter systems come as interesting alternatives 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>

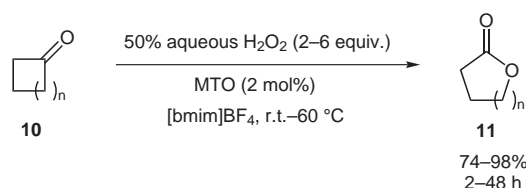


(D) Oxidation of glycols by MTO-hydrogen peroxide in methanol provides direct access to methyl glycosides.<sup>16</sup> Moreover, the application of the MTO/UHP system for the oxidation of glycols **8** in the presence of dibutylphosphate as activating protector of the anomeric position afforded glycosyl 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>



a) MTO (cat.), UHP (3 equiv), DBP, ionic liquid, r.t.  
b) Py, Ac<sub>2</sub>O, r.t.

(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.



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