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Bi(III) as New Catalyst for the Selective Hydrolysis of Esters

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Abstract : The selective hydrolysis of esters has been carried out in a reaction catalyzed by Bi(III)-mandelate in DMSO. The reaction is specific of aryl esters. Competition tests resulted in the quantitative hydrolysis of p-nitrophenyl acetate in the presence of ethyl benzoate or other aryl acetates.

The search for efficient methods of protection and deprotection of functional groups in organic chemistry constitutes a topic of constant interest[1,2]. In particular, alcohol and phenol protection as acetates, benzoates, carbonates or carbamates is frequently utilized, and selective procedures of hydrolysis of such esters or derivatives under mild, neutral and catalytic conditions are most useful[3].

In the field of selective ester saponification, cyclodextrins[4] or some specific micelles[5] have been reported as good catalysts for the hydrolysis of phenyl esters, without altering aliphatic ones; this reaction selectivity is interesting for biomimetic reactions in polyfunctional molecules. On the other hand, metalloenzymes[6], and more recently antibodies[7] have been described for their specific hydrolytic action towards some aryl ester functions. Metallic complexes that mimic the active centers of such enzymes have been prepared[8], and particularly, Zn^{2+} complexes have been reported to present a selective reactivity towards hydrolysis of aryl esters as compared to aliphatic ones[9]. Activated zinc in methanol also constitutes an efficient reagent for the selective hydrolysis of aryl acetates[10].

In our ongoing research on the catalytic activity of Bi(III) derivatives in organic synthesis[11], we have found that Bi(III)-mandelate, **1**, constituted a selective catalyst for the hydrolysis of specific ester functions.

The use of Bi(III) derivatives as catalysts in organic reactions has only scarcely been reported. Some recent examples concern some oxidation[12] and condensation reactions[13]. We have tested the activity of Bi(III) complexes in the hydrolysis of several ester functions and we present here our preliminary results. No example on the use of Bi(III) complexes in ester hydrolysis reactivity has, to our knowledge, been previously reported.

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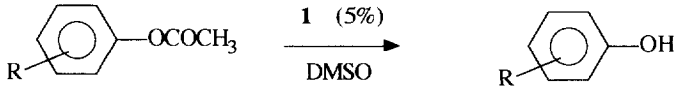
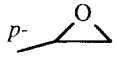
The hydrolysis of *p*-nitrophenyl acetate, **2**, was carried out in DMSO under oxygen (1 atm) with a catalytic amount of **1** (5% molar with respect to the ester), and afforded *p*-nitrophenol in 96% yield (see Table 1). The catalyst, Bi(III)-mandelate, $[(PhCH(OH)COO)_2Bi]_2(\mu\text{-}O)$, is a white powder, easily prepared in 93% yield from Bi_2O_3 and (L)-mandelic acid in refluxing water [14]. Bi(III)-mandelate is insoluble in most commun organic solvents, but it is soluble in DMSO at above 80 °C. Moreover the coordination of Bi(III) carboxylates to DMSO has been shown by X-ray christallography[15]. The presence of molecular oxygen (1 atm) slightly increased the yield of the reaction (from 80% under nitrogen to 96% under O_2, in the case of ester **2**), whereas the additional introduction of water (up to 6 equiv. with respect to the ester) drastically decreased the catalytic activity. The activation of Bi-complexes by molecular oxygen has recently been reported[12].

Table 1 : Hydrolysis of aryl acetates catalyzed by Bi(III)-mandelate, **1**[a].



Acetate	R	T (°C)	Reaction time (h)	Isolated Yield (%)
2	*p*-NO_2	95	31	96
3	*p*-COOH	95	24	73
4	H	125	24	44
5	*o*-F	95	24[b]	55
6	*p*- 	80	4.5	61[c]

a) General experimental procedure: DMSO (5 ml) was stirred in the presence of Bi(III)-mandelate, **1** , (156 mg, 0.15 mmol) at 80° C for 30 min under oxygen (1 atm), followed by the addition of the ester (3 mmol). The reaction mixture was stirred at the desired temperature and followed by GC analysis of aliquots. Acidic hydrolysis by aqueous 0.1N HCl solution, ether extraction, treatment of the organic layer by aqueous 0.1N NaOH solution until pH =12-14 and ether reextraction gave the neutral products of the reaction, e.g. the recovered esters. Acidification of the basic aqueous phase with 1N HCl solution to pH 1-2 followed by a final ether extraction afforded the phenol derivatives and the carboxylic acids, which were precipited in ether-pentane mixtures and filtered off. The products were analyzed by GC, ^1H and ^{13}C NMR, and mass spectra, and their spectral data compared to those of authentic samples.

b) After 15 hours reaction, a new portion of Bi(III)-mandelate, **1** (156 mg, 0.15 mmol) was added. Without the second Bi(III) addition, a yield of 30% of *o*-fluorophenol was attained after 24 hours.

