

Highly efficient C–H insertion reactions of hydrogen peroxide catalyzed by homogeneous and heterogeneous methyltrioxorhenium systems in ionic liquids

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Abstract—A convenient and efficient C–H insertion reaction of environment friendly H₂O₂ into representative hydrocarbon derivatives by homogeneous methyltrioxorhenium (MTO), heterogeneous poly(4-vinylpyridine)/methyltrioxorhenium (PVP/MTO) and microencapsulated polystyrene/methyltrioxorhenium (PS/MTO) systems in ionic liquids, is described. In some cases a higher activity was observed if compared with the same reaction in molecular solvents. The heterogeneous catalysts are stable systems under the reaction conditions and can be recycled for more transformations.

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In recent years the need for designing ‘clean’ and ‘green’ industrial processes has created a very significant amount of interest in the use of non-volatile ionic liquids in chemical synthesis and catalysis.¹ Ionic liquids possess, inter alia, the following desirable properties: they are liquids below 100 °C and with a relative low viscosity, allowing kinetic control; they are solvents for a wide range of inorganic, organic and polymeric materials;² they can exhibit Brønsted and Lewis acidity as well as superacidity, enabling many catalytic processes. Finally, some ionic liquids are commercially available since they can be prepared readily and economically. As such, ionic liquids are thought to offer a range of significant improvements compared to conventional molecular solvents especially in view of the fact that there are several ionic liquids that can be synthesized, making it possible to design an ionic liquid, which is specific with the reaction requirements (‘designer solvent’).

Advances in oxidation chemistry that utilize ionic liquids have been obtained with 1-*n*-butyl-3-methylimi-

dazolium hexafluorophosphate [BMIM][PF₆],³ 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄]⁴ and 1-ethyl-3-methylimidazolium bis-triflic amide [EMIM][Tf₂N]⁵ salts, which are oxygen and water stable compounds. Although some attention has been focused on catalytic oxidations in ionic liquids,⁶ to date there are no examples of C–H insertion reactions of environment friendly hydrogen peroxide (H₂O₂) into hydrocarbon derivatives. The oxidation of hydrocarbons is an important and challenging area in industrial and commodity chemistry.⁷ Most of the existing processes use toxic and often stoichiometric oxidants and molecular solvents eventually producing wastes.

In the last decade methyltrioxorhenium (MTO) has been used in several organic transformations.⁸ Furthermore, MTO showed excellent conversions and selectivities for the epoxidation of olefins in ionic liquids. Under these experimental conditions, the bis-peroxo [MeReO(O₂)₂] η^2 -rhenium complex was more reactive than the monoperoxo [MeRe(O)₂O₂] complex, while the opposite is true for the reaction conducted in conventional molecular solvents.^{9,10}

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

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solvents.^{11b} Thus, novel synthetic strategies should be designed to obtain MTO catalytic systems that are really immobilized in ionic liquids. Recently, we described the first example of oxidation of hydrocarbons with H_2O_2 and heterogeneous MTO systems in ethanol and acetic acid.¹² These catalysts showed to be efficient systems also for the activation of H_2O_2 in the oxidation of aromatic derivatives, alkenes and terpenes.¹³ Heterogeneous catalysis allows the easy separation of products making possible the recycling and reuse of the catalyst with environmental and economical advantages.

Herein we describe the unprecedented catalyzed C–H insertion reactions of environment friendly H_2O_2 into representative hydrocarbon derivatives, by means of heterogeneous MTO systems in ionic liquids. Reactions were performed using catalysts based on the heterogenization of MTO on easily available, nontoxic and low expensive poly(4-vinylpyridine) and poly(4-vinylpyridine *N*-oxide) 2% [PVP-2/MTO (**I**) and PVPN-2/MTO (**II**), respectively], and 25% [PVP-25/MTO (**III**) and PVPN-25/MTO (**IV**), respectively], cross-linked with divinylbenzene.¹⁴ Microencapsulated catalyst PS-2/MTO (**V**) based on the physical entrapment of MTO on polystyrene 2% cross-linked with divinylbenzene was also used.¹⁵ The structures of catalysts are reported in Figure 1.

