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Homogeneous and heterogeneous catalytic oxidation of benzylic and secondary alcohols with a metal dioxygenato complex in the presence of 2-methylpropanal and dioxygen

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Abstract

The oxidation of benzylic and secondary alcohols under homogeneous conditions was achieved at 40°C using molecular oxygen as the oxidant in the presence of excess 2-methylpropanal and catalytic amount of Co(acac)$_2$. The oxidation reactions were also carried out with a heterogeneous analogue of Co(acac)$_2$ revealing that the supported cobalt polymer acts as an active and reusable catalyst. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Secondary alcohols; Benzylic alcohols; Metal β-diketonates; Supported metals

1. Introduction

Metal-catalysed oxidation of alcohols to carbonyl compounds in combination with molecular oxygen as the oxidant represents a significant step in synthetic organic chemistry for both environmental and economical reasons. Although much attention has recently focused on the aerobic catalytic oxidation of secondary alcohols to the corresponding ketones under homogeneous conditions [1–8], however, few reactions of aerobic oxidation of alcohols in heterogeneous phase are known. For example, aerobic catalytic procedures involving fixed giant Pd cluster [9], polymer supported perruthenate compound [10,11] and heterogeneous systems based on copper chloride/ phenanthroline [12] or CeO$_2$/Ru systems [13] have been reported. More recently, a heterogeneous Ru–Al–Co hydrotalcites catalytic system showed high activity toward the aerobic oxidation of allylic and benzylic alcohols [14].

In our previous works, we have investigated the oxidation of various organic substrates using the catalytic system based on a metal β-dioxygenato complexes, a sacrificial aldehyde and oxygen or air [15–22]. During the course of these studies, the aerobic oxidation of cyclohexanol to cyclohexanone at room temperature catalysed by nickel(II), iron(III) and cobalt(II) β-ketoesterate complexes in the presence of excess 3-methylbutanal has been reported. However, the maximum turnover, obtained with Co(II) catalytic system, was

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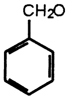
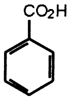
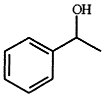
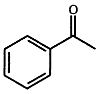
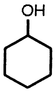
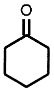
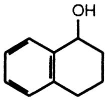
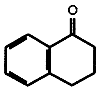
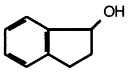
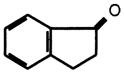
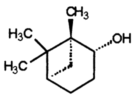
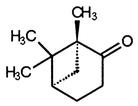
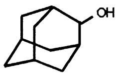
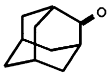
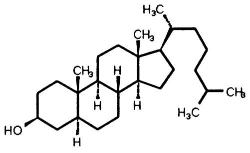
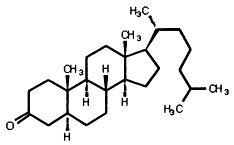
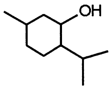
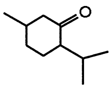
only 1.5 h^{-1} [16]. Iqbal and co-workers reported a similar type of catalytic aerobic oxidation of various alcohols to carbonyl compounds using a cobalt–Schiff base complex in the presence of 2-methylpropanal [23].

Starting from those preliminary results, in this paper we present an efficient method for the oxidation of benzylic and secondary alcohols catalysed by dioxygenato complexes under homogeneous and heterogeneous conditions.

Commercially available metal acetylacetonato complexes in the presence of excess 2-methylpropanal were used for the aerobic oxidations in homogeneous phase, while the copolymer obtained by reaction of $Co(AAEMA)_2$ [$AAEMA^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate)] with *N*,*N*-dimetylacrylamide and *N*,*N*′-methylenebisacrylamide in *N*,*N*-dimethylformamide was the catalyst used for the same reactions in heterogeneous phase.

