

Bi⁰/O₂ as a New Catalytic System for the Oxidation of α -Ketols, α -Hydroxy Acids and Epoxides

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Bi⁰ has been used as a catalyst for the oxidative C–C bond cleavage under O₂ of α -ketols, α -hydroxy acids and terminal epoxides, to give the corresponding carboxylic acids. The results are compared to those obtained in similar oxidation re-

actions catalysed by Bi^{III} carboxylates. These reactions constitute the first example of the catalytic use of Bi⁰ in oxidation reactions, and the first evidence for a Bi^{III}/Bi⁰ redox couple under molecular oxygen.

Introduction

Although bismuth is regarded as a relatively nontoxic heavy metal, its application to organic chemistry has been rather neglected until recently, although it is likely now to find new applications in low-toxicity catalytic processes.^[1–3] Organic chemistry involving bismuth derivatives has largely been devoted to oxidation reactions,^[4–6] particularly with the use of stoichiometric amounts of Bi^V derivatives that involve the redox couple Bi^V/Bi^{III}.^[7–9]

In the field of oxidation by Bi^{III} derivatives, a few mediated processes have been described,^[10–12] but their use in oxidation catalysis has not yet been widely explored.^[13–15] Recently, Bi^{III} has been reported as an efficient catalyst in Friedel–Crafts^[16] and other aldol-type reactions.^[17]

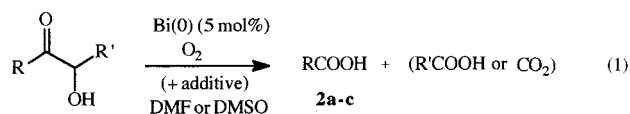
Bismuth(III) carboxylates (α -hydroxycarboxylates, pyridine-carboxylates, salicylates) have recently been found to be efficient catalysts for the oxidative C–C bond cleavage of epoxides to carboxylic acids in O₂/DMSO media.^[18] Furthermore, dioxygen was found to be the oxidant in the Bi^{III} mandelate-catalysed oxidative transformation of α -ketols into carboxylic acids.^[19] The Bi^{III} carboxylate/O₂ system offers a different and new activity as an oxidizing system, as compared with all previously described bismuth(V) or bismuth(III) reagents.

We now present a novel extension of the catalytic oxidation reactions of α -ketols, α -hydroxy acids and epoxides by Bi⁰ under molecular oxygen and give some evidence for a Bi^{III}/Bi⁰ redox system. To the best of our knowledge, no report in the literature deals with the oxidation of organic compounds with the Bi⁰/O₂ catalytic system.

Results and Discussion

Oxidation of α -Ketols by Bi⁰/O₂

The oxidation of α -ketol **1a** in the presence of a catalytic amount of Bi^{III} mandelate (5 mol-%)^[20] in DMSO under dioxygen (1 atm.) at 80 °C resulted, after 4.5 h, in a complete conversion of the ketol, with the formation of benzoic acid in 63% yield.^[19] The process involves the C–C bond cleavage of the α -ketol, with formation of carbon dioxide [see Equation (1)].



1a R = Ph, R' = H

1b R = C₈H₁₇, R' = H

1c R = R' = C₄H₉

The addition of α -hydroxy ketones **1a–c** to a Bi^{III} mandelate solution, in either DMF or DMSO, resulted in the immediate formation of a grey-black precipitate. Under dioxygen, this precipitate rapidly dissolved and the medium was kept homogeneous during the reaction. Under N₂, however, the initial precipitate persisted and could not be redissolved. This precipitate was filtered off and was analysed as Bi⁰, recovered quantitatively (by EDTA complexometry, 98 ± 2% of Bi, IR).

Under N₂, the reaction was stoichiometric in Bi^{III} (which resulted in black metallic bismuth) and produced the α -diketone. Under O₂, further C–C bond cleavage occurred. This bond cleavage was catalytic in Bi^{III} and presumably involved the Bi^{III}/Bi⁰ redox couple with a Bi⁰ to Bi^{III} reoxidation by dioxygen.