Briefly, triphenylmethane **1**, benzhydrol **2**, 1-phenyl-ethanol **3**, *cis*-1,2-dimethylcyclohexane **4** and adamantane **5** (1 mmol) dissolved in [BMIM][PF₆] or [EMIM][Tf₂N] (1 mL; in the case of **1** a low amount of CHCl_3 was used in order to increase the solubility of the substrate) were added portionwise with supported catalysts **I–V** (100 mg, loading factor 1) and H_2O_2 (4–6 equiv) at 25–60 °C. At the end of the reaction, the mixture was extracted with diethyl ether. After separation, the ethereal layer was added with a catalytic amount of MnO_2 , filtrated and evaporated. The ionic liquid layer containing catalysts **I–V** may be used in successive experiments without further purification (see forward). Reaction products were characterized by GC–MS analyses and by comparison with authentic samples.¹⁶ Oxidations with MTO under similar experimental conditions were performed as references. In the absence of catalyst, less

than 5% conversion of substrates took place under otherwise identical conditions. The oxidation results are summarized in Tables 1–6 and Schemes 1–5.

The oxidation of triphenylmethane **1** with MTO and heterogeneous MTO catalysts **I–V** in [BMIM][PF₆] and CHCl_3 (25% v/v) at 45 °C, yielded benzophenone **6** as the only recovered product (Scheme 1). In accordance with the data previously reported,¹² it is reasonable to suggest that triphenyl carbinol (not shown) was a reactive intermediate in the oxidation. To the best of our knowledge, this is the first example of oxidative dearylation of tertiary aromatic hydrocarbon to ketone in ionic liquid. Catalysts **I–V** showed both conversion values of substrate (45–53%) and yield of product (80–91%) comparable with MTO (Table 1, entries 2–6 vs 1). In the family of poly(4-vinylpyridine) catalysts, pyridine *N*-oxide derivatives **II** and **IV** were less efficient than parent pyridine derivatives **I** and **III** (e.g., Table 1, entries 2–4 vs 3–5), compound **III** being the best catalyst. The behaviour of microencapsulated **V** was similar to poly(4-vinylpyridine) catalysts affording **6** in 45% conversion and 88% yield (Table 1, entry 6). It is interesting to note that catalysts **I–V** showed a higher reactivity in the oxidation of **1** in [BMIM][PF₆]- CHCl_3 than in ethanol.¹² Comparable results in molecular solvents were obtained only in acetic acid, which is known to efficiently increase the reactivity of MTO.^{12,17}

To evaluate the generality of this procedure, benzhydrol **2** and 1-phenyl-ethanol **3** were oxidized under similar experimental conditions. The oxidation of **2** with H_2O_2 and catalysts **I–V** in [BMIM][PF₆] at 45 °C gave **6** in 76–83% yield and 73–94% conversion of substrate (Scheme 2, Table 2, entries 2–6). Catalysts **I–V** showed both conversion values of substrate and yields of product comparable with MTO. Again, pyridine *N*-oxide derivatives were less efficient than parent pyridine derivatives (e.g., Table 2, entries 2–4 vs 3–5), compounds **I** and **III** being the best catalysts. Microencapsulated catalyst **V** showed a similar behaviour (Table 2, entry 6). The equilibrium constant for the interaction between pyridine *N*-oxide and MTO is of the same order of magnitude than that measured for pyridine.¹⁸ On the other hand, the pyridine *N*-oxide/MTO adduct shows

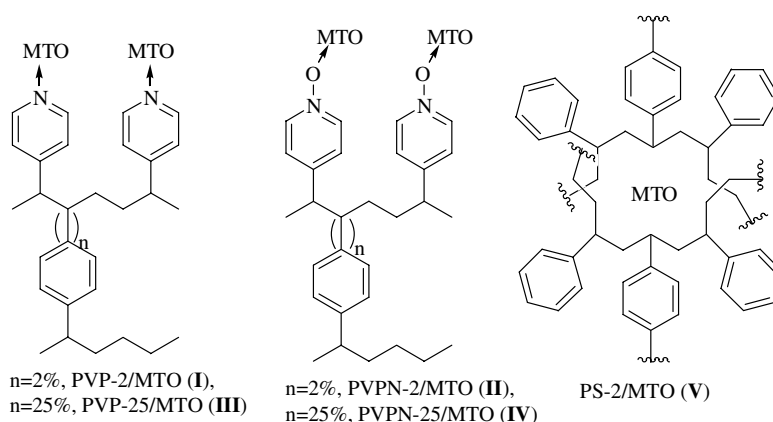


Figure 1.

