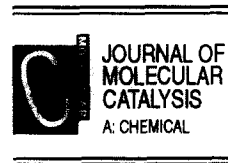




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# Aerobic oxidation of $\alpha$ -hydroxyketones catalysed by cobalt(II) and iron(III) complexes under homogeneous and heterogeneous conditions

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## Abstract

Aromatic  $\alpha$ -hydroxyketones were easily oxidized by dioxygen in the presence of excess aldehyde or aldoacetal with catalytic amount of Co(II) or Fe(III) complexes, under homogeneous and heterogeneous conditions. Co(acac)<sub>2</sub> or Fe(acac)<sub>3</sub> were the catalysts used in homogeneous phase reactions whereas Co(II) or Fe(III) supported complexes, obtained by copolymerization of Co(AAEMA)<sub>2</sub> or Fe(AAEMA)<sub>3</sub> (AAEMA<sup>-</sup> = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate) with acrylamides, were the heterogeneous catalysts. The supported metal complexes were recyclable and did not suffer from metal leaching.

**Keywords:** Oxidation; Ketones; Hydroxyketones; Diketones; Metal  $\beta$ -diketonates; Heterogeneous reactions; Polymer; Supported catalysts

## 1. Introduction

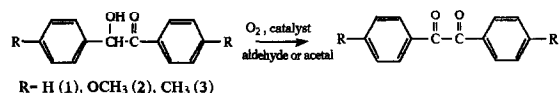
The oxidation of  $\alpha$ -hydroxyketones represents the most direct route to  $\alpha$ -diketones. The commonly used procedure for the synthesis of benzils from benzoin and derivatives is the cupric acetate promoted reaction with ammonium nitrate [1]. Other catalytic methods more recently developed to oxidize benzoin to benzils employ air, perchloric acid or *p*-benzoquinone as the oxidants and nickel [2], thallium [3], ytterbium [4], iron [5] or molybdenum [6] complexes as the catalysts.

Following our study on the catalytic activity of  $\alpha$ -diketonato complexes [7] and of their heterogeneous analogues [8] in oxidation reactions under Mukaiyama's conditions [9] (e.g. aerobic oxidations carried out in the presence of excess sacrificial aldehyde or aldoacetal) we discovered a new method for the oxidation of  $\alpha$ -hydroxyketones such as benzoin, 4,4'-dimethylbenzoin and 4,4'-dimethoxybenzoin (anisoin) to the corresponding  $\alpha$ -diketones (Scheme 1).

## 2. Results and discussion

The catalytic activity of several metal diketonates was explored using anisoin as the sub-

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Scheme 1.

strate. When  $\text{Co}(\text{acac})_2$  or  $\text{Fe}(\text{acac})_3$  were employed, high yields of anisoil (> 88%) were obtained after 4 h and 5 h respectively. On the contrary,  $\text{Ni}(\text{acac})_2$  and  $\text{Cu}(\text{acac})_2$  in the same conditions, gave high conversions of the starting material but in both cases the major reaction product was *p*-anisic acid deriving from cleavage of the C–C bond. The same product was also obtained when the reaction was performed under Mukaiyama's conditions but in the absence of any metal catalyst, or when the oxidation was carried out by *m*-chloroperbenzoic acid procedure.

The results obtained when benzoin (1), anisoil (2), and 4,4'-dimethylbenzoin (3) were exposed to oxidizing conditions in reactions catalysed by  $\text{Co}(\text{acac})_2$  and  $\text{Fe}(\text{acac})_3$  are summarized in Table 1.  $\text{Co}(\text{acac})_2$  was more active compared to  $\text{Fe}(\text{acac})_3$  and the reactivity of the tested substrates followed the order: benzoin > anisoil > 4,4'-dimethylbenzoin.

