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Molybdenum(VI)-peroxo complex catalyzed oxidation of alkylbenzenes with hydrogen peroxide

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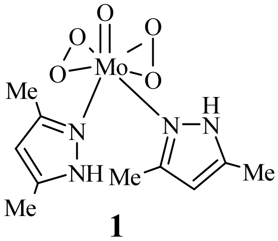
Abstract—The molybdenum(VI) peroxo complex **1**, synthesized from the reaction of MoO_3 with H_2O_2 and 3,5-dimethylpyrazole (dmpz), selectively oxidizes benzylic C-H bonds of alkylbenzenes to the corresponding alcohols and ketones in moderate to good yields in the presence of H_2O_2 in acetonitrile under reflux (ca. 80°C). © 2003 Elsevier Science Ltd. All rights reserved.

Metal catalyzed oxidation of organic compounds with hydrogen peroxide is rapidly gaining importance as a viable alternative to the environmentally hazardous metal promoted stoichiometric oxidations.[1,2] Recent studies have shown that transition metals in combination with various oxidizing agents can convert a wide range of hydrocarbons into the corresponding oxidized products.[3] These metal-catalyzed oxidations are modeled on certain enzymes which perform the oxidation of hydrocarbons in natural systems.[4] In spite of many studies, to the best of our knowledge, there is only one report which uses hydrogen peroxide, in addition to molecular oxygen, as the source of oxygen for the oxidation of the benzylic C–H bond of alkyl benzenes with a molybdenum complex under homogeneous conditions.[5] We now report that the new molybdenum(VI) oxo-diperoxo complex[6] **1**, synthesized from the reaction of MoO_3 with H_2O_2 and dmpz, has been found to catalyze the oxidation of the benzylic C–H bond of alkylbenzenes with hydrogen peroxide to the corresponding alcohols and ketones in moderate to good yields. This is the first example of a molybdenum catalyzed oxidation reaction that employs a molybdenum complex as the catalyst with H_2O_2 as the oxidant under atmospheric oxygen for the oxidation of alkylbenzenes.

The oxidation of diphenylmethane was first examined as a standard substrate with H_2O_2 in the presence of a catalytic amount of **1** in acetonitrile under atmospheric oxygen (Table 1). As anticipated the oxidation occurred selectively at the benzylic C–H bond and afforded a 3:2 mixture of diphenylmethanol and benzophenone in 62% yield when the reaction was allowed to reflux at ca. 80°C in the presence of 5 mol% of **1** for 12 h.[7] The reaction conditions with catalyst **1** and H_2O_2 are summarized in Table 1.



1

Table 1. Oxidation of diphenyl methane with **1** and H_2O_2

Entry	Catalyst **1** (mol%)	H_2O_2 (mmol)	Products (yield, %)[a,b]	
			Ph_2CHOH	Ph_2CO
1	5	20	30	9
2	5	40	38	24
3	5	60	43	25

[a] A solution of the catalyst **1**, diphenylmethane (1 mmol), H_2O_2 (30%) and acetonitrile (1 ml) was refluxed at ca. 80°C for 12 h under atmospheric oxygen.

[b] Isolated yield.

Keywords: alkylbenzene; selective oxidation; molybdenum peroxo complex; hydrogen peroxide.

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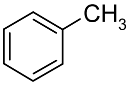
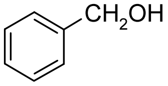
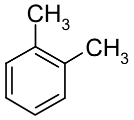
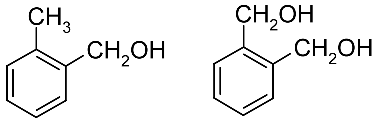
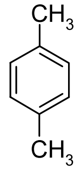
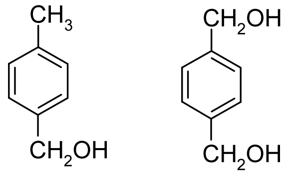
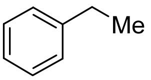
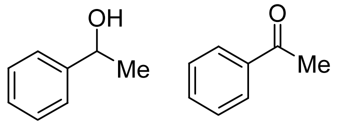
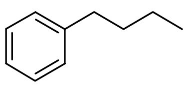
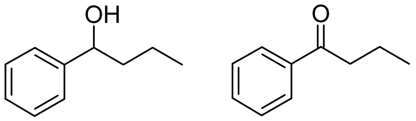
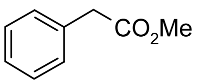
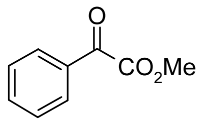
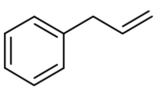
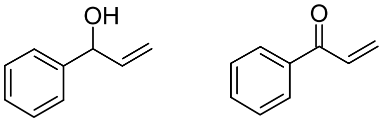
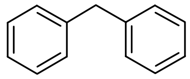
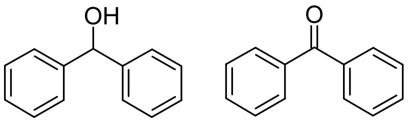
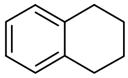
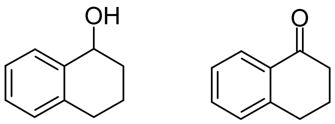
To evaluate the scope of this reaction, the oxidation of allylbenzene, butylbenzene, ethylbenzene, tetralin, toluene and xylenes (*ortho* and *para*) were studied further (entries 1–5, 7 and 9, Table 2). As described above, the oxidation consistently took place at a benzylic C–H bond. The substrates containing secondary C–H bonds, allylbenzene, butylbenzene, ethylbenzene and tetralin, were oxidized to a mixture of the corresponding alcohols and ketones in high yields (entries 4–5, 7 and 9, Table 2). However, toluene and xylenes were less reactive affording the corresponding alcohols as the products thereby suggesting that the ease of oxidation is a

