

New efficient catalysts for the aerobic oxidation of ethers

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Abstract

Some nickel, copper, and silver salts or complexes are efficient catalysts for the oxidation of benzylic ethers with oxygen in 1,2-dimethoxyethane. Salts of the weakly coordinating anion trifluoroacetate are particularly efficient, approaching (and, in some cases, improving) the yields obtained with cobalt(II) chloride, the best catalyst so far reported.

Keywords: Aerobic oxidation; Ethers; Nickel; Copper; Silver

1. Introduction

The oxidation of ethers to the corresponding esters is an important reaction usually accomplished by using stoichiometric amounts of oxidants such as chromium trioxide or ruthenium tetroxide [1]. A greatly improved procedure uses catalytic amounts of ruthenium compounds together with a suitable oxidant, mainly sodium periodate or an alkaline (or calcium) hypochlorite [2]. However, the use of an inexpensive oxidant such as dioxygen (aerobic oxidation) remains an obvious goal and a number of papers appeared describing catalysis of this reaction by iron [3], ruthenium [4], cobalt [5], rhodium [3,4,6], iridium [4], and palladium [7] salts or complexes, and metallic platinum [8]. Particularly good results were obtained by using anhydrous cobalt(II) chloride [5].

We now report that salts or complexes of

other metals (nickel, copper, and silver) also catalyse the aerobic oxidation of ethers, approaching, in some cases (particularly with copper salts), the efficiency of cobalt compounds in promoting such a reaction.

2. Results and discussion

A cyclic benzylic ether, isochroman (1), was chosen as a model substrate. It was reacted with oxygen (1 atm), at 80°C, in 1,2-dimethoxyethane as the solvent [5,7], in the presence of several nickel, copper or silver salts or complexes. Significant results are collected in Table 1, together with those obtained with cobalt(II) chloride, included for comparison purposes. Although, in principle, oxidations products could arise from attack to both the methylene groups α to the oxygen atom, only products originated from attack to the benzylic CH_2 were detected. 1-Isochromanone (2) was always the main reaction product, although low amounts of 1-

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methoxyisochroman and 1,1-dimethoxyisochroman were also detected, possibly arising from reactions with the solvent.

Nickel chloride catalysed the oxidation, but nickel acetate was a better catalyst and nickel trifluoroacetate turned out to be even more efficient. On the other hand, a nickel complex with a tetradentate ligand [salen: *N,N'*-ethylenebis(salicylideneaminato)] afforded 1-isochromanone in only 3% yield, the same result obtained in a blank experiment without any catalyst.

Moving from nickel to cupric salts, the chloride turned out to be quite ineffective while, again, the acetate was a better catalyst. Best results, however, were obtained with $\text{Cu}(\text{acac})_2$ (acac: acetylacetonato) and with cupric trifluoroacetate. The latter catalyst gave a fairly excellent yield (83%) of 1-isochromanone and, in our hands (with a freshly distilled, peroxide-free 1,2-dimethoxyethane as the solvent), it turned

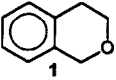
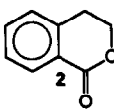
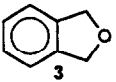
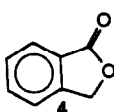
out to be even more efficient than anhydrous cobalt(II) chloride. It should be noted, however, that the catalytic activity of cobalt(II) chloride can be significantly higher when even small amounts of peroxide compounds are present in the 1,2-dimethoxyethane used as solvent [5].

Copper(I) chloride turned out to be a much better catalyst than copper(II) chloride. On the other hand, the catalytic activities of copper(I) and copper(II) trifluoroacetates were quite similar.

Finally, some silver salts were also evaluated: the chloride, quite insoluble in the reaction medium, was completely ineffective, while acetate and trifluoroacetate turned out to be, again, a reasonable and a good catalyst, respectively.

When phthalan (**3**) was used as the substrate and cupric trifluoroacetate was chosen as the catalyst, phthalide (**4**) was obtained in reasonable yield (Table 1), together with traces of phthalic anhydride. On the other hand, an acyclic

Table 1
Oxidation of cyclic ethers catalysed by cobalt, nickel, copper or silver compounds ^a

Substrate	Catalyst	Conversion (%)	Product	Yield (%) ^b
 1	—	30	 2	3
	CoCl_2	94		68 ^c
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	86		35
	$(\text{CH}_3\text{COO})_2\text{Ni} \cdot 4\text{H}_2\text{O}$	87		68
	$(\text{CF}_3\text{COO})_2\text{Ni} \cdot 3\text{H}_2\text{O}$	97		79
	Ni(salen)	23		3
	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	36		2
	$(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$	89		38
	$(\text{CF}_3\text{COO})_2\text{Cu} \cdot 2\text{H}_2\text{O}$	97		83 ^d
	$\text{Cu}(\text{acac})_2$	91		64
	CuCl	88		66
	CF_3COOCu	96		80 ^d
	CH_3COOAg	43		21
	CF_3COOAg	98		73
 3	CoCl_2	99 ^e	 4	55 ^f
	$(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$	89 ^e		16
	$(\text{CF}_3\text{COO})_2\text{Cu} \cdot 2\text{H}_2\text{O}$	97 ^e		57

^a Substrate, 10 mmol; catalyst, 0.1 mmol; solvent (1,2-dimethoxyethane), 25 ml; O_2 (1 atm); 80°C; 10 h.

