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Addendum

Addendum to “CH_3ReO_3/H_2O_2 in room temperature ionic liquids: an homogeneous recyclable catalytic system for the Baeyer–Villiger reaction”

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Additional explanations and experimental data regarding our previously published letter [*Tetrahedron Lett.* **2003**, *44*, 8991] are herein described.

We report here additional explanations and experimental details about our previously published work[1] in light of a recent *Tetrahedron Lett.* article entitled ‘Highly efficient C–H insertion reactions of hydrogen peroxide catalyzed by homogeneous and heterogeneous methyltrioxorhenium systems in ionic liquids’ by Bianchini, G.; Crucianelli, M.; De Angelis, F.; Neri, V.; Saladino, R.[2]

In the Bianchini et al. letter, the authors stated “As erroneously reported in a recent communication,[11a] MTO cannot be retained into ionic liquids during liquid/liquid extraction of the reaction mixture, due to its known high solubility in a wide range of molecular solvents[11b]” (page 2427, column 2), in which Ref. 11a is our **2003** *Tetrahedron Lett.* article. Furthermore, in Ref. 11b the same authors reported “In our hands, an extraction yield major than 85% of MTO from [EMIM][BF_4] was measured using diethyl ether as mobile phase, with a concomitant dramatic decrease of the catalytic activity”.

We mention these statements because in our **2003** *Tetrahedron Lett.* article, we described the catalytic Baeyer–Villiger oxidation of cyclic ketones with methyltrioxorhenium (CH_3ReO_3, MTO)/hydrogen peroxide (H_2O_2). This clearly means that the oxidation catalyst was not MTO but rather the methyltrioxorhenium (CH_3ReO_3, MTO)/hydrogen peroxide (H_2O_2) complex in [bmim]BF_4.

During the course of our work, we verified that a partial leaching of the MTO/H_2O_2 complex (rhenium species) could occur by extraction with diethyl ether. Nevertheless, the ionic liquid solution remained catalytically active after the products were extracted with diethyl ether as shown by the results obtained in the successive recycles. Moreover, we observed that the ionic liquid solution, initially yellow due to the formation of the diperoxorhenium complex in situ,[3] was bleached during the first run. Further changes in colour were not observed in the subsequent recycles. This suggests that rhenium species different from the diperoxorhenium complex were generated under these conditions. More work is in progress to verify this hypothesis.

In an effort to avoid any further misinterpretations, we report here in detail the experimental procedure of the oxidations. [bmim]BF_4 was synthesized in our laboratory according to the literature.[4] The ketone (0.2–0.3 mmol) was dissolved in 1 mL of [bmim]BF_4 at 25–60 °C. Then, CH_3ReO_3 (2%) and hydrogen peroxide (50% aqueous solution, 2–6 equiv, 2 equiv. each time) were added in 1–48 h depending on the substrate. The oxidation reaction was monitored by GC or by TLC. After the reaction was completed, the ionic liquid solution was extracted with diethyl ether (5 × 1 mL). Subsequently, the combined ethereal layer was washed twice with 1 mL of saturated NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The

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oxidation products were characterized by GC–MS analysis and NMR spectroscopy. The ionic liquid solution can be reused at least five times with no loss of activity simply by adding fresh substrate and hydrogen peroxide. Indeed, the yields and reaction times were equivalent for each of the subsequent recycles, which are crucial to evaluate the effectiveness of recycling processes.

In addition, we would like to comment on the term 'immobilized,' used by us on page 8993, column 2, and commonly used even in classical textbooks.[5] It conventionally refers to a methodology that allows the recycle of the catalyst in a synthetic heterogeneous or homogeneous process. Usually small losses of metal do not change the efficiency of the recycle to a significant extent, as we clearly observed in our process.

Finally, we note that Bianchini, G.; Crucianelli, M.; De Angelis, F.; Neri, V. and Saladino R. in their letter (see Ref. 21) overlooked our recent contributions to the ionic liquids research area.[6]

References and notes

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