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Bi(III)-mandelate/DMSO : A New Oxidizing System for the Catalyzed C-C Cleavage of Epoxides

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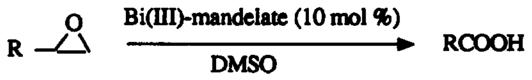
Abstract : *Bi(III)-mandelate was found to be an effective catalyst for the oxidative C-C bond cleavage of epoxides and their transformation into carboxylic acids in anhydrous DMSO medium.*

Bismuth (V) derivatives constitute interesting, though stoichiometric oxidants in organic synthesis[1]. Thus, sodium bismutate/AcOH allows the cleavage of 1,2-diols and acyloins[2], while zinc bismutate[3] in aprotic solvents has been described to smoothly oxidize alcohols into carbonyl compounds. On the other hand, Barton has reported a series of pentavalent organobismuth compounds derived from Ph_3BiCl_2[4], which are efficient for the mild and selective oxidation of allylic alcohols, among others.

Homogeneous oxidations by Bi(III) derivatives are poorly documented ; the few examples reported so far concern the Bi(III) mediated oxidation of acyloins to α-diketones with the formation of black bismuth[5] and the $Bi(OAc)_3$/AcOH diacetylation of some olefins in the presence of iodine[6]. Triphenylbismuth associated to NBS has been reported to catalyze the cleavage of α-glycols to carbonyl compounds[7].

During the course of our studies on bismuth precursors as selective oxidation reagents, we became interested in the synthesis[8,9], structural characterization[10] and reactivity of complexes containing multidentate carboxylic acids. While studying the reactivity of such complexes, we found that Bi(III)-mandelate[9,11] constitutes an efficient catalyst for the oxidative C-C cleavage of epoxides into carboxylic acids by DMSO (eq. 1). We herein report this novel oxidizing system.



(eq. 1)

DMSO is a well known oxidizing agent for alkyl halides in the presence of a base, and for alcohols in the presence of stoichiometric amounts of oxalyl chloride (Swern oxidation)[12] or other activating agents[13]. Epoxides, through treatment with DMSO in the presence of acids, are converted into the corresponding α-ketols[14].

To the best of our knowledge, the conversion of epoxides to carboxylic acids, with C-C cleavage, is unprecedented : up to now, this transformation required a several-step sequence.

In a typical procedure, anhydrous DMSO is stirred at 80°C in the presence of a catalytic amount of Bi(III)-mandelate for 30 min, before addition of the epoxide. The reaction is carried out in air and stopped after total epoxide consumption (according to GC analysis). Our preliminary results are summarized in Table I.

Styrene oxide (entry 1) was quantitatively converted after a 22 h reaction at 75°C and benzoic acid was formed in 60% yield. In the same experimental conditions but in the absence of the Bi(III)-carboxylate, the conversion of styrene oxide was only 50% and phenacyl alcohol was the major product (29%). Terminal aliphatic epoxides such as 1-octene epoxide (entry 2) or 1-decene epoxide (entry 3) required longer reaction times for complete consumption, respectively 30 and 46 hours at 75-80°C. The corresponding carboxylic acids (n-1) were isolated in *ca* 40% yield. The by-products in these reactions were essentially the 1,2-diol and some sulfur-containing derivatives. Starting with 2,3-epoxypropyl-4 methoxyphenyl ether (entry 4), aryloxy acetic acid was formed in 10% yield only: the reaction mainly led to p-methoxyphenol (85%) through a rearrangement-elimination reaction[15].

It is noteworthy that when the reaction of styrene oxide with DMSO was conducted in the presence of $Bi(OAc)_3$, only traces of benzoic acid were found after 22 h contact at 70°C. With Bi_2O_3, no reaction occured after 4 h contact at 75°C, while prolonged heating of the reactants (90°C, 22 h) resulted in inextricable polymeric material with only 16% benzoic acid. On the other hand, heating styrene oxide in DMSO in the presence of mandelic acid and no bismuth, afforded essentially $PhCOCH_2OH$ and no benzoic acid. These results demonstrate that the bimuth mandelate complex plays an important role in the C-C oxidative cleavage of epoxides.