^b Yields (based on the charged substrate) were determined by GLC with internal standard.

^c After 6.5 h.

^d After 9 h.

^e 75°C.

^f After 18 h.

Table 2
Oxidation of dibenzyl ether catalysed by nickel, copper or silver compounds ^a

Catalyst	Time (h)	Conversion (%)	Yields (%) ^b	
			Benzoic acid ^c	Benzyl benzoate
–	10	12	10	1
NiCl ₂ · 6H ₂ O ^d	10	15	12	2
CuCl ₂ · 2H ₂ O ^e	20	14	5	9
(CH ₃ COO) ₂ Cu · H ₂ O	8	70	46	15
(CF ₃ COO) ₂ Cu · 2H ₂ O	8 ^f	72	57	10
CH ₃ COOAg ^g	15	55	43	7

^a Substrate, 10 mmol; catalyst, 0.1 mmol; solvent (1,2-dimethoxyethane), 25 ml; O₂(1 atm); 60°C.

^b Yields (based on the charged substrate) were determined by GLC with internal standard.

^c 2 mol of benzoic acid were assumed to form upon oxidation of 1 mol of substrate.

^d 0.25 mmol.

^e 0.33 mmol.

^f 70°C.

^g 0.07 mmol.

ether, dibenzyl ether, turned out to be, by far, less reactive than cyclic substrates, particularly when metal chlorides were used as catalysts (Table 2). Moreover, the main reaction product was usually benzoic acid rather than the expected ester, benzyl benzoate.

Attempts to oxidise formaldehyde acetals, either cyclic (1,3-dioxolane, 1,3-benzodioxole) or not (diphenoxymethane), resulted in very slow reactions and very poor selectivities.

Among the salts of the metals used as catalyst, the catalytic efficiency increased in the order: chloride < acetate < trifluoroacetate.

So, less coordinating anions are required in order to achieve efficient catalysis. This could be also confirmed by the lack of any catalytic activity exhibited by the nickel complex of the strongly coordinating, tetradentate salen ligand, although this point has to be interpreted with some caution, since it is unlikely that the salen ligand survived for a long time under the strongly oxidising reaction conditions. The negative influence of the coordinating chloride anion could also explain the different efficiencies observed with cuprous and cupric chlorides, but not with the corresponding trifluoroacetates.

It is well known that ethers, upon exposure to oxygen, undergo autoxidation via α -alkoxy (or aryloxy) substituted radicals which, reacting with molecular oxygen, afford hydroperoxides

which, in turn, often decompose to complex products mixtures, so that the reaction is usually of poor preparative value [9]. Formation of benzoic acid in the oxidation of dibenzyl ether suggests that, also in the presence of metal compounds, the reaction involves a radical intermediate which can either react with oxygen or undergo fragmentation [5]. So, the role of the metal could be to catalyse the hydroperoxide decomposition (and, possibly, also its formation), thus enhancing the selectivity of the overall process.

3. Experimental

¹H-NMR and mass spectra were recorded on a Bruker AC 200 and a Finnigan Incos 50 spectrometer, respectively. GLC analyses were performed on a Carlo Erba HRGC 5300 instrument using a Supelco SPB-5 column. Products were isolated by column chromatography on silica gel (4/1 n-hexane/ethyl ether as the eluant), and identified by their spectral data, in comparison with authentic samples.

Diphenoxymethane [10], hydrated nickel(II) and copper(II) trifluoroacetates [11], anhydrous copper(I) trifluoroacetate [12], salen [13] and Ni(salen) [14] were prepared as previously described. Freshly opened 1,2-dimethoxyethane

was distilled over sodium, under nitrogen atmosphere: potassium iodide test was used in order to confirm the absence of peroxides. Oxygen (Rivoira), and all other chemicals (Aldrich) were used as purchased.

3.1. General procedure for the oxidation of ethers

A 100 ml round-bottomed flask equipped with a magnetic stirring bar, thermometer, reflux condenser and gas sparger, was charged with 1,2-dimethoxyethane (25 ml), the substrate (10 mmol), and the catalyst (0.1 mmol). Oxygen was allowed to bubble through the sparger and the mixture was heated, under vigorous stirring, at the reaction temperature. The reaction progress was monitored either by GLC or by TLC (silica plates; 4/1 n-hexane/ethyl ether; spots detected by spraying with a KMnO_4 solution). After the required time, the reaction mixture was cooled to room temperature and analysed by GLC with n-decane as internal standard.

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