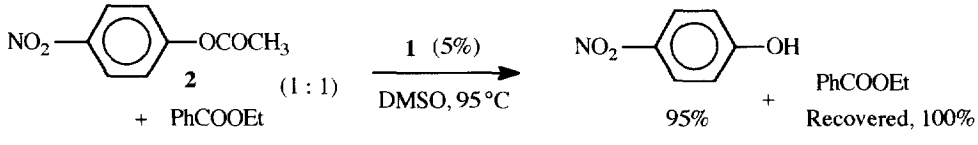
c) The product is *p*-hydroxy benzoic acid.

Table 1 shows the results obtained from the hydrolysis of several aryl acetates catalyzed by **1**. A carboxylic acid function in the *para* position (**3**) afforded 73% acetate hydrolysis after 24 hours, and phenyl (**4**) or *o*-fluorophenyl (**5**) acetates could also be hydrolyzed. The hydrolysis of *p*-acetoxy styrene epoxide (**6**) was effected through a first acetate hydrolysis (as shown by the GC analysis), followed by an oxidative cleavage of the oxirane ring. Thus, epoxide (**6**) led directly to *p*-hydroxy benzoic acid (R = *p*-COOH) in 61% yield. The oxidative cleavage of aryl epoxides to benzoic acid derivatives by the Bi(III)/DMSO/O_2 system has been previously reported[16].

The presence of the Bi(III) catalyst was essential for the reaction; in the absence of the catalyst, *p*-acetoxy styrene epoxide, **6**, was recovered unreacted in 94% yield under the same conditions of Table 1. Only a partial hydrolysis was observed in the case of *p*-nitrophenyl acetate, **2**, with recovery of 40% of unreacted ester. However, the use of mandelate as counter-ion was not essential for the reaction, and Bi(III)-salicylate could also be used as the catalyst. Thus, the hydrolysis of phenyl acetate led to 45% of phenol with 5 molar % of Bi(III)-salicylate (DMSO, 125 °C, 24 h).

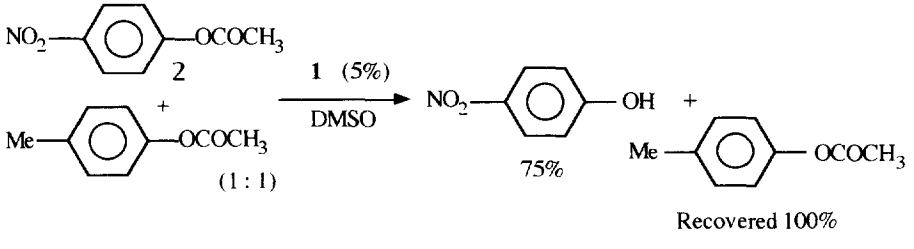
The selectivity of the Bi(III) catalytic system is remarkable : no hydrolysis of alkyl esters, such as ethyl benzoate, was observed. Moreover, the bismuth catalyst was most active for the hydrolysis of electron-deficient aromatic esters, and electron-rich aryl esters showed very low reactivity. Thus, *p*-hydroxyphenyl, *p*-tolyl or *p*-aminophenyl acetates could be quantitatively recovered after 24 hours reaction with **1** at 95 °C.

In a first series of competition experiments, we found that aryl esters could be completely hydrolyzed in the presence of alkyl esters (eq. 1). Thus, when a 1:1 mixture of acetate **2** and ethyl benzoate were reacted with 5% of **1** (DMSO, O_2, 95 °C, 68 h), ethyl benzoate could be quantitatively recovered and *p*-nitrophenol was isolated in 95% yield.



(1)

The competition test with a 1:1 mixture of **2** and *p*-tolyl acetate led to complete recovery of this last compound and 75% of *p*-nitrophenol after 31 h at 95 °C (eq. 2). Similar reactivity was observed in competition tests of **2** with phenyl or *p*-carboxymethylphenyl acetates.



(2)

These preliminary results indicate that Bi(III) complex **1** constitutes a good catalyst for the specific hydrolysis of some aryl esters. The method is extremely simple and the catalyst is a stable compound of easy preparation[14].

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