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Novel Polyaniline-Supported Molybdenum-Catalyzed Aerobic Oxidation of Alcohols to Aldehydes and Ketones

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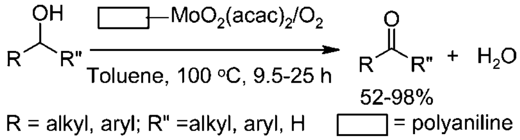
ABSTRACT



Oxidation of alcohols to aldehydes and ketones has been studied in high yields using molecular oxygen and a catalytic amount of 1 in toluene under stirring (ca. 100 °C). The reactions of primary alcohols are faster compared to secondary alcohols and the catalyst 1 can be recycled without loss of activity.

Oxidation of alcohols to carbonyl compounds is a fundamental functional transformation in organic chemistry.[1] Numerous oxidizing agents are available to effect this transformation. However, most of these oxidizing reagents are often required in stoichiometric quantities and are sometimes toxic. From an economical and environmental viewpoint, catalytic oxidation processes are thus valuable, and those employing molecular oxygen or air are particularly attractive. Recently, Ru,[2] Ru−Co,[2c] Co,[3] Cu,[4] and Zr[5] complexes have been shown to catalyze the aerobic oxidation of alcohols in the presence of co-reductants such as aldehydes, *N*-hydroxyphthalimide, diethyl azodicarboxylate, *β*-ketoesters, hydroquinone, or nitrosonium ions, while molecular oxygen as the sole oxidant is sufficient when catalysts based on V,[6] Pt,[7] Rh,[8] Pd,[9] Ru,[10] Co,[11] Ni,[12] Cu,[13] Os,[14] and polyoxometalates[15] are used.

The use of heterogeneous catalysts in the liquid phase offers several advantages over homogeneous ones, such as ease of recovery and recycling, atom utility, and enhanced stability.[9g,10b,h] During the course of our investigation on the oxidation of organic compounds,[6d,16] we have found that polyaniline-supported $MoO_2(acac)_2$ **1** is recyclable and catalyzes efficiently the oxidation of alcohols to aldehydes and ketones with molecular oxygen in high yields (Scheme 1). This is a clean technology process where compounds are

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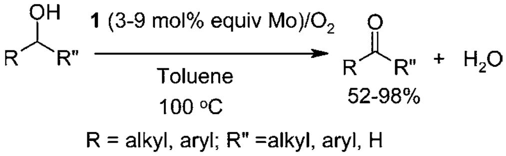
10.1021/ol048195t CCC: $27.50

Scheme 1



formed free from any contaminated byproducts. To the best of our knowledge, no report is available in the literature in regard to the aerobic oxidation of alcohols with molecular oxygen using a recyclable molybdenum catalyst. Furthermore, this is the first example for the activation of molecular oxygen using a polymer-supported molybdenum catalyst.[17]

Catalyst **1** was prepared by stirring a 1:1 mixture of the commercially available polyaniline[18] and $MoO_2(acac)_2$[19] in acetonitrile for 50 h at ambient temperature, and a tentative structure is shown in Figure 1. The oxidation of 4-methoxybenzyl alcohol was then examined as a standard substrate in the presence of a catalytic amount of **1** in toluene under molecular oxygen. As expected, the oxidation took place affording 4-methoxybenzaldehyde in 96% yield when the reaction mixture was allowed to stir at 100 °C for 9.5 h. In contrast, the corresponding homogeneous process using $MoO_2(acac)_2$ was less effective and provided a mixture of 4-methoxybenzaldehyde and 4-methoxybenzoic acid in 58% and 13% yield, respectively (Scheme 2).

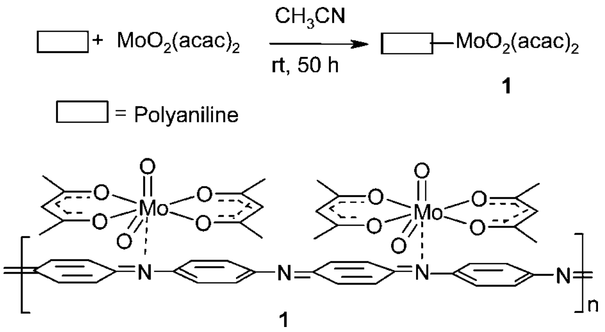
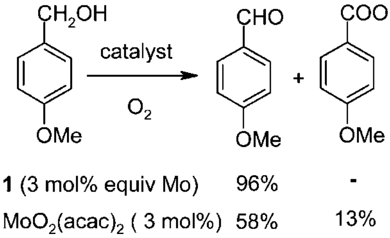


Figure 1. Proposed polyaniline-supported $MoO_2(acac)_2$ structure.

Scheme 2



To study the scope of this procedure, the oxidation of other alcohols was next studied (Table 1, entries 1−16). Benzyl

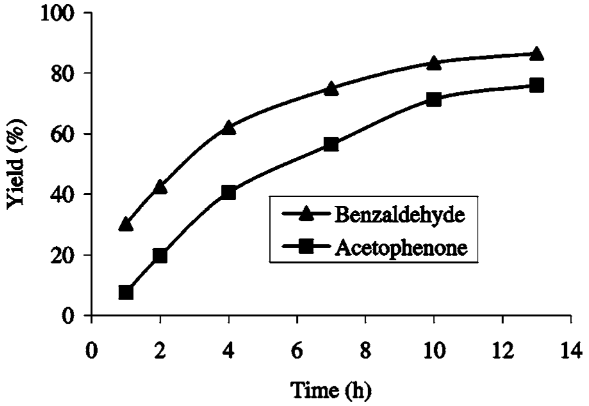


Figure 2. Progress of the oxidation of benzyl alcohol and phenylethanol.