Table 1

Oxidation of alcohols (1.2 mmol) with dioxygen ($p = 1$ atm) and 2-methylpropanal (3.6 mmol present at the beginning of the reaction plus that added as indicated in the notes) in the absence of metal catalyst; solvent: 1,2-dichloroethane (8 ml); $T = 40°C$

Entry	Substrate	Product	Time (h)	Yield (%)
1[a]			6	4[a]
2[b]			7	20
3[b]			7	22
4			5	20
5			5	58
6			4	32
7[b]			7	9
8[b]			7	33
9[c]			9	17

[a] The relevant yield in benzaldehyde was 29%.

[b] 1.2 mmol aldehyde added after 6 h reaction.

[c] 1.2 × 2 mmol aldehyde added at reaction times: 6 and 8 h.

2. Experimental

2.1. Materials and apparatus

The metal acetylacetonates, the substrates, the standards and 2-methylpropanal were purchased by Aldrich. Chromatographic analyses were carried out on a Hewlett Packard 6890 instrument using a capillary 30 m HP-5 (5% phenyl methyl siloxane) column or a capillary 30 m SPB-1 column. GCMS data (EI, 70 eV) were acquired on a HP 6890 instrument using a HP 19091S-433 HP-5MS 5% phenyl methyl siloxane 30.0 m × 250 μm × 0.25 μm coupled with a mass spectrometer HP 5973. The oxidised products were identified by comparison of their MS spectra and retention times in GC analyses with those of authentic samples. The yields were calculated by GLC analyses as moles of oxidised product per mole of starting alcohol by using the internal standard method.

2.2. Catalytic runs

2.2.1. Homogeneous phase

A three-necked flask equipped with a dropping funnel was wrapped with aluminium foil and charged with the substrate (1.2 mmol), the metal acetylacetonate (0.020 mmol, when present), 2-methylpropanal (added dropwise as specified in the caption of Tables 1, 2 and 3) in 1,2-dichloroethane (8 ml) and the mixture was vigorously stirred under dioxygen ($p = 1$ atm) at 40°C, and monitored by GLC and GCMS.

Table 2
Oxidation of benzyl alcohol (1.2 mmol) with dioxygen ($p = 1$ atm) and 2-methylpropanal (3.6×4 mmol added at times: 0, 5, 24 and 31 h); solvent: 1,2-dichloroethane (8 ml); $T = 40$°C; catalyst/substrate = 1/60 mol/mol

Entry	Catalyst	Time (h)	Yield (%)
1[a]	Co(acac)$_2$	6	96
2	Cu(acac)$_2$	32	90
3	Ni(acac)$_2$	32	96
4	Pd(acac)$_2$	32	10
5	Fe(acac)$_3$	32	54
6	Mn(acac)$_3$	32	49

[a] 3.6 mmol × 2 mmol aldehyde added at reaction times: 0 and 5 h.

2.2.2. Heterogeneous phase

A three-necked flask equipped with a dropping funnel was wrapped with aluminium foil and charged with the substrate (1.2 mmol), the supported cobalt catalyst (26.4 mg, 4.47% of Co), 2-methylpropanal (added dropwise as specified in the caption of Table 4) in 1,2-dichloroethane (8 ml) and the mixture was vigorously stirred under dioxygen ($p = 1$ atm) at 40°C until completion of the reaction as monitored by GLC. The supported catalyst was recovered after duty by addition of diethyl ether to the suspension and subsequent centrifugation. The recovered resin was washed with 1,2-dichloroethane and diethyl ether, dried under vacuum and recycled.

