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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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Abstract—The Baeyer–Villiger oxidation of cyclic ketones can be effected by methyltrioxorhenium/hydrogen peroxide in the ionic liquid [bmim]BF_4. After simple extraction of the lactone with diethyl ether, the catalyst can be repeatedly recycled and efficiently reused for the lactonisation process in the same reaction medium.

The Baeyer–Villiger oxidation of ketones is a reaction of considerable interest in organic chemistry, the corresponding lactones being important synthetic intermediates in the agrochemical, chemical and pharmaceutical industries.[1]

Developing green chemistry methodologies is one of the main themes of modern synthetic chemistry. In this context, catalysis is a powerful tool because it offers numerous benefits including lower energy requirements, increased selectivity, catalytic versus stoichiometric amounts of materials and the minimal production of hazardous and toxic wastes.[2] Heterogeneous catalysis, in particular, addresses the targets of green chemistry by allowing the easy separation of the products and permitting the recycling and reuse of the catalyst with operational and economical advantages. Polymer-anchored platinum complexes,[3] solid acids,[4] Sn-β zeolite,[5] Sn-MCM-41,[6] sulphonated resins[7] and silica-supported transition metal ions[8] are some of heterogeneous catalysts used to perform the Baeyer–Villiger reaction with benign oxidants such as hydrogen peroxide or molecular oxygen as alternatives to the use of organic peroxy acids. Recently, we established conditions for converting some flavanoid ketones into the corresponding lactones using hydrogen peroxide activated by methyltrioxorhenium (CH_3ReO_3) supported on poly(4-vinylpyridine) polymers.[9] However, under these conditions simple cyclic ketones such as cyclobutanone **1** reacted slowly or were unreactive such as cyclopentanone **3** and cyclohexanone **9**.[10]

A good alternative to heterogeneous catalysis would involve the possibility of reusing an efficient homogeneous catalyst in ionic liquids. Recently, a simple and practical approach to immobilizing OsO_4 for olefin dihydroxylation has been reported and the catalyst as well as the solvent were recycled and reused.[11] Other examples are reported in the literature.[12]

We report here the first catalytic Baeyer–Villiger oxidation of cyclic ketones with the recyclable catalytic system methyltrioxorhenium(CH_3ReO_3)/H_2O_2 in 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4.

To the best of our knowledge, only the methyltrioxorhenium-catalyzed epoxidation of highly reactive olefins in ionic liquids with urea–H_2O_2 adduct (UHP) has been reported but no recycling of the catalyst was described nor applications to other reactions.[15] As expected, among the simple ketones the highest activity was found for ring-strained cyclobutanone **1**. In fact, after only 1 h, γ-butyrolactone **2** was quantitatively isolated from the reaction mixture by simple extraction with diethyl ether (Table 1, entry 1). A second run was then performed by adding fresh substrate and oxidant

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Keywords: Baeyer–Villiger reaction; cyclic ketones; lactones; ionic liquids; [bmim]BF_4.

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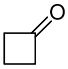
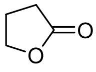
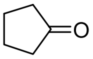
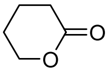
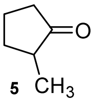
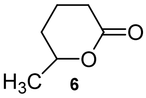
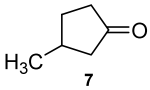
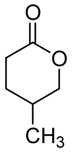
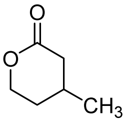
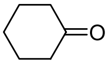
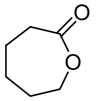
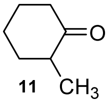
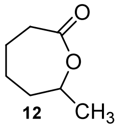
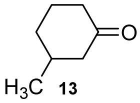
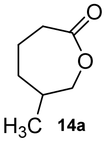
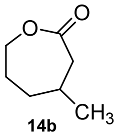
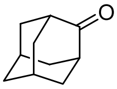
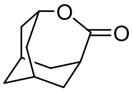
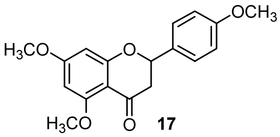
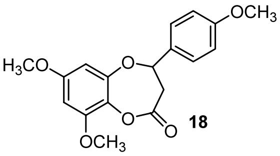
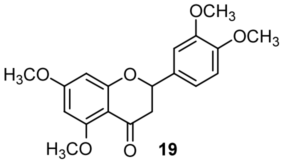
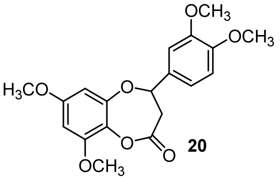
Table 1. Oxidation of ketones with CH_3ReO_3 (2%)/H_2O_2 (50% water solution) in [bmim]BF_4