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Table 1. Aerobic Oxidation of Alcohols to Aldehydes and Ketones Using Catalyst **1**[a]

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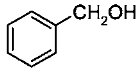
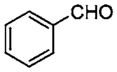
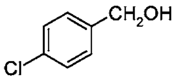
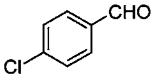
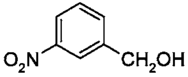
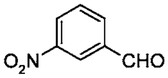
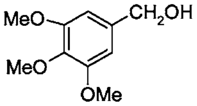
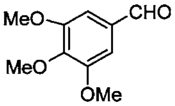
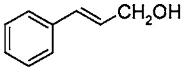
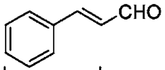
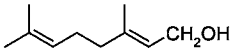
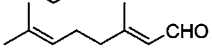
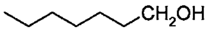
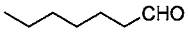
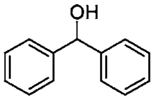
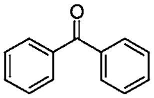
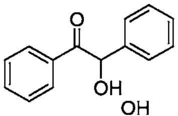
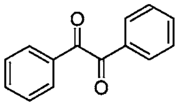
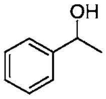
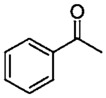
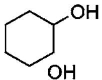
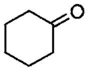
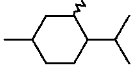
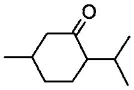
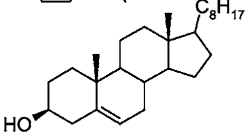
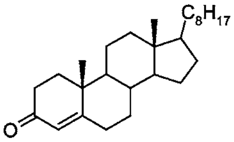
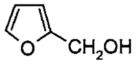
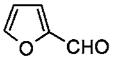
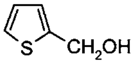
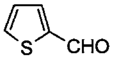
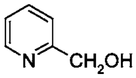
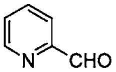
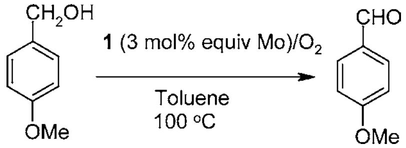
1		12	86(92)[c]	>98	
2		13	85	>99	
3		12	69	100	
4		10	89	>99	
5[d]		16	75	86	
6[d]		19	77	77	
7[e]		17	80(86)[c]	100	
8		18	85	100	
9		14	90	99	
10		18	80(89)[c]	100	
11		15	59(68)[c]	100	
12		21	52	100	
13[f,g]		25	72	100	
14		11	98	99	
15		11	88	99	
16		20	72	99	

[a] Substrate (1 mmol) and catalyst **1** (22 mg, 3 mol equiv of Mo) were stirred at ca. 100 °C under oxygen balloon for the appropriate time. [b] Isolated yield. [c] GC yield. [d] Accompanied 5−10% of unidentified products. [e] Catalyst **1** (44 mg, 6 mol equiv of Mo) used. [f] 1,2-Dichloroethane was employed as solvent. [g] Catalyst **1** (66 mg, 9 mol equiv of Mo) used. [h] Determined by GC (except entry 13).

alcohol was oxidized to benzaldehyde in 92% conversion and 98% selectivity. A similar reactivity was observed with the substrates having electron-withdrawing and -donating groups in the aromatic ring, i.e., 4-chloro-, 3-nitro-, and 3,4,5-trimethoxybenzyl alcohols. Allylic alcohols, geraniol, and cinnamyl alcohol were oxidized to the corresponding aldehydes in moderate selectivity. An aliphatic alcohol, heptanol, could be oxidized to heptanal in 86% yield. Secondary alcohols such as phenylethanol, diphenylmethanol, benzoin, cyclohexanol, and (±)-menthol required a slightly longer reaction time compared to primary alcohols to afford the corresponding ketones in 52−90% yields. The oxidation profile of a 1:1 mixture of benzyl alcohol and phenylethanol is shown in Figure 2. In the case of cholesterol, the carbon−carbon double bond migrated to give 4-cholesten-3-one in 72% yield. Heterocyclic alcohols, 2-furfurol, 2-thiophenemethanol, and 2-pyridinemethanol, were oxidized to the corresponding aldehydes in high yields. No oxidation was

Table 2. Recycling of the Catalyst **1**



run	product (%, yield)[b]	recovery (%)
1	96	>99
2	95	>98
3	94	>97

observed with S and N heteroatoms. However, diols, 1,3-dihyroxybutane and 1,2-dihydroxypropane, were less reactive and provided a trace (<3%) of mixture of the corresponding keto and hydroxy aldehydes after 50 h.

The catalyst **1** could be filtered and recycled (Table 2). For example, the oxidation of 4-methoxybenzyl alcohol was performed up to three runs with no loss of activity. Furthermore, to study the leaching of the metal complex, catalyst **1** was stirred at 100 °C for 10 h and the filtrate was used for the oxidation of 4-methoxybenzyl alcohol. No reaction was observed, indicating that leaching of the metal complex has not occurred.

In conclusion, the oxidation of alcohols to aldehydes and ketones has been studied with molecular oxygen in the presence of recyclable catalyst **1** in high yields. This reaction provides a new environmentally friendly route to the conversion of alcoholic functions to carbonyl groups. Aldehydes do not undergo further oxidation to carboxylic acids.

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Supporting Information Available: General experimental procedure and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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