In the case of benzoin the reaction reached completion after 1.5 h ( $\text{Co}(\text{acac})_2$ , entry 1) or 4 h ( $\text{Fe}(\text{acac})_3$ , entry 2). In the other cases the reactions stopped before completion at a maximum 86% conversion obtained with anisoil in the presence of  $\text{Co}(\text{acac})_2$  (entry 3), due to the

Table 1  
Oxidation of benzoins under Mukaiyama's conditions<sup>a</sup>

Entry	Substrate	Catalyst	Time (h)	Conversion %	Yield %
1	benzoin	$\text{Co}(\text{acac})_2$	1.5	100	94
2	benzoin	$\text{Fe}(\text{acac})_3$	4	100	85
3	anisoil	$\text{Co}(\text{acac})_2$	4	86	96
4	anisoil	$\text{Fe}(\text{acac})_3$	5	52	89
5	4,4'-dimethyl-benzoin	$\text{Co}(\text{acac})_2$	2	70	95
6	4,4'-dimethyl-benzoin	$\text{Fe}(\text{acac})_3$	2	43	97

<sup>a</sup> 1.2 mmol substrate, 0.020 mmol metal complex, 3.6 mmol *i*-butyraldehyde, 5.0 ml 1,2-dichloroethane, room temperature, atmospheric pressure of O<sub>2</sub>.

Table 2

Oxidation of benzoins by  $\text{Fe}(\text{acac})_3$  and  $\text{Co}(\text{acac})_2$  under Mukaiyama's conditions<sup>a</sup>

Entry	Substrate	Catalyst	Time (h)	Conversion %	Yield %
1	anisoil	$\text{Co}(\text{acac})_2$	1	96	94
2	anisoil	$\text{Fe}(\text{acac})_3$	1.5	84	97
3	4,4'-dimethyl-benzoin	$\text{Co}(\text{acac})_2$	4	94	95
4	4,4'-dimethyl-benzoin	$\text{Fe}(\text{acac})_3$	6	82	94

<sup>a</sup> 1.2 mmol substrate, 0.020 mmol catalyst, 4.0 ml 1,2-dichloroethane, room temperature, 1 atm O<sub>2</sub>. 3.6 mmol *i*-butyraldehyde was added as follows: 0.9 mmol were present at the beginning of the reaction and 2.7 mmol dissolved in 2.0 ml of 1,2-dichloroethane were added dropwise in the course of the reaction at a rate of 2.7 mmol/h.

untimely consumption of the sacrificial aldehyde.

To overcome this inconvenience we have carried out the oxidations of (2) and (3) by dropping part of the aldehyde in the course of the reaction, thus achieving much higher conversions of the starting material and high yields in the desired  $\alpha$ -diketone (Table 2). The same expedient has been used for the first time by us in the  $\text{Co}(\text{acac})_2$  catalysed oxidation of diphenylsulfide under Mukaiyama's conditions [10].

We have carried out additional tests using propionaldehyde diethyl acetal in the place of *i*-butyraldehyde. Preliminary experiments showed that in the absence of metal catalysts negligible conversion was achieved and that catalytic reactions run at room temperature were quite slow. Anisoil gave 98% conversion after 45 h with  $\text{Co}(\text{acac})_2$  and 76% conversion after 62 h with  $\text{Fe}(\text{acac})_3$ . Carrying out the reactions at 50°C and using 3.6 mmol acetal with  $\text{Co}(\text{acac})_2$  and 6.0 mmol acetal with  $\text{Fe}(\text{acac})_3$  it was possible to achieve 100% conversions and quantitative yields in benzils for all the substrates (Table 3).

Table 4 summarizes the results obtained in the heterogeneous phase, using as catalysts the insoluble copolymers deriving from reaction of  $\text{Co}(\text{AAEMA})_2$  or  $\text{Fe}(\text{AAEMA})_3$  with *N,N*-di-

Table 3

Catalytic oxidation of benzoin by Fe(acac)<sub>3</sub> and Co(acac)<sub>2</sub> with acetal catalyst

Entry	Substrate	Catalyst	Time (h)	Yield %
1 <sup>a</sup>	benzoin	Co(acac) <sub>2</sub>	1	100
2 <sup>b</sup>	benzoin	Fe(acac) <sub>3</sub>	6	97
3 <sup>a</sup>	anisoin	Co(acac) <sub>2</sub>	1.5	98
4 <sup>c</sup>	anisoin	Fe(acac) <sub>3</sub>	6	97
5 <sup>a</sup>	4,4'-dimethyl-benzoin	Co(acac) <sub>2</sub>	2.5	100
6 <sup>b</sup>	4,4'-dimethyl-benzoin	Fe(acac) <sub>3</sub>	6	99

Conditions: 1.2 mmol substrate, 0.020 mmol catalyst, 5.0 ml 1,2-dichloroethane,  $T = 50^{\circ}\text{C}$ , 1 atm O<sub>2</sub>. The conversions for all the experiments were 100%.