These observations prompted us to examine the behaviour of α -hydroxy ketones in the presence of a catalytic amount of Bi⁰. Thus, when **1a** was added to a suspension of commercially available Bi⁰ powder (relative molar ratio 10:1) in DMF under O₂ at 80 °C, a slow dissolution of Bi⁰

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Table 1. Bi-catalysed oxidation of α -ketols under O₂ (1 atm)

Entry	Substrate	Catalyst ^[a]	Additive (equiv.) mandelic acid/Bi ⁰	Solvent, time	Product, Yield
1	1a	Bi ⁰	—	DMF, 3 h	2a , 81%
2	1a	Bi ⁰	2:1	DMF, 3 h	2a , 71%
3	1b	Bi ⁰	2:1	DMF, 5 h	2b , 60%
4	1a	Bi ⁰	2:1	DMSO, 3 h	2a , 84%
5	1b	Bi ⁰	2:1	DMSO, 5 h	2b , 60%
6	1a	Bi ^{III} mandelate	—	DMSO, 4.5 h	2a , 63%
7	1b	Bi ^{III} mandelate	—	DMSO, 4.5 h	2b , 63%
8	1c	Bi ^{III} mandelate	—	DMSO, 4.5 h	2c , 66%
9	1a	Bi ^{III} mandelate	—	DMF, 4.5 h	2a , 58%
10	1b	Bi ^{III} mandelate	—	DMF, 4.5 h	2b , 76%
11	1c	Bi ^{III} mandelate	—	DMF, 51 h	2c , 50%
12	1b	Bi ^{III} mandelate ^[b]	—	DMSO, 4.5 h	2b , <5%, + Bi(0)

^[a] Reactions run with 5 mol-% Bi^{III} and with 10 mol-% of Bi⁰ catalysts at 80 °C. The Bi⁰ or Bi^{III} concentration was of 3–6·10^{−2} M. —

^[b] Reaction runs under nitrogen.

was observed and, after 3 h reaction, benzoic acid was isolated in 81% yield [Equation (1)]. No reaction occurred in the absence of O₂. This novel Bi⁰-catalysed process involves the oxidative C–C bond cleavage of the α -ketol to the corresponding carboxylic acid under molecular oxygen.

In order to mimic better the related Bi^{III} mandelate oxidation of the same substrates, the Bi⁰/O₂ oxidations were carried out in the presence of added mandelic acid (relative molar ratio 1:Bi⁰:mandelic acid of 10:1:2). The yields of carboxylic acid **2a** and **2b** were 71 and 60%, respectively. Table 1 summarizes these results.

The oxidation of α -hydroxy ketones could also be carried out in DMSO. The Bi⁰/O₂ system in DMSO produced **2a** and **2b** in 84 and 60% yield, respectively.

In contrast, when metallic bismuth was added to a DMF or a DMSO solution at 80 °C under dioxygen but without the organic substrate, no apparent dissolution occurred. After 4 h, Bi⁰ was filtered off and recovered quantitatively. The medium also remained heterogeneous and no reaction occurred when mandelic acid (2 equiv./Bi, which mimics the stoichiometry of the Bi^{III} mandelate complex^[20]) was added. After 3.5 h at 80 °C, mandelic acid remained unchanged and Bi⁰ could be recovered in 83% yield. However, as indicated, a catalytic oxidation involving Bi⁰ dissolution occurred when an α -ketol was added to the DMF solution under O₂.

Similar behaviour, with rapid formation of Bi⁰ upon addition of α -hydroxy ketones **1** and its further dissolution when under O₂, was also observed for other Bi^{III} carboxylates that we tested, such as Bi salicylate, Bi phthalate or Bi pinacolate.

For comparison, the behaviour of α -ketols in the presence of Bi^{III} catalysts was examined. Treatment of substrates **1a–c** with Bi^{III} mandelate (5 mol-%) in DMSO under O₂ resulted in the C–C bond cleavage with the formation of the corresponding carboxylic acids **2a–c** in 63–66% yields (Table 1). The α -diketone (or α -ketoaldehyde) was an intermediate in this reaction. In the absence of Bi^{III}, no reaction occurred. Under N₂, less than 5% of **2b** was formed in the oxidation of **1b**; starting **1b** was recovered in 56%

yield and only ketol adducts of high molecular mass were formed.

The Bi^{III} mandelate oxidation of **1a–c** under O₂ in DMF afforded **2a–c** in 58, 76 and 50% yields, respectively. In this Bi^{III}-catalysed oxidation in DMF, dioxygen is the oxidant in the process and its consumption was measured in the case of **1c** as 1.5 mol O₂/mol of substrate. CO₂ was the by-product of the oxidation of **1b** in DMF, as was established from the quantitative precipitation of BaCO₃ when bubbling the gaseous effluents over a Ba(OH)₂ solution.

