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# A novel catalyzed C–H insertion reactions of hydrogen peroxide by poly(4-vinylpyridine)/methyltrioxorhenium systems

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**Abstract**—Novel poly(4-vinylpyridine) supported MTO compounds were effective heterogeneous catalysts for the C–H insertion reactions of $H_2O_2$ into some representative hydrocarbon derivatives. The most relevant outcomes of these oxidations are described.

The oxidation of hydrocarbons is an important and challenging areas in industrial and commodity chemistry.[1] Most of the existing processes for the oxidation of hydrocarbons use toxic and often stoichiometric oxidants eventually producing wastes. For this reason, novel efficient and selective methodologies using environmentally friendly $H_2O_2$ as primary oxidant and heterogeneous recoverable catalysts are desirable. In the last decade methyltrioxorhenium (MTO) has been used for several organic transformations such as the oxidation of alkenes, alkynes, aromatic derivatives, phosphine, sulfur derivatives and also for the Baeyer–Villiger rearrangement.[2] The reactive intermediates for these oxidations are a monoperoxo [$MeRe(O)_2O_2$] and a bis-peroxo [$MeReO(O_2)_2$] $\eta^2$-rhenium complexes.[3] Only a few examples describing the use of MTO for the oxidation of hydrocarbons appeared. Murray et al. reported the $H_2O_2$ oxygen atom insertion into the C–H bond of hydrocarbon derivatives catalyzed by MTO.[4] Successively, Schuchardt et al. reported that alkanes and aromatic compounds are oxidized by anhydrous $H_2O_2$ in air by use of MTO as catalyst.[5] It must be observed that, in these latter applications, the use of homogeneous MTO along with anhydrous $H_2O_2$ represents a major drawback for a potential large scale industrial exploitation. Recently, we have reported the synthesis of novel heterogeneous rhenium catalysts based on the heterogenization of MTO on easily available, not toxic and low expensive poly(4-vinylpyridine) derivatives.[6] These catalysts showed to be efficient systems for the activation of $H_2O_2$ in the oxidation of aromatic derivatives, alkenes, terpenes and in the Baeyer–Villiger rearrangement.[7] Herein, we describe the use of poly(4-vinylpyridine) 2% cross-linked (with divinylbenzene)/MTO (PVP-2/MTO, **I**) and poly(4-vinylpyridine) 25%/MTO (PVP-25/MTO, **II**) compounds,[8] for the oxidation with $H_2O_2$ of triphenylmethane **1a**, benzhydrol **1b** and adamantane **2**. In our protocol the reactions with MTO, performed under the experimental conditions described by Murray et al.,[4] have been used as references. Briefly, 1 mmol of substrate dissolved in 2 mL of solvent, was added portionwise with supported catalyst (100 mg, loading factor 1) and $H_2O_2$ (4–6 equiv) (for specific conditions see Tables 1 and 2). At the end of reaction a low amount of $MnO_2$ was added and the solvent evaporated after filtration. The reaction products have been characterized by GC–MS analyses and by comparison with authentic samples.[9] Results of the oxidation of compounds **1a**,**b** and **2** are reported in Schemes 1 and 2 and Tables 1 and 2. Murray et al. described that the oxidation of **1a** with MTO gives triphenylcarbinol (not shown) as the only recovered product.[4] In our hand, under the same experimental conditions, benzophenone **3** was obtained as major product in the presence of low amount of benzoate **4** (Table 1, entry 1). Traces of triphenylcarbinol and phenol were detected in the reaction mixture by GC–MS analysis. A similar behavior was observed with heterogeneous catalysts **I** and **II**. In these latter cases, the reaction performed with catalyst **I** at

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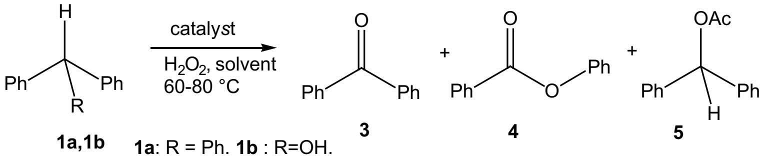