The new Bi(III)-mandelate/DMSO catalytic oxidizing system shows an interesting functional group selectivity. Thus, typical substrates oxidized by DMSO[12,13], such as benzyl alcohol, did not react in the presence of Bi(III)-mandelate : only traces of benzaldehyde were detected by GC after 24 h contact with Bi(III) in a 5% molar ratio in DMSO at 70°C. Furthermore, 2-cyclohexenol was recovered unchanged after 48 h under the same reaction conditions. Importantly enough, olefins were found to be inert and the selective C-C cleavage of the oxirane function in oct-7-en-1,2-epoxide could be carried out without attack on the double bond (entry 5).

The method is also suitable for internal epoxides, but it then requires higher temperatures and/or longer reaction times to reach completion. Thus, trans-4,5-decene epoxide (entry 6) was totally converted after 50 h at 85°C to afford pentenoic acid (60%) accompanied by 4,5-decadione (10%).

The yield in pentenoic acid unambiguously shows that the epoxide cleavage produces two molecules of carboxylic acids corresponding to each of the R_1 and R_2 substituent sides (see Table 1): the Bi(III)/DMSO oxidizing system is capable of incorporating 3 oxygen atoms into the epoxidic substrate in a single step.

The α-diketone seems to be an intermediate in this oxidation. Thus, during the reaction of cis or trans-stilbene oxides (entry 7), benzil was the only product formed when the oxidation of either isomer was performed at 70°C, though with poor conversions (30% for the cis derivative and only 5% for trans-stilbene oxide). The less reactive trans-stilbene oxide could nevertheless be totally converted when the reaction mixture was kept at 110°C for 12 days to afford benzil (60%), and benzoic acid (30%, entry 8).

In conclusion, we have found a simple, one-step procedure which affords carboxylic acids from epoxides. It represents one of the first examples where a Bi(III) derivative is used as the catalyst in an oxidation reaction.

References and Notes

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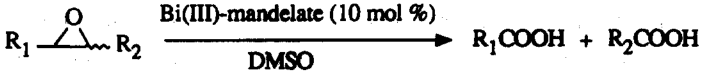
Table 1 : Bi(III)-mandelate catalyzed epoxide cleavage in DMSO[a]



Entry	**R1**	**R2**	**Reaction Conditions**	**Product (% isolated yield)**
1	C_6H_5	H	75°C 22 h	C_6H_5COOH (60%)
2	n-C_6H_{13}	H	80°C 30 h	n-$C_6H_{13}COOH$ (42%)
3	n-C_8H_{17}	H	75°C 46 h	n-$C_8H_{17}COOH$ (40%)
4	$MeOC_6H_4OCH_2$	H	80°C 48 h	p-$MeOC_6H_4OH$ (85%) p-$MeOC_6H_4OCH_2COOH$ (10%)
5	$CH_2=CH(CH_2)_4$	H	90°C 24 h	$CH_2=CH(CH_2)_4COOH$ (50%)
6	n-C_4H_9 (trans)	n-C_4H_9	85°C 50 h	n-C_4H_9COOH (60%) n-$C_4H_9COCOC_4H_9$ (10%)
7	C_6H_5 (cis or trans)[b]	C_6H_5	70°C 55 h	$C_6H_5COCOC_6H_5$ (90%)
8	C_6H_5 (trans)	C_6H_5	110°C 12 days	$C_6H_5COCOC_6H_5$ (65%) C_6H_5COOH (30%)

[a] General procedure :

Anhydrous DMSO (5 ml) was stirred in the presence of Bi(III)-mandelate ($[Bi(mand)_2]_2O$, 392 mg, 0.4 mmol) at 80°C for 30 min under air, followed by the addition of the epoxide (4 mmol). At the adequate temperature, the reaction was followed by GC until complete consumption of the substrate. Acidic hydrolysis, ether extraction, treatment of the organic layer by aqueous 0.1 NaOH solution, acidification of the aqueous phase to pH 1-2 and final ether extraction afforded the corresponding carboxylic acids.

[b] Conversion 30% for the cis epoxide and 5% for the trans isomer. Yield of benzil based on the reacted epoxide.

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