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

Entry	Catalyst ^a	Solvent ^b	Time (h)	<i>T</i> (°C)	Conv. (%)	Yield (%)
1	MTO	[BMIM][PF ₆]	65	45	57	93
2	PVP-2/MTO (I)	[BMIM][PF ₆]	48	45	48	89
3	PVPN-2/MTO (II)	[BMIM][PF ₆]	48	45	51	81
4	PVP-25/MTO (III)	[BMIM][PF ₆]	48	45	51	91
5	PVPN-25/MTO (IV)	[BMIM][PF ₆]	48	45	53	80
6	PS-2/MTO (V)	[BMIM][PF ₆]	48	45	49	88

^a PVP-2/MTO: poly(4-vinylpyridine) 2% cross-linked. PVP-25/MTO: poly(4-vinylpyridine) 25% cross-linked. PVPN-2/MTO: poly(4-vinylpyridine *N*-oxide) 2% cross-linked. PVPN-25/MTO: poly(4-vinylpyridine *N*-oxide) 25% cross-linked. PS-2/MTO: polystyrene 2% cross-linked.

^b Ionic liquid mixed with 25% v/v of CHCl₃.

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

Entry	Catalyst ^a	Solvent	Time (h)	<i>T</i> (°C)	Conv. (%)	Yield (%)
1	MTO	[BMIM][PF ₆]	24	45	98	88
2	PVP-2/MTO (I)	[BMIM][PF ₆]	24	45	78	83
3	PVPN-2/MTO (II)	[BMIM][PF ₆]	24	45	73	79
4	PVP-25/MTO (III)	[BMIM][PF ₆]	24	45	91	82
5	PVPN-25/MTO (IV)	[BMIM][PF ₆]	24	45	81	76
6	PS-2/MTO (V)	[BMIM][PF ₆]	24	45	94	78

^a PVP-2/MTO: poly(4-vinylpyridine) 2% cross-linked. PVP-25/MTO: poly(4-vinylpyridine) 25% cross-linked. PVPN-2/MTO: poly(4-vinylpyridine *N*-oxide) 2% cross-linked. PVPN-25/MTO: poly(4-vinylpyridine *N*-oxide) 25% cross-linked. PS-2/MTO: polystyrene 2% cross-linked.

Table 3. Oxidation of **3** with MTO and polymer supported MTO catalysts

Entry	Catalyst ^a	Solvent	Time (h)	<i>T</i> (°C)	Conv. (%)	Yield (%)
1	MTO	EtOH	24	60	35	12
2	PVP-2/MTO (I)	EtOH	24	60	26	10
3	PVPN-2/MTO (II)	EtOH	24	60	20	8
4	PVP-25/MTO (III)	EtOH	24	60	22	10
5	PVPN-25/MTO (IV)	EtOH	24	60	22	8
6	PS-2/MTO (V)	EtOH	24	60	18	8
7	PVP-2/MTO (I)	AcOH	24	60	23	12
8	MTO	[BMIM][PF ₆]	44	rt	98	91
9	PVP-2/MTO (I)	[BMIM][PF ₆]	48	rt	80	84
10	PVPN-2/MTO (II)	[BMIM][PF ₆]	48	rt	84	82
11	PVP-25/MTO (III)	[BMIM][PF ₆]	48	rt	75	86
12	PVPN-25/MTO (IV)	[BMIM][PF ₆]	48	rt	80	80
13	PS-2/MTO (V)	[BMIM][PF ₆]	48	rt	88	85

^a PVP-2/MTO: poly(4-vinylpyridine) 2% cross-linked. PVP-25/MTO: poly(4-vinylpyridine) 25% cross-linked. PVPN-2/MTO: poly(4-vinylpyridine *N*-oxide) 2% cross-linked. PVPN-25/MTO: poly(4-vinylpyridine *N*-oxide) 25% cross-linked. PS-2/MTO: polystyrene 2% cross-linked.

Table 4. Stability of catalysts **III** and **V** in the oxidation of **1** and **2** in [BMIM][PF₆]

Entry	Reagent	Product	Catalyst	Conversion (%)			
				Run no. 1 ^a	Run no. 2	Run no. 3	Run no. 4
1	1	6	III	51 (91) ^b	35 (80)	33 (78)	—
2	1	6	V	49 (88)	47 (88)	45 (86)	—
3	2	6	III	91 (82)	32 (76)	30 (75)	—
4	2	6	V	94 (78)	85 (78)	83 (77)	82 (76)

^a After the first reaction, following runs were performed adding only fresh substrate and oxidant to the ionic liquid, and working under the same experimental conditions.