The comparison of yields in Table 1 should be taken with some caution, because the reaction times and the catalyst concentrations were not the same in all the examples.

Our results indicate that oxidative cleavage by O₂ of α -hydroxy ketones in the presence of bismuth can be carried out using either a Bi^{III} carboxylate or Bi⁰.

Bi-Catalysed Oxidations of Styrene Oxide

The oxidation of styrene oxide in the presence of a catalytic amount of Bi^{III} mandelate in DMSO under dioxygen (1 atm.) has been reported.^[18b] The reaction, carried out at 80 °C, resulted after 4.5 h in complete conversion of the epoxide, with the formation of benzoic acid in 58% yield. The process involves the C–C bond cleavage of the epoxide and the incorporation of three oxygen atoms per epoxide molecule ([Equation (2)]).

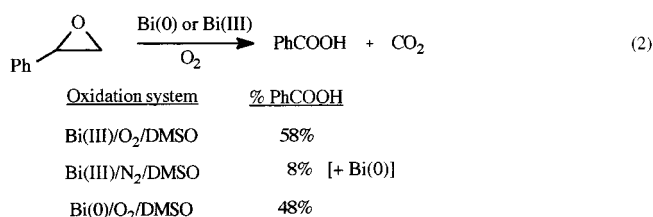
The same treatment under air (20 atm.) afforded 64% of carboxylic acid. DMSO was necessary for the reaction; no epoxide conversion occurred with DMF as the solvent.

Here, again, when the same reaction was carried out under N₂, a grey precipitate was formed; it could be filtered off and identified as metallic bismuth (IR, elemental analysis). No precipitate of Bi⁰ could be observed in other epoxide reactions, either under O₂ or under air. Under N₂, benzoic acid was obtained from styrene oxide in only 8% yield, together with phenacyl alcohol (28%), which was presumably formed from the direct DMSO oxidation of the oxirane ring.^[21]

The formation of Bi⁰ from Bi^{III} in reactions under N₂ suggests that reduced bismuth species might be interme-

diates in the catalytic oxidation reaction of epoxides under dioxygen, and that Bi^{III} could be recycled under O_2 .

As mentioned in the case of α -hydroxy ketones, when metallic bismuth was added to a DMSO solution containing mandelic acid (as the additive) under dioxygen, no apparent Bi^0 dissolution occurred. However, catalytic oxidation and Bi^0 dissolution occurred in the presence of the epoxide. Thus, when styrene oxide was added to a Bi^0/DMSO solution with mandelic acid (relative molar ratio 10:1:2) under O_2 at 80 °C, the solution slowly became homogeneous (Bi^0 dissolution), and benzoic acid was isolated in 48% yield after 4.5 h [Equation (2)]. The yield of benzoic acid was lower, but comparable to that obtained in the Bi^{III} mandelate oxidation (58%). No benzoic acid was formed in the absence of Bi^0 or in the absence of O_2 or DMSO.



The Bi^0/O_2 system with DMF as the solvent was not efficient, and unchanged styrene oxide could be recovered quantitatively, whether in the presence or the absence of additive. DMSO was necessary for both the Bi^0 and the Bi^{III} epoxide oxidations. Our results indicate that the epoxide oxidation to carboxylic acids involves the system Bi^0 or $\text{Bi}^{\text{III}}/\text{O}_2/\text{DMSO}$, and that oxidants DMSO and O_2 are both necessary for the reaction, in contrast with the oxidation of α -hydroxy ketones, for which O_2 was the only oxidant required. We suggest that DMSO is necessary for the first step of oxirane ring-opening in a Swern-type oxidation to a ketol,^[22,23] and that dioxygen is needed for further oxidative C–C bond cleavage and for the recycling of the reduced bismuth species.

Styrene oxide oxidation by $\text{Bi}^0/\text{O}_2/\text{DMSO}$ in the absence of mandelic acid resulted in poor reproducibility, with yields of benzoic acid in the range of 0–52%.

Several carboxylic acids, Bi^{III} complexes of which had previously been prepared and tested in oxidation reactions,^[18c] were used as additives in the Bi^0 -catalysed oxidation of styrene oxide in DMSO under oxygen. The results are presented in Table 2.

For Bi^0 systems with salicylic, *m*-nitrosalicylic, phthalic or benzoic acids, as well as with mandelic acid, the yields (37–50%) and the rate of the reactions were slightly lower but in the same range as those of the corresponding Bi^{III} -catalysed oxidations (44–58%).