Entry	Ketone	Lactone	Conditions	Conversion (%)	Yield (%)
1	 **1**	 **2**	H_2O_2 (2 eq.), r.t, 1 h	> 98[a]	> 98[a]
2	 **3**	 **4**	H_2O_2 (6 eq.), 60°C, 24 h	> 98[a]	70[a]
3	 **5**	 **6**	H_2O_2 (6 eq.), 60°C, 24 h	> 98[a]	75[a]
4	 **7**	 **8a**  **8b**	H_2O_2 (6 eq.), 60°C, 24 h	90[a,b]	74[a,b]
5	 **9**	 **10**	H_2O_2 (6 eq.), 60°C, 48 h	40[a]	20[a]
6	 **11**	 **12**	H_2O_2 (6 eq.), 60°C, 48 h	38[a]	20[a]
7	 **13**	 **14a**  **14b**	H_2O_2 (6 eq.), 60°C, 48 h	36[a,b]	18[a,b]
8	 **15**	 **16**	H_2O_2 (4 eq.), 60°C, 12 h	> 98[a]	> 98[a]
9	 **17**	 **18**	H_2O_2 (2 eq.), 40°C, 2 h	85[c]	> 98[c]
10	 **19**	 **20**	H_2O_2 (2 eq.), r.t, 2 h	82[c]	95[c]

[a] Conversions and yields were calculated by gas chromatography.

[b] Ratio of two regioisomers **8a**/**8b**=1/1 and **14a**/**14b**=4/1 were calculated from the ^{1}H-NMR spectrum of the oxidation products. Structures **8a**, **8b**, **14a** and **14b** have been reported in the literature.[13,14]

[c] Conversions and yields were calculated after chromatographic purification of the reaction mixture.

Table 2. Baeyer–Villiger oxidation of the ketones **1** and **17** in [bmim]BF_4 using CH_3ReO_3 as a recyclable catalyst

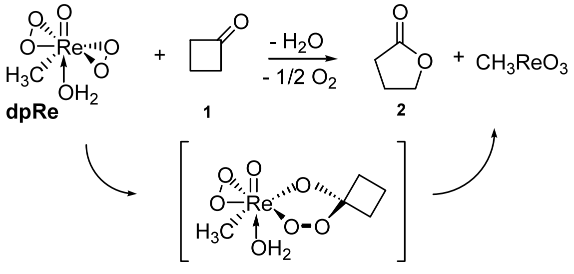
Entry	Ketone	Lactone	Conversions and yields (%)[a]					
			Run no. 1[b]	Run no. 2[b]	Run no. 3[b]	Run no. 4[b]	Run no. 5[b]	Run no. 6[b]
1	**1**	**2**	>98 (>98)	95 (>98)	95 (>98)	95 (>98)	88 (92)	65 (80)
2	**17**	**18**	85 (>98)	85 (95)	85 (95)	85 (95)	82 (90)	60 (85)

[a] Yields of the lactones **2** and **18** are given in parentheses. They were measured by gas chromatography after chromatographic purification of the reaction mixture.

[b] After the first run, successive runs were performed adding only fresh substrate and oxidant to the ionic liquid under the same experimental conditions.

to the ionic liquid under the same experimental conditions. It was noteworthy that the γ-butyrolactone **2** was isolated in the same yield without addition of CH_3ReO_3, indicating that both the ionic liquid and the catalyst were recyclable and reusable. This catalytic system was stable and efficient for five recycling experiments (Table 2, entry 1). Under the same experimental conditions, the cyclopentanones **3**, **5** and **7** reacted in good yield to give the corresponding lactones **4**, **6**, **8** (Table 1, entries 2–4), the cyclohexanones **9**, **11** and **13** being less reactive (Table 1, entries 5–7). The strained adamantanone **15** presented a high reactivity (Table 1, entry 8). This new oxidative methodology was tested on the methylated flavanones naringenin **17** and hesperetin **19** (Table 1, entries 9 and 10) which had been previously lactonized under heterogeneous conditions.[9] Experimental data indicated that the catalytic system CH_3ReO_3/H_2O_2 in [bmim]BF_4 was more efficient than CH_3ReO_3 supported on poly(4-vinylpyridine) polymers/H_2O_2 in *t*-butanol. In fact, the lactonization proceeded under milder conditions (40°C and room temperature versus 80°C, 2 equiv. versus 6–10 equiv. of oxidant), faster (2 h versus 6–12 h) and more efficiently (yields 85% and 82% versus 42–80% and 35–72% according to the polymers used).[9] The experimental data for recycling of the catalyst in [bmim]BF_4 starting from naringenin **17** confirms the recyclability of the catalyst in the same reaction medium (Table 2, entry 2).

Similarly, as reported by Herrmann on the homogeneous catalytic Baeyer–Villiger oxidation promoted by CH_3ReO_3 in conventional solvents,[16] the diperoxorhenium complexe **dpRe** could be the active species which operates a nucleophilic C-attack at the polar carbonyl group of the ketone (Scheme 1).



Scheme 1. Mechanistic pathway for the oxidation of cyclobutanone **1** catalysed by CH_3ReO_3.

In conclusion, the oxidative catalyst CH_3ReO_3 can be immobilized in ionic liquids and used to perform an efficient Baeyer–Villiger oxidation of cyclic ketones with hydrogen peroxide. This new catalytic system permits recycling both of the catalyst and of the reaction medium. Work is in progress in our laboratory to evaluate the possible chemo- and regioselectivity of this reaction in different ionic liquids.

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