<sup>a</sup> In the presence of 3.6 mmol propionaldehyde diethyl acetal.

<sup>b</sup> In the presence of 5.2 mmol propionaldehyde diethyl acetal.

<sup>c</sup> In the presence of 6.0 mmol propionaldehyde diethyl acetal.

methylacrylamide and *N,N'*-methylenebisacrylamide.

The reactivity order of the substrates and of the catalysts was the same as observed in the homogeneous reactions. The heterogeneous catalysts could be recovered by simple filtration after duty. They maintained nearly unvaried their metal content and were recyclable with negligible loss of activity (entries 2, 4).

Table 4

Catalytic oxidation of benzoin by supported Fe(III) and Co(II) complexes under Mukaiyama's conditions

Entry	Substrate	Supported metal	Time (h)	Conversion %	Yield %
1 <sup>a</sup>	anisoin	cobalt	3	96	91
2 <sup>a,b</sup>	anisoin	cobalt	3	88	90
3 <sup>a</sup>	anisoin	iron	2	70	93
4 <sup>a,b</sup>	anisoin	iron	3	65	90
5 <sup>c</sup>	benzoin	cobalt	3	100	94
6 <sup>c</sup>	benzoin	iron	6	100	95
7 <sup>a</sup>	4,4'-dimethyl-benzoin	cobalt	3	72	92
8 <sup>a</sup>	4,4'-dimethyl-benzoin	iron	2	46	100

1.2 mmol substrate, 0.020 mmol supported metal, 5.0 ml 1,2-dichloroethane, ambient conditions.

<sup>a</sup> In the presence of 3.6 mmol *i*-butyraldehyde which was added as follows: 0.9 mmol were present at the beginning of the reaction and 2.7 mmol dissolved in 2.0 ml of 1,2-dichloroethane were added dropwise in the course of the reaction at a rate of 2.7 mmol/h.

<sup>b</sup> Recycle of the previous run.

<sup>c</sup> In the presence of 3.6 mmol *i*-butyraldehyde.

### 3. Experimental

#### 3.1. Materials and apparatus

Chromatographic analyses were carried out on a Hewlett Packard 5890 instrument using a 25 m SPB-1 capillary column. GC-MS data were acquired on a HP 5890 chromatograph (30 m SE30 column) coupled with a mass selective detector HP 5970B, 70 eV.

The oxidized products were identified by comparison of their MS spectra and retention times in GC analyses with those of authentic samples.

Conversions and yields were calculated by GLC analyses as moles of oxidized product per mole of starting  $\alpha$ -hydroxyketone by using the internal standard method. The difference to 100% in the reported yields was ascribable to small amounts of *para*-substituted benzaldehyde and *para*-substituted benzoic acid.

The metal acetylacetonates, benzoin and propionaldehyde diethyl acetal were purchased by Aldrich and used as received; *i*-butyraldehyde was distilled prior to use. The supported Co(II) and Fe(III) complexes were prepared as described by us elsewhere [8].

#### 3.2. Catalytic runs: homogeneous phase

A Schlenk tube was charged with the substrate (1.2 mmol), the metal complex (0.02 mmol), the sacrificial aldehyde (added, for the substrates (2) and (3), as described in the caption of Table 2) or propionaldehyde diethyl acetal (3.2 mmol in the presence of Co(acac)<sub>2</sub> and 5.2–6.0 mmol in the Fe(acac)<sub>3</sub>) in 1,2-dichloroethane (4–5 ml) and stirred under dioxxygen at the desired temperature till completion of the reaction, as monitored by GLC analysis.

#### 3.3. Catalytic runs: heterogeneous phase

A Schlenk tube was charged with the substrate (1.2 mmol), the supported metal complex (0.02 mmol), the sacrificial aldehyde (added, for

the substrates (2) and (3), as described in the caption of Table 4) in 1,2-dichloroethane (4 ml) and stirred under dioxygen at room temperature till completion of the reaction, as monitored by GLC analysis. After reaction, to the suspension was added cold petroleum ether and filtered. The solid was treated with acetone causing the extraction of the diketone and the separation of the supported catalyst. The resin was washed with acetone and diethyl ether, dried under vacuum and opportunely recycled. The acetone solution was evaporated or added to water and the solid residue was purified by column chromatography on silica gel (hexane–diethyl ether) to afford the desired  $\alpha$ -diketone.

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