Bi^0/AcOH (1:3) was also an active catalytic system (entry 8), affording 40% of benzoic acid, although no clean reaction could be found with $\text{Bi}(\text{OAc})_3$ under our experimental conditions.

In the case of salicylic acid (entries 2, 3), the ratio of Bi^0 to carboxylic acid was changed from 1:1 to 1:5, but without

Table 2. Oxidation of styrene oxide catalysed by Bi^0 or by Bi^{III} under O_2 (1 atm)^[a]

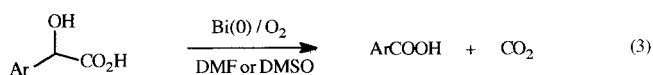
Entry	Additive	$\text{Bi}^0/\text{additive}^{[c]}$ (molar ratio)	Yield of PhCOOH	
			with Bi^0	with $\text{Bi}^{\text{III}}^{[d]}$
1		1 : 2	48%	58%
2		1 : 1	49%	54%
3	"	1 : 5	45%	---
4		1 : 1	50%	58%
5	$\text{PhCOOH}^{[b]}$	1 : 2	38%	44%
6		1 : 3	32%	45%
7		1 : 1	37%	49%
8	AcOH	1 : 3	40%	---

^[a] Reactions were carried out in DMSO at 80 °C over 4.5 hours. – ^[b] In this example, 4-methylstyrene oxide was used as the substrate. – ^[c] Bi^0 was used in 10 mol-% ratio with respect to styrene oxide. – ^[d] Yields taken from refs.^[18c,18d] for comparison, in Bi^{III} -catalysed reactions (10 mol-%) run under the same conditions (1 atm O_2 , DMSO, 80 °C, 2.5–4.5 h).

any improvement in the final yield of benzoic acid on increasing the additive concentration.

Bi^0 and Bi^{III} Oxidation of α -Hydroxy Acids

The use of the Bi^0/O_2 system was extended to the oxidative cleavage of the C–C bond of several α -hydroxy acids, as shown in Equation (3).



Several substituted aryl derivatives were oxidized to the corresponding benzoic acid derivatives with good yields and selectivities. The oxidative cleavage reaction was carried out at 125 °C, with DMSO or DMF as the solvents. The Bi^0/O_2 catalytic system was shown to be more efficient in the presence of acetic acid as the additive (1.5 equiv./ Bi). Table 3 summarizes the results for Bi^0 and Bi^{III} -catalysed oxidations of several α -aryl- α -hydroxy acids.

The oxidation of 4-chloromandelic acid with Bi^0/O_2 in DMSO (entry 1) afforded 4-chlorobenzoic acid, with 98% selectivity and 56% conversion after 24 h. The alternative use of Bi^{III} phthalate as the catalyst produced the carboxylic acid with 99% selectivity and 68% conversion (entry 2). The same oxidation in DMF (entry 3) afforded 4-chlorobenzoic acid with 70% selectivity.

Excellent carboxylic acid selectivities were also obtained for the Bi^0/O_2 oxidation of the 4-fluoro- or 4-trifluoromethyl-substituted aromatic derivatives (entries 4,5), or with unsubstituted mandelic acid (entry 6) in DMSO. In DMF, oxidative cleavage occurred but the selectivities were lower. For comparison, in the case of entry 5 with DMF as solv-

Table 3. Bi-catalysed oxidative cleavage of α -hydroxy acids under O_2 (1 atm)

Entry	Substrate	Catalyst ^[a]	Additive	Solvent, time	Conversion	Product selectivity
1	4-Cl-C ₆ H ₄	Bi ⁰	AcOH	DMSO, 24 h	56%	98%
2	4-Cl-C ₆ H ₄	Bi ^{III} -phthalate	—	DMSO, 24 h	68%	99%
3	4-Cl-C ₆ H ₄	Bi ^{III} -phthalate	—	DMF, 48 h	100%	70%
4	4-F-C ₆ H ₄	Bi ⁰	AcOH	DMSO, 24 h	72%	97%
5	4-CF ₃ -C ₆ H ₄	Bi ⁰	AcOH	DMSO, 24 h	97%	99%
6	C ₆ H ₅	Bi ^{III} mandelate	AcOH	DMSO, 24 h	52%	90%
7	4-MeO-C ₆ H ₄	Bi ^{III} mandelate	AcOH	DMSO, 6 h	77%	62%

^[a] Reactions carried out with 10 mol-% Bi catalyst at 125 °C and 1.5 equiv. of additive/Bi⁰.

ent, 4-trifluoromethylbenzoic acid was obtained with 100% conversion and 33% selectivity.

