Bi^0-Catalyzed Oxidation of Mandelic Acid Derivatives: Substrate Selectivity

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A series of mandelic acid derivatives was oxidized with a bismuth-catalyzed oxidation system based on Bi^0/DMSO/O_2. Benzaldehyde and/or benzoic acid derivatives could be obtained chemoselectively depending on the catalytic system and the substitution on the aromatic ring. A strong substrate selectivity was observed, suggesting different oxidation mechanisms.

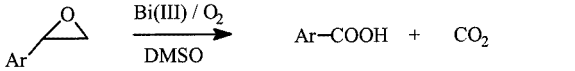
Introduction

In the last few years, we have been interested in the Bi^{III}-catalyzed oxidation of organic substrates by molecular oxygen.[1,2] Despite its low toxicity, the use of bismuth derivatives in catalysis has not been thoroughly explored until recently.[3,4]

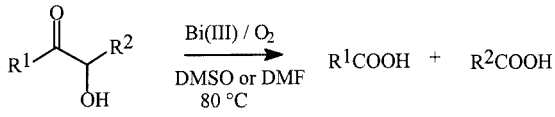
In the field of oxidation, Bi^V derivatives are well-known for their oxidizing power in stoichiometric reactions. Thus, oxidation of alcohols to carbonyl compounds, of phenols to quinones, of thiols to disulfides or the oxidative cleavage of 1,2-diols or acyloins to carbonyl compounds has been reported.[5–8] These systems are based on the redox couple Bi^V/Bi^{III}.

In contrast, only a few examples have been described of the use of Bi^{III} in oxidation reactions. Among them, Bi_2O_3/AcOH has been reported for the stoichiometric oxidation of α-hydroxy ketones to α-diketones,[9] and $BiPh_3$ catalyzes the cleavage of 1,2-diols in the presence of NBS as the oxidant.[10]

We have developed a new catalytic system based on Bi^{III}/O_2, able to oxidatively cleave epoxides, α-hydroxy acids and α-ketols to carboxylic acids [Equation (1) and (2)],[11–13] and to transform epoxides into α-diketones in DMSO[14] or into cyclic carbonates in DMF.[15]



(1)



(2)

The catalysts are Bi^{III} carboxylates, easily prepared from Bi_2O_3 and the corresponding carboxylic acids.[16,17]

We have recently shown that these processes [Equation (1) and (2)] involved the Bi^{III}/Bi^0 redox couple and that molecular oxygen was able to effect the reoxidation of Bi^0 to Bi^{III} under the reaction conditions. It was recently reported that both Bi^{III} or Bi^0 could be used as starting catalysts for these oxidations.[13]

We present here our recent results on the oxidative cleavage of mandelic acid derivatives using a catalytic amount of commercial bismuth powder in a DMSO/O_2 system. The oxidation of mandelic acid derivatives has been widely examined and essentially reported in the patent literature,[18] but to the best of our knowledge, no example of bismuth-catalysed reactions of these substrates has been described.

Results and Discussion

Oxidation of Mandelic Acid and Vanillic Mandelic Acid (VMA)

The oxidation of mandelic acid (**1a**) with either Bi^0 or Bi^{III} as the catalyst in a DMSO/O_2 medium afforded, after 24 hours at 125 °C, a mixture of carboxylic acid **1b** and

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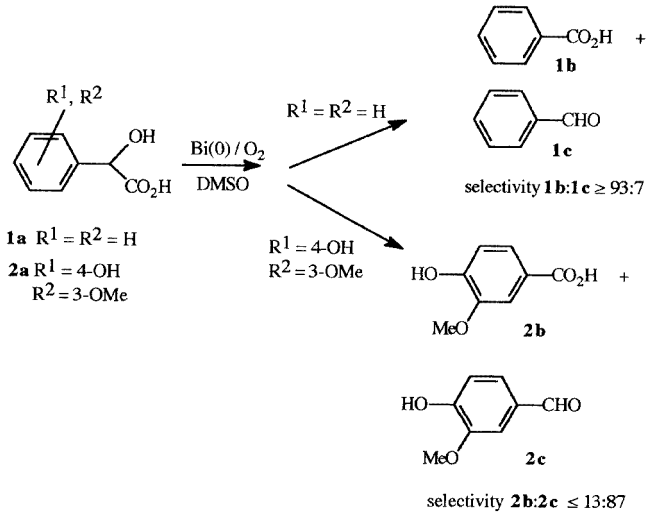


Scheme 1. Substrate selectivity in the Bi^0-catalyzed oxidation of mandelic acid substrates **1a** and **2a**

aldehyde **1c** (Scheme 1). The main product was benzoic acid (**1b**), obtained with excellent selectivities of 93−99%.

No oxidation of unsubstituted mandelic acid could be observed in water, although the reaction could be run in DMF or DMSO. The oxidation of VMA was more efficient in DMSO than in DMF (Table 1, entries 5, 6).

The selective formation of the carboxylic acid was in sharp contrast to the results of the oxidation of some substituted mandelic acid derivatives, for which the corresponding aldehyde was obtained selectively.[19] Thus, the oxidation of 4-hydroxy-3-methoxy-mandelic acid (**2a**; VMA) has been thoroughly studied for the synthesis of the corresponding aromatic aldehyde vanillin (**2c**).

When **2a** was oxidized in reactions catalyzed by Bi^0 or Bi^{III}, under DMSO/O_2 conditions, the aldehyde **2c** was the main product and was obtained with high selectivities (Scheme 1). Some representative results of the mandelic acid and VMA oxidations are reported in Table 1.

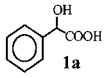
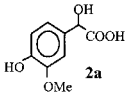
Optimization of the reaction conditions (solvent, temperature, catalyst ratio, additives) was carried out for the oxidation of **1a** catalyzed by either Bi^0 or Bi^{III}. The use of bismuth powder gave the best results in DMSO/AcOH, whereas Bi^{III}-phthalate worked best in neutral DMSO. The influence of acid or base additives on mandelic acid oxidations has already been reported for other catalytic systems.[20]

Unsubstituted mandelic acid afforded incomplