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Oxidation of aromatic aldehydes and ketones by H_2O_2/CH_3ReO_3 in ionic liquids: a catalytic efficient reaction to achieve dihydric phenols

Roberta Bernini,[a,*] Antonietta Coratti,[a] Gianfranco Provenzano,[a] Giancarlo Fabrizi[b] and Daniela Tofani[c]

[a] *Dipartimento A.B.A.C, Università degli Studi della Tuscia, Via S. Camillo De Lellis, 01100 Viterbo, Italy*
[b] *Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università degli Studi di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy*
[c] *Dipartimento di Ingegneria Meccanica e Industriale, Università "Roma Tre", Via della Vasca Navale 79, 00146 Roma, Italy*

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Abstract—A convenient and efficient application of hydrogen peroxide/methyltrioxorhenium in ionic liquids [bmim]BF_4 and [bmim]PF_6 for the oxidation of hydroxylated and methoxylated benzaldehydes and acetophenones to the corresponding phenols is described. Good yields of products were obtained in short reaction times.

1. Introduction

The dihydric phenols such as catechol, hydroquinone and their methyl ethers, are high value chemicals. They are widely used as agrochemicals, antioxidants, pharmaceuticals, flavoring agents, polymerization inhibitors. For example, catechol is the basic chemical for the synthesis of the 4-*tert*-butylcatechol, an industrial antioxidant for foods and cosmetics[1] and for the synthesis of the pharmaceutical adrenalone;[2] guaiacol is used as good starting material for the industrial synthesis of vanillin, a prime flavor molecule;[3] hydroquinone is largely employed in photographic processes.[4]

Classical synthesis of this kind of phenols can be performed by catalytic oxidation of aromatic hydrocarbons,[5] hydroxylation of phenols,[6] oxidative decarboxylation of aryl carboxylic acids,[7] hydrolysis of halobenzenes.[8] Alternatively, the oxidation of benzaldeydes and acetophenones with alkaline hydrogen peroxide was an easy synthetic pathway (Dakin reaction).[9] However, under these conditions, reactions were too slow to be commercially attractive. Hydrogen peroxide/boric acid,[10] hydrogen peroxide/selenium compounds,[11] sodium perborate and sodium percarbonate,[12] *m*-chloroperbenzoic acid[13] were other useful reagents to convert aromatic aldehydes to the corresponding phenols, but these procedures required long reactions time, in some cases up to 30 h. Recently, Sn-Beta zeolites were used to activate hydrogen peroxide[14] providing an interesting example of good reactivity of aromatic aldehydes in short reaction times.

In recent years, methyltrioxorhenium (CH_3ReO_3, MTO)[15] has been shown to possess interesting catalytic properties in oxidation reactions with hydrogen peroxide as oxygen atom donor.[16] The reactive intermediate is a bis-peroxo metal [$CH_3ReO(O_2)_2$] complexes **dpRe** (Fig. 1) whose structure was established by X-ray analysis.[17] Recently, an efficient oxidation of hydroxylated and methoxylated benzaldeydes with hydrogen peroxide/methyltrioxorhenium in conventional solvents was described: under these conditions between 16 and 24 h were necessary to achieve complete oxidation.[18]

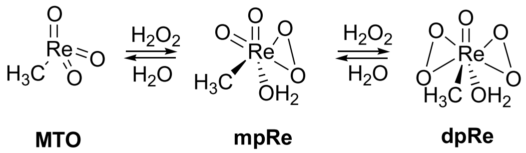

Figure 1. Catalytic system H_2O_2/CH_3ReO_3.

Keywords: Oxidation; Hydrogen peroxide/methyltrioxorhenium; Ionic liquids; Benzaldehydes; Acetophenones; Dihydric phenols.

* Corresponding author. Tel.: +39 0761357230; fax: +39 0761357230; e-mail: berninir@unitus.it

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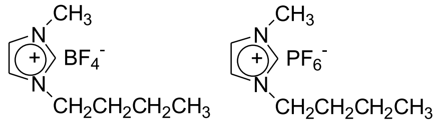
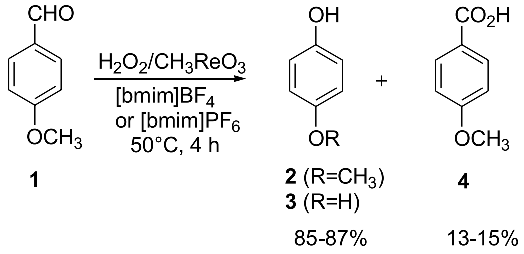
During recent years, the ionic liquids [bmim]BF_4 and [bmim]PF_6, where [bmim]$^+$ is the 1-butyl-3-methylimidazolium cation, were used as substitutes for molecular solvents in catalytic reactions (Fig. 2).[19] These kind of liquids have several interesting and benign properties: they show low volatility, chemical, physical and thermal stability and can furthermore be recycled and reused.[20] Moreover, catalytic oxidations proceed faster than in conventional solvents.[21] For example, hydrogen peroxide/boric acid in [bmim]PF_6 converted aromatic aldehydes into phenols very quickly (1–2 h)[22] and the *m*-chloroperbenzoic acid promoted Baeyer–Villiger oxidation of simple ketones and benzaldehydes was achieved in 2–4 h.[23]