3. Results and discussion

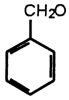
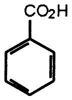
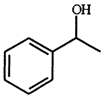
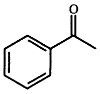
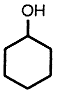
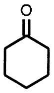
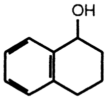
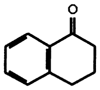
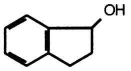
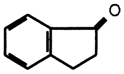
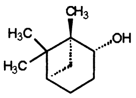
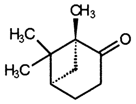
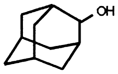
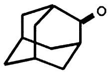
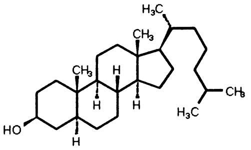
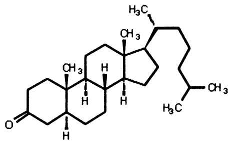
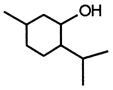
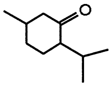
3.1. Oxidation of alcohols in homogeneous phase

It is known that the autoxidation of aldehyde to a peracid species in the presence of molecular oxygen can lead to the oxidation of alkenes [24–26], ketones [27,28] and hydrocarbons [18] even in the absence of a metal catalyst. Aerobic oxidations of several alcohols with sacrificial aldehyde were carried out in the absence of metal catalyst and the results are collected in Table 1. It is apparent that the non-catalysed reactions proceed sluggishly, with a maximum yield of 58% obtained in the case of 1-indanol (entry 5).

The aerobic oxidation of alcohols, with or without catalyst, was generally carried out at 40°C in the dark and in the presence of an initial aldehyde/substrate ratio equal to 3. When the reactions stopped before completion, as monitored by GLC analyses, fresh aldehyde was added to the reaction mixture as indicated in the captions of the Tables 1–4. This procedure was found to be the best compromise between the requirement of continuous feeding of aldehyde together with the need of minimising the amount of 2-methylpropanoic acid that continuously forms in the reaction medium and can give rise to undesired esterification of the unreacted starting alcohol.

A screening of various metal acetylacetonates was performed to compare their catalytic activity in the oxidation of benzyl alcohol to benzoic acid. The relevant results are summarised in Table 2. Among the metal acetylacetonates tested, Co(acac)$_2$ was shown to be the

Table 3
Oxidation of alcohols (1.2 mmol) with dioxygen ($p = 1$ atm), Co(acac)$_2$, 2-methylpropanal (3.6 mmol present at the beginning of the reaction plus that added as indicated in the notes); solvent: 1,2-dichloroethane (8 ml); $T = 40^\circ$C, Co(acac)$_2$/substrate = 1/60 mol/mol

Entry	Substrate	Product	Time (h)	Yield (%)
1[a]			6	96
2[b]			7	82
3[b]			7	89
4			5	93
5			4	98
6			4	97
7[b]			7	90
8[b]			7	85
9[c]			9	54

[a] 1.2 mmol aldehyde added after 5 h reaction.

[b] 1.2 mmol aldehyde added after 6 h reaction.

[c] 1.2 × 2 mmol aldehyde added at reaction times: 6 and 8 h.

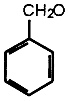
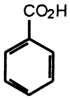
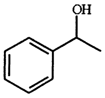
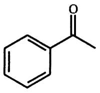
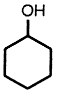
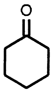
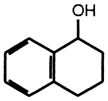
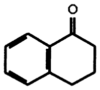
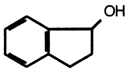
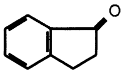
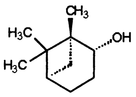
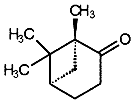
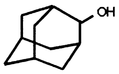
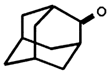
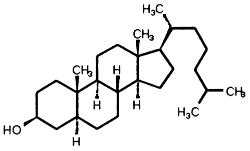
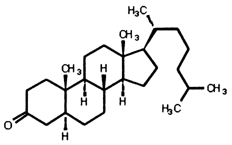
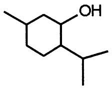
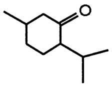
most active catalyst, affording 96% conversion in 6 h (entry 1). Cu(acac)$_2$ and Ni(acac)$_2$ gave high yields (90% and 96%, respectively), but the reactions were quite slow (32 h, entries 2, 3). Pd(acac)$_2$, Fe(acac)$_3$ and Mn(acac)$_2$ based catalytic systems were less effective giving yields ranging between 10 and 54% in 32 h (entries 4–6).