^b Yields of benzophenone **6** are given in parentheses.

the highest value of the energy for the transition state in the epoxidation of olefins¹⁹ and oxygen-donor adducts of MTO usually show lower reactivity than MTO.²⁰

The oxidation of **3** with H₂O₂ and catalysts **I–V** in [BMIM][PF₆], at room temperature, afforded acetophenone **7** as the only recovered product in 80–86% yield and 75–88% conversion of substrate depending on the

catalyst used (Scheme 3, Table 3, entries 9–13). Noteworthy a higher reactivity was observed if compared to that showed in both ethanol and acetic acid at 60 °C (less than 5% conversion of substrates took place at room temperature). Under these latter conditions compound **7** was recovered in 8–12% yield and 18–26% conversion of substrate (see Table 3, entries 2–7).²¹

Table 5. Oxidation of **4** with MTO and polymer supported MTO catalysts

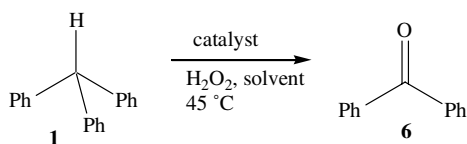
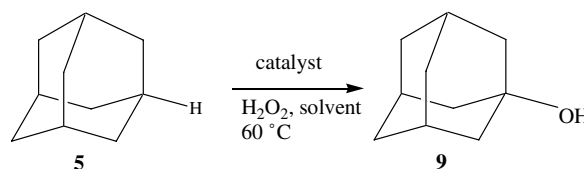
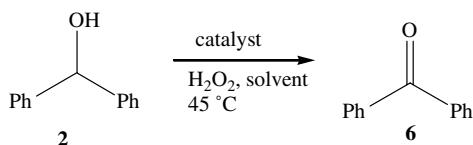
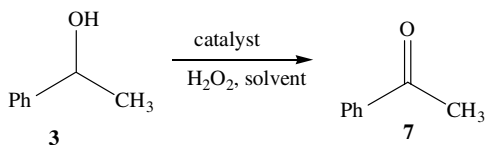
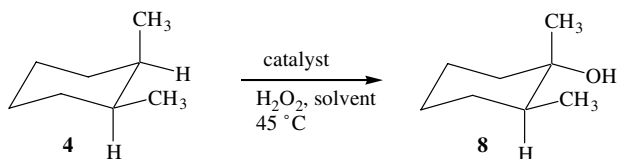
Entry	Catalyst ^a	Solvent	Time (h)	<i>T</i> (°C)	Conv. (%)	Yield (%)
1	MTO	[BMIM][PF ₆]	72	45	87	88
2	PVP-2/MTO (I)	[BMIM][PF ₆]	72	45	81	79
3	PVPN-2/MTO (II)	[BMIM][PF ₆]	72	45	78	75
4	PVP-25/MTO (III)	[BMIM][PF ₆]	72	45	68	78
5	PVPN-25/MTO (IV)	[BMIM][PF ₆]	72	45	71	76
6	PS-2/MTO (V)	[BMIM][PF ₆]	72	45	80	81

^a PVP-2/MTO: poly(4-vinylpyridine) 2% cross-linked. PVP-25/MTO: poly(4-vinylpyridine) 25% cross-linked. PVPN-2/MTO: poly(4-vinylpyridine *N*-oxide) 2% cross-linked. PVPN-25/MTO: poly(4-vinylpyridine *N*-oxide) 25% cross-linked. PS-2/MTO: polystyrene 2% cross-linked.

Table 6. Oxidation of **5** with MTO and polymer supported MTO catalysts

Entry	Catalyst ^a	Solvent	Time (h)	<i>T</i> (°C)	Conv. (%)	Yield (%)
1	MTO	[EMIM][Tf ₂ N]	48	60	43	68
2	PVP-2/MTO (I)	[EMIM][Tf ₂ N]	48	60	63	79
3	PVPN-2/MTO (II)	[EMIM][Tf ₂ N]	48	60	78	68
4	PVP-25/MTO (III)	[EMIM][Tf ₂ N]	48	60	69	75
5	PVPN-25/MTO (IV)	[EMIM][Tf ₂ N]	48	60	79	69
6	PS-2/MTO (V)	[EMIM][Tf ₂ N]	48	60	72	72

^a PVP-2/MTO: poly(4-vinylpyridine) 2% cross-linked. PVP-25/MTO: poly(4-vinylpyridine) 25% cross-linked. PVPN-2/MTO: poly(4-vinylpyridine *N*-oxide) 2% cross-linked. PVPN-25/MTO: poly(4-vinylpyridine *N*-oxide) 25% cross-linked. PS-2/MTO: polystyrene 2% cross-linked.