Table 2. Oxidation of alkylbenzenes with **1** and H_2O_2

Entry	Substrate	Time (h)	Product(s)	Yield (%)[a,b]
1		12		37[c,d]
2		14		23 (2:1)[d]
3		14		27 (2:1)[d]
4		15		64(9:1)[c]
5		13		75(8:1)
6		10		82
7		8		81 (5:2)
8		12		62 (3:2)
9		9		84 (9:1)

[a] A solution of the catalyst **1** (5 mol%), alkylbenzene (1 mmol), H_2O_2 (30%, 40 mmol) and acetonitrile (1 ml) was heated under reflux at *ca.* 80 °C under atmospheric oxygen. [b] Isolated yield. [c] GC yield. [d] Catalyst **1** (6 mol%) used. No oxidation was observed in the absence of **1**. The identity of the products was ascertained by IR, ^{1}H NMR and mass spectroscopy and by comparison with authentic samples.

direct reflection of the C–H bond strength (entries 1–3, Table 2). In the case of allylbenzene no double bond oxidation was observed. Similarly, methyl phenylacetate afforded the corresponding α-keto ester selectively as the product, no oxidative cleavage being observed (entry 6, Table 2).

Notably, the yields of the oxidized products were significantly reduced when the reactions were carried out under a nitrogen atmosphere. Additionally, the oxidation of diphenylmethanol was carried out separately and benzophenone (90%) was obtained. This study suggested that the ketones produced in the oxidation of the substrates having secondary C–H bonds are derived from in situ oxidation of the respective secondary alcohols.

In conclusion, the studies described herein indicate that the molybdenum complex **1** catalyses the oxidation of alkylbenzenes in the presence of hydrogen peroxide under atmospheric oxygen in moderate to good yields. The system is mild and selective in so far as benzylic C–H bond oxidation is concerned. Further investigation is in progress to determine the detailed mechanism and the exact chemical nature of the active oxidant in these oxidations.

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6. *Preparation of* **1**. MoO_3 (22.22 mmol) was dissolved in 30% H_2O_2 (220 mmol). The solution was cooled in an ice-bath and then dmpz (44.93 mmol) was added in portions. A red suspension was obtained at this stage which was stirred for 1 h and then left overnight at ca. 4°C to afford a lemon yellow colored microcrystalline complex, $[MoO(O_2)_2(dmpz)_2]$ **1**, in 57% yield. Mp 91°C; IR(KBr) v/cm^{-1}: 935 (Mo=O), 882 (O-O), 592 (Mo-O_2, sym.), 665 (Mo=O_2, asym.), 1568 (C-N), 3323, (N-H), 303 (Mo-N);[8] Raman (KBr) v/cm^{-1}: 956 (Mo=O), 886 (O-O), 320 (Mo-N), 674 (Mo-O_2, asym), 595 (Mo-O_2, sym); electronic spectrum[9] λ/nm: 332 ($\pi^*_v \rightarrow d^*_\sigma$), 216 ($\pi^*_h \rightarrow d^*_\sigma$). Anal. calcd for $C_{10}H_{16}O_5N_4Mo$: C, 32.62; H, 4.39; N, 15.21; O_2^{2-}, 17.38; Mo, 26.05. Found: C, 32.39; H, 4.58; N, 15.15; O_2^{2-}, 16.89; Mo, 26.40.
7. Alkylbenzene (1 mmol), $MoO(O_2)_2(dmpz)_2$ **1** (5 mol%) and hydrogen peroxide (30%, 40 mmol) were dissolved in acetonitrile (1 ml) and the homogeneous solution was heated at ca. 80°C under atmospheric oxygen for the appropriate time (see Table 2). The products were then either identified by GC analysis or the aqueous CH_3CN was removed on a rotary evaporator and the residue was passed through a short pad of silica gel using a mixture of ethyl acetate and hexane as eluent to afford the corresponding alcohols and ketones.
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