Next, we have carried out aerobic oxidation of various alcohols catalysed by Co(acac)$_2$ under homogeneous conditions. The results are reported in Table 3.

The phenethyl alcohol was smoothly oxidised to the corresponding carbonyl compound in 82% yield (entry 2). Small amounts of styrene (10% ca.), deriving from acid catalysed dehydration of the starting alcohol was also detected in the reaction mixture.

Cyclohexanol was converted into cyclohexanone in 7 h, with a yield of 89% (entry 3). The selectivity of the reaction was slightly lowered by the formation of the cyclohexyl ester of *i*-butyrric acid (ca. 4%).

Table 4
Oxidation of alcohols (1.2 mmol) with dioxygen ($p = 1$ atm) and 2-methylpropanal (3.6 mmol present at the beginning of the reaction plus that added as indicated in the notes) in the presence of supported cobalt; solvent: 1,2-dichloroethane (8 ml); $T = 40°\text{C}$, Co/substrate $= 1/60$ mol/mol

Entry	Substrate	Product	Time (h)	Yield (%)
1[a]			6	94
2[b]			7	94
3[b]			7	92
4			5	95
5			2	99
6			4	97
7[b]			7	95
8[b]			7	86
9[c]			9	75

[a] 1.2 mmol aldehyde added after 5 h reaction.
[b] 1.2 mmol aldehyde added after 6 h reaction.
[c] 1.2 × 2 mmol aldehyde added at reaction times: 6 and 8 h.

The oxidation of 1,2,3,4-tetrahydro-1-naphtol, 1-indanol, isopinocampheol to the corresponding ketones was achieved in high yield (93–98%) and in 100% selectivity (entries 4–6).

2-Adamantanol and 5α-cholestan-3β-ol yielded in 7 h 90% and 85%, respectively of the corresponding carbonyl compounds (entries 7, 8). The oxidation of menthol was relatively slow and gave 54% conversion into menthone after 9 h (entry 9).

3.2. Oxidation of alcohols in heterogeneous phase

Our interest was focused on two aspects of the heterogeneous reactions of alcohols oxidation carried out with the copolymer obtained from Co(AAEMA)$_2$ and the aforementioned acrylamides [19]: the activity and the recyclability of the supported catalyst. The results obtained in the heterogeneous oxidation of alcohols are summarised in Table 4 and show that in all cases,

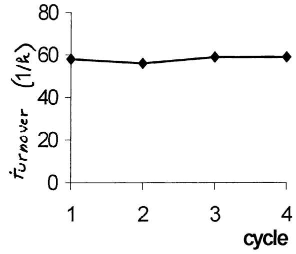


Fig. 1. Recyclability of the cobalt-polymer in the oxidation of indanol (1.2 mmol) with O_2 ($p = 1$ atm), 2-methylpropanal (3.6 mmol) in 1,2-dichloroethane (8 ml) at room temperature; supported cobalt/substrate = 1/60 mol/mol. Yield in indanone ≥97% in each run.

high yields in the desired carbonyl compounds were achieved. It is noteworthy that 1-indanol and menthol gave higher turnovers compared to those obtained in homogeneous phase.

As to recyclability, turnovers ranging between 56 and 59 h^{-1} were obtained in four subsequent reaction cycles of the oxidation of 1-indanol to 1-indanone, reusing the same batch of supported complex (Fig. 1).

Moreover, for all the oxidation reactions shown in Table 4 the supported catalyst was easily separated from the reaction mixture and was recycled at least once without appreciable loss of activity and selectivity.

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