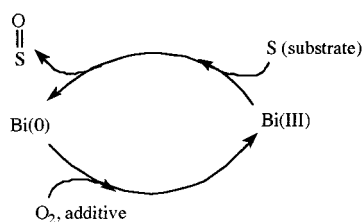
The C–C cleavage reaction of the tested α -hydroxy acids proceeded through the formation of the α -keto acid intermediate, which, under specific reaction conditions, could be isolated in several cases.

The presence of an electron-donating substituent such as methoxy on the aromatic ring also permitted the formation of the corresponding carboxylic acid (entry 7), but with a selectivity of only 62%. The remaining by-product was 4-methoxybenzaldehyde.

The oxidation of α -aryl- α -hydroxy acids to the corresponding benzoic acids required more forcing reaction conditions (125 °C, 24 h) than those used for the oxidation of α -ketols or aryl epoxides (80 °C, 4 h). Bi^{III} mandelate as catalyst or mandelic acid as the additive could be therefore be used in the oxidation of α -ketols or aryl epoxides without decomposition.

Mechanistic Considerations

Our results indicate that the oxidative cleavage by O_2 of α -hydroxy ketones, epoxides and α -hydroxy acids in the presence of bismuth can be carried out using either a Bi^{III}-carboxylate or Bi⁰ (Scheme 1).



Scheme 1. Involvement of Bi^{III}-carboxylate and Bi⁰ in the catalytic oxidation of a substrate (S) (e.g. α -ketols, α -hydroxy acids or epoxides) under O_2

Comparing the experiments carried out with or without O_2 , we can summarize our results as follows: the oxidation of α -ketols **1** can be carried out under O_2 (1 atm) with a catalytic amount (5–10 mol-%) of either Bi^{III} or Bi⁰, with either DMF or DMSO as solvents (80 °C, 3–5 h). This treatment resulted in the oxidative C–C bond cleavage of the α -ketol, and in the formation of carboxylic acids **2** in yields of 50–84% [Equation (1)]. The consumption of O_2 was measured, for the oxidation of **1c** with Bi^{III} mandelate, as 1.5 mol of O_2 per mol of substrate.

Under N_2 , the same treatment of ketol **1b** with Bi^{III} mandelate (5 mol-%) afforded less than 5% of carboxylic acid **2b**, and 56% of **1b** could be recovered (DMSO, 80 °C, 4 h). Also, under N_2 , treatment of ketols **1a** or **1b** with Bi⁰ (10 mol-%), with or without additive (mandelic acid, 20 mol-%) resulted in no oxidation (DMF or DMSO, 80 °C, 4 h) and in the complete recovery of the starting materials. Under O_2 (1 atm), these same processes afforded carboxylic acid **2a** in 71–84% yield (DMF or DMSO, 80 °C, 3 h), and **2b** in 60% yield (DMF or DMSO, 80 °C, 5 h).

The catalytic oxidation of styrene oxide to benzoic acid (10 mol-% catalyst) could be effected either by the system Bi^{III}/ O_2 in DMSO or by the system Bi⁰/ O_2 /additive in DMSO (additive = carboxylic acid, see Table 2). Benzoic acid yields of 32–58% were obtained.

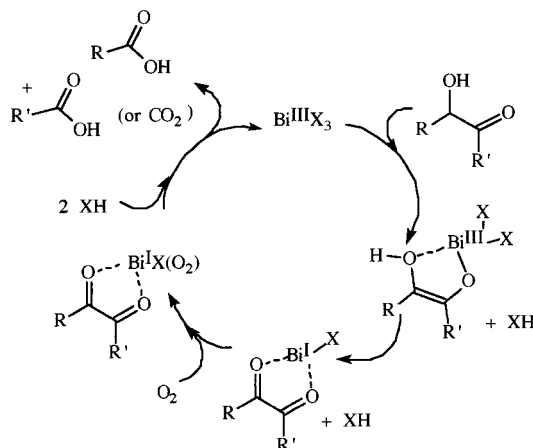
The same reaction under N_2 , catalysed by Bi^{III} in DMSO, afforded only 8% of benzoic acid, together with a black precipitate of Bi(0). Also, under N_2 , the Bi⁰/additive system in DMSO produced no epoxide oxidation and no Bi⁰ dissolution.