[bmim]BF_4 **[bmim]PF_6**

Figure 2. Ionic liquids [bmim]BF_4 and [bmim]PF_6.

By continuing our studies into oxidations using the catalytic system hydrogen peroxide/methyltrioxorhenium in ionic liquids,[24] we report now the results on the oxidative conversion of substituted aromatic aldehydes and ketones in [bmim]BF_4 and [bmim]PF_6 to the corresponding phenols. Good yields of products in short reaction times and under controlled conditions were obtained.



Scheme 1. Oxidative conversion of 4-methoxybenzaldehyde **1**.

2. Results and discussion

As a model substrate, for the initial investigations, we chose 4-methoxybenzaldeyde **1** (Scheme 1). Our results are summarized in Table 1. Both in [bmim]BF_4 and [bmim]PF_6, the oxidation to 4-methoxyphenol **2** are faster at 50 °C and better in terms of yield and selectivity (entries 3, 4), than at 25 °C (entries 1, 2); small amount of hydroquinone **3** and 4-methoxybenzoic acid **4** were also isolated. Our results also showed that the nature of the anion of the ionic liquid was not important for the reactivity of the substrate and the reaction times. When the experiments were carried out under identical conditions but omitting the catalyst, we found that 4-methoxyphenol **2** was formed only in traces ($<5\%$). Experimentally, all the reactions were carried out at 50 °C for 4 h, the products were then selectively and quantitatively extracted from the ionic liquid solution by several extractions with small portions of diethyl ether. The second run was performed by adding fresh substrate and hydrogen peroxide to the ionic liquid solution: the catalytic system was still stable and efficient for five successive recycling experiments as reported in Table 2. However as general trend, we found a small increase in the yield of the 4-methoxybenzoic acid **4**, most probably as a consequence of added water.

Good results were obtained with activated benzaldehydes such as **5**, **7**, **11** and **13**. The corresponding phenols **3**, **8**, **9**, **14** were obtained in good yields (Scheme 2, Table 3, entries 1–8). Nevertheless, benzaldehydes with *meta*-substituted electron-donating groups **16**, **19** and unsubstitued benzaldehyde **22**, failed to oxidize to the Dakin products: in these

Table 1. Oxidation of 4-methoxybenzaldeyde **1** with hydrogen peroxide/methyltrioxorhenium in [bmim]BF_4 and [bmim]PF_6[a]

Entry	Ionic liquid	Conv. (%)	Yield (%) of **2**	Yield (%) of **3**	Yield (%) of **4**
1[b]	[bmim]BF_4	20	95	—	—
2[b]	[bmim]PF_6	18	98	—	—
3[c]	[bmim]BF_4	>98	77	10	13
4[c]	[bmim]PF_6	>98	75	10	15

[a] Conversions and yields were determined after chromatographic purification of reaction mixtures.
[b] H_2O_2 (35% water solution): 8 equiv; CH_3ReO_3 (2%), 25 °C, 24 h.
[c] H_2O_2 (35% water solution): 4 equiv; CH_3ReO_3 (2%), 50 °C, 4 h.

Table 2. Oxidation of 4-methoxybenzaldeyde **1** with H_2O_2/CH_3ReO_3 in [bmim]BF_4 and in [bmim]PF_6 as a recyclable system[a]

Run no.[b]	Conv. (%)[c]	Yield (%) of **2**[c]	Yield (%) of **3**[c]	Yield (%) of **4**[c]	Conv. (%)[d]	Yield (%) of **2**[d]	Yield (%) of **3**[d]	Yield (%) of **4**[d]
1	>98	77	10	13	>98	75	10	15
2	95	76	13	11	95	75	10	15
3	90	77	11	12	88	73	8	19
4	88	60	16	24	85	64	11	25
5	84	64	14	22	80	60	12	28
6	66	68	11	22	68	56	14	30

[a] Yields and conversions were calculated after chromatographic purification of the reaction mixture.
[b] After each run, the successive one was performed adding only fresh substrate and oxidant to the ionic liquid solution under the same experimental conditions.
[c] Data in [bmim]BF_4.
[d] Data in [bmim]PF_6.