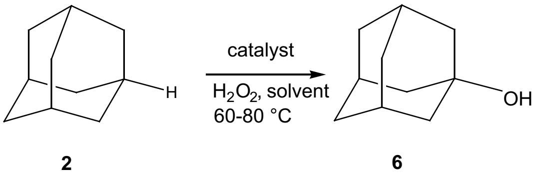
**Scheme 1.**

**Table 1.** Oxidation of **1a**,**b** with MTO and polymer supported MTO catalysts

| Entry | Substrate | Catalyst[a] | Solvent | $H_2O_2$ (equiv) | *T* (°C) | Conv. (%) | Product(s) | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | MTO | EtOH | 6 | 60 | 95 | **3** (**4**) | 73 (8) |
| 2 | **1a** | PVP-2/MTO (**I**) | EtOH | 6 | 60 | 23 | **3** (**4**) | 71 (6) |
| 3 | **1a** | PVP-2/MTO (**I**) | EtOH | 6 | 80 | 27 | **3** (**4**) | 75 (9) |
| 4 | **1a** | PVP-25/MTO (**II**) | EtOH | 6 | 80 | 23 | **3** (**4**) | 74 (8) |
| 5 | **1a** | No catalyst | AcOH | 6 | 80 | <5 | **3** | <2 |
| 6 | **1a** | PVP-2/MTO (**I**) | AcOH | 6 | 80 | 49 | **3** (**4**) | 82 (8) |
| 7 | **1a** | PVP-25/MTO (**II**) | AcOH | 6 | 80 | 65 | **3** (**4**) | 86 (6) |
| 8 | **1b** | MTO | EtOH | 5 | 60 | 95 | **3** | 90 |
| 9 | **1b** | No catalyst | AcOH | 5 | 80 | <5 | **3** | <2 |
| 10 | **1b** | PVP-2/MTO (**I**) | AcOH | 5 | 80 | 56 | **3** (**5**) | 50 (20) |
| 11 | **1b** | PVP-25/MTO (**II**) | AcOH | 5 | 80 | 67 | **3** (**5**) | 55 (22) |

[a] PVP-2/MTO: poly(4-vinylpyridine) 2% cross-linked. PVP-25/MTO: poly(4-vinylpyridine) 25% cross-linked.

60 °C in EtOH afforded a low conversion of **1a** and appreciable yield of **3** (Scheme 1; Table 1, entry 2). Irrespective from the catalyst used, an increase of both, substrate conversion and product yield, was observed increasing the reaction temperature at 80 °C (Table 1, entries 3 and 4). It is known that acidic solvents enhance the reactivity of MTO.[1] Accordingly, the oxidation of **1a** was performed in acetic acid (AcOH) to give 49–65% conversion of substrate and 82–86% yield of **3** (Table 1, entries 6 and 7), compound **II** being the best catalyst. These data are in accordance with our previous findings on the effect of the reticulation grade of the poly(4-vinylpyridine) (that is 2% vs 25% cross-linked) for the efficiency and selectivity of polymer supported MTO catalysts.[6] Less than 5% conversion of **1a** was observed in the absence of the catalyst (Table 1, entry 5). Compounds **I** and **II** were stable systems under previously described reaction conditions and were recovered and recycled for at least five times without any appreciable loss in efficiency. The oxidative dearylation of tertiary aromatic hydrocarbons to ketones has been performed by use of stoichiometric oxidants or homogeneous catalysts, but there are not quite general examples describing the use of $H_2O_2$ with heterogeneous systems.[10] It is reasonable to suggest that triphenylcarbinol is a reactive intermediate in the oxidation. In fact, triphenylcarbinol was efficiently oxidized to **3** with MTO under previously reported experimental conditions. Moreover, compound **4** is probably due to the known MTO-promoted Baeyer–Villiger rearrangement of ketone derivatives.[7d] To evaluate the generality of this procedure, benzhydrol **1b** and adamantane **2** were oxidized under similar experimental conditions. The oxidation of **1b** with $H_2O_2$ in the presence of compounds **I** and **II** as catalysts in AcOH gave **3** in 50–55% yield and 56–67% conversion of substrate, respectively (Scheme 1; Table 1, entries 10 and 11). In this latter case, an appreciable amount of **5** was recovered from the reaction mixture, probably as a consequence of the catalysis of MTO in the formation of the ester moiety.[1] The oxidation of **2** with MTO afforded 1-adamantanol **6** in excellent yield (Scheme 2; Table 2, entry 1). Heterogeneous catalysts **I** and **II** showed a similar behavior (Table 2, entries 2, 3 and 5, 6). Again, AcOH was the most appropriate solvent to obtain highest yield of **6**