In summary: Under O_2 , Bi^{III}- or Bi⁰-catalysed oxidation of α -ketols, epoxides and α -hydroxy acids takes place with oxidative C–C bond cleavage, whereas under N_2 almost no reactivity was observed for the same systems.

From a mechanistic point of view, one of the key steps lies in the coordination of Bi^{III} to the α -hydroxy derivative (e.g., α -hydroxy ketone) in its hydroxy enolate form, followed by a redox step in which the α -diketone is formed and the Bi^{III} is formally reduced to Bi^I. We propose that under O_2 , this reduced Bi^I species is readily reoxidized to Bi^{III}. Under nitrogen, a dismutation can occur into Bi⁰, which precipitates as black, metallic bismuth, and Bi^{III}. The activation and transfer of molecular oxygen in the reoxidation step of either the Bi^I intermediate or Bi⁰ remains uncertain. However, α -diketones were found to be the intermediates in the oxidation of α -ketols and epoxides, and α -keto acids were also found as intermediates in the oxidations of α -hydroxy acids.

It is noteworthy that the isolation of Bi⁰ from stoichiometric Bi^{III} oxidations under N_2 does not rule out passage through Bi^I intermediate species. Bi^I complexes are very unstable, but their intermediate formation has been evoked for several processes.^[24]

A catalytic cycle for the oxidation of by Bi^{III} is proposed in Scheme 2.

Scheme 2. Mechanism of the oxidation of α -ketols

Several attempts were made to precipitate the complexes formed from the reaction of Bi^0 and **1a** in DMF under O_2 , but no clean complex could be isolated. Studies on mechanistic aspects of the Bi^0/O_2 catalytic system are currently underway.

Conclusions

In conclusion, this work constitutes the first example of oxidation reactions by molecular oxygen involving Bi^0 as the catalyst. We have shown that the Bi^0/O_2 system was efficient for the oxidative C–C bond cleavage of α -hydroxy ketones, α -hydroxy acids and aryl epoxides to the corresponding carboxylic acids. These oxidations could be carried out independently using either the $\text{Bi}^{\text{III}}/\text{O}_2$ or the Bi^0/O_2 systems.

Oxidative cleavage of α -hydroxy ketones or α -hydroxy acids can be carried out either in DMF or in DMSO. However, the presence of DMSO is required for the oxidative cleavage of epoxides, which can be effected using either $\text{Bi}^{\text{III}}/\text{O}_2/\text{DMSO}$ or $\text{Bi}^0/\text{O}_2/\text{DMSO}$ systems.

The $\text{Bi}^{\text{III}}/\text{Bi}^0$ redox couple has been proposed for the first time in catalytic reactions involving dioxygen. To the best of our knowledge, no catalytic cycle involving $\text{Bi}^{\text{III}}/\text{Bi}^0$ in oxidation reactions has yet been reported in the literature. Moreover, the possibility of using O_2 as the oxidant opens new perspectives in the field of clean and catalytic oxidation processes.

Experimental Section

General: The different Bi^{III} -carboxylates were prepared from Bi_2O_3 and the corresponding carboxylic acids, according to refs.^[18c,20] Other products were used as supplied. DMSO and DMF were distilled under vacuum in the presence of CaH_2 .

General Procedure for Oxidations with Bi^0 : Anhydrous DMSO or DMF (5 mL) was stirred under oxygen (1 atm) in the presence of commercial Bi^0 powder (0.3 mmol) and in the absence or in the presence of the desired additive (0.3 mmol or the equivalents used

in Table 1) at 80 °C for 30 min. This was followed by the addition of the α -ketol or the epoxide (3 mmol). The solution was maintained at 80 °C for α -ketols or epoxides and at 125 °C for α -hydroxy acids. The reaction was followed by GC or by ^1H NMR until complete consumption of the substrate. Acidic hydrolysis using aqueous 0.1 N HCl solution, diethyl ether extraction, treatment of the organic layer with aqueous 0.1 N NaOH solution until pH = 12–14 was reached, and ether reextraction gave the neutral products of the reaction. Acidification of the basic aqueous phase with 1 N HCl solution to pH 1–2, followed by a final ether extraction, afforded the carboxylic acids **2**, which were precipitated using ether-pentane mixtures and filtered off. The products were analysed by GC, ^1H and ^{13}C NMR and mass spectroscopy, and their spectral data compared to those of authentic samples.

The same procedure was used for Bi^{III} -catalysed oxidations, with 5–10 mol-% of the catalyst.

Acknowledgments

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