**Scheme 1.****Scheme 5.****Scheme 2.****Scheme 3.****Scheme 4.**

To evaluate the stability of heterogeneous MTO catalysts in ionic liquids the oxidation of **1** and **2** with catalysts **III** and **V** in [BMIM][PF₆], was repeated in successive trans-

formations. It is noteworthy that the recycled catalyst **V** showed comparable selectivity in the oxidation even after four runs, affording acetophenone **6** as the only recovered product in high yield (see Table 4, entries 2 and 4). However, in the case of the recycled catalyst **III**, a decrease of the reactivity was observed during the first recycling step (run no. 2), after which the value of conversion of substrates **1** and **2** become constant in the range of 30–35% (see Table 4, entries 1 and 3). Probably, a partial leaching of the catalyst was responsible for this behaviour.

The efficiency of oxygen-atom insertion by MTO and heterogeneous MTO catalysts in ionic liquids was further demonstrated through their ability to oxidize saturated hydrocarbons, such as *cis*-1,2-dimethylcyclohexane **4** and adamantane **5**. The reaction of **4** with both MTO and heterogeneous MTO catalysts **I–V** performed in [BMIM][PF₆] at 45 °C, gave the corresponding *cis*-1,2-dimethylcyclohexan-1-ol **8** both in high yield and conversion of substrate (Scheme 4, Table 5), showing a selective oxidation at the tertiary C–H bond. As shown in Table 5, compounds **I** and **V** were the best heterogeneous catalyst systems affording **8** in 79% and 81% yield, and 81% and 80% conversion, respectively (Table 5, entries 2 and 6). A similar selectivity in the oxidation of **4** was previously observed with dimethyldioxirane,²² a stoichiometric oxidant characterized by a ‘butterfly’ transition state, in the oxygen-atom insertion reaction, similar to that hypothesized for MTO.⁸

In the oxidation of adamantane **5** the ionic liquid [EMIM][Tf₂N] was used as reaction solvent in order to increase the solubility of substrate. When the reaction was performed at 60 °C in the presence of both MTO and heterogeneous MTO catalyst systems **I–V**, 1-adamantanol **9** was selectively obtained in acceptable yield and conversion of substrate (Scheme 5, Table 6). Noteworthy, in these latter cases catalysts **I**, **III** and **V** were found more reactive and selective than MTO (Table 6, entry 1 vs entries 2, 4 and 6), even if usually a catalytic species loses part of its catalyst efficiency after the heterogenization process. An enhancement of the reactivity of heterogeneous MTO catalysts with respect to parent MTO was previously observed in the oxidation of phenol and anisole derivatives to quinones with hydrogen peroxide.^{13a} Catalysts **II** and **IV** showed a reactivity similar to MTO (Table 6, entries 3 and 5). Again, poly(4-vinylpyridine) catalysts **I** and **III** were more selective than their corresponding *N*-oxide derivatives **II** and **IV** (Table 6, entries 2 and 4 vs entries 3 and 5), catalyst **I** being the best reactive system.

In conclusion, various hydrocarbons can be efficiently oxidized to corresponding ketones or alcohols by MTO and heterogeneous MTO catalyst systems **I–V** in ionic liquids using H₂O₂ as environment friendly oxidant. The efficiency and selectivity of catalysts **I–V** were sensitive to the nature of the polymeric support, poly(4-vinylpyridine) and polystyrene affording the best performances. In several cases the activity of catalysts **I–V** in ionic liquids was greater than that observed in molecular solvents. Moreover, in the oxidation of adamantane catalysts **I**, **III** and **V** were more reactive and selective than parent MTO. While MTO was not entirely retained in ionic liquids during extraction of the reaction mixtures with diethyl ether, catalyst **V** was easily recycled and used for successive transformations with similar selectivity and reactivity. Future work is therefore in progress, in order to exploit further on this efficient and environment respectful procedure.

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- The reaction mixtures were 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–MS instrument, using the same column. Yields and conversions of the reactions have been quantified using *n*-octane

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