**Scheme 2.**

**Table 2.** Oxidation of **2** with MTO and polymer supported MTO catalysts

| Entry | Catalyst | Solvent | $H_2O_2$ (equiv) | *T* (°C) | Conv. (%) | Product | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | MTO | EtOH | 4 | 60 | 45 | **6** | 77 |
| 2 | PVP-2/MTO (**I**) | EtOH | 4 | 80 | 31 | **6** | 69 |
| 3 | PVP-25/MTO (**II**) | EtOH | 4 | 80 | 33 | **6** | 62 |
| 4 | No catalyst | AcOH | 4 | 80 | <5 | **6** | <2 |
| 5 | PVP-2/MTO (**I**) | AcOH | 4 | 80 | >98 | **6** | 81 |
| 6 | PVP-25/MTO (**II**) | AcOH | 4 | 80 | >98 | **6** | 85 |

(Table 2, entries 2, 3 vs 5, 6). It is noteworthy to emphasize that, in the oxidation of **2**, catalysts **I** and **II** showed both high conversion values of substrate and very good yields of product **6** (Table 2, entries 5, 6), even if usually a catalytic species loses part of its activity after the heterogenization process. These results are in accordance with data previously obtained by us, in the oxidation of cardanol derivatives with $H_2O_2$ by use of poly(4-vinylpyridine) supported MTO systems.[7b] In conclusion, to the best of our knowledge, this article describes the first reported example in literature dealing with the C–H insertion reactions of $H_2O_2$ by means of heterogeneous rhenium derivatives. Further work is therefore in progress, in order to exploit further on this efficient and environmentally friendly procedure.

## Acknowledgement

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## References and notes

1. For some recent examples of $H_2O_2$ oxidation of hydrocarbons, see: (a) Shul'pin, G. B. *Comptes Rendus Chimie* **2003**, *6*, 163–178; (b) Nizova, G. V.; Bolm, C.; Ceccarelli, S.; Pavan, C.; Shul'pin, G. B. *Adv. Synth. Catal.* **2002**, *344*, 899–905.
2. For general reviews, see: (a) Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197–3246; (b) Owens, G. S.; Arias, J.; Abu-Omar, M. M. *Catal. Today* **2000**, *55*, 317–363.
3. Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rouch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157–1160.
4. Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *Tetrahedron Lett.* **1995**, *36*, 6415–6418.
5. Schuchardt, U.; Mandelli, D.; Shul'pin, G. B. *Tetrahedron Lett.* **1996**, *37*, 6487–6490.
6. Saladino, R.; Neri, V.; Pelliccia, A. R.; Caminiti, R.; Sadun, C. *J. Org. Chem.* **2002**, *67*, 1323–1332.
7. (a) Saladino, R.; Neri, V.; Mincione, E.; Filippine, P. *Tetrahedron* **2002**, *58*, 8493–8500; (b) Saladino, R.; Mincione, E.; Attanasi, O. A.; Filippone, P. *Pure Appl. Chem.* **2003**, *75*, 261–268; (c) Saladino, R.; Neri, V.; Pelliccia, A. R.; Mincione, E. *Tetrahedron* **2003**, *59*, 7403–7408; (d) Bernini, R.; Mincione, E.; Cortese, M.; Saladino, R.; Gualandi, G.; Belfiore, M. C. *Tetrahedron Lett.* **2003**, *44*, 4823–4825.
8. Compounds **I** and **II** were prepared as reported in Ref. 6. In summary, MTO (256 mg, 1.0 mmol) was added to a suspension of the appropriate resin (1.0 g) in ethanol (4 mL). The mixture was stirred for 1 h using a magnetic stirrer. The solvent was removed by filtration, and the catalyst was washed with ethyl acetate and finally dried under high vacuum.
9. The reaction mixtures have been analyzed by a Hewlett Packard 6890 Series gas chromatograph equipped with a FID, using a 30 m × 0.32 mm × 0.25 μm film thickness (cross-linked 5% phenylmethylsiloxane) column and nitrogen as carrier gas. The identification of the peaks by GC–MS has been performed by means of a Varian 2000 GC-MAS instrument, using the same column. Yields and conversions of the reactions have been quantified using *n*-octane as internal standard, or when necessary, after chromatographic purification.
10. See for recent examples: (a) Revital, B. D.; Ronny, N. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 92–95; (b) Ishii, Y.; Nakayama, K.; Takeno, M.; Sakaguchi, S.; Iwahama, T.; Nishiyama, Y. *J. Org. Chem.* **1995**, *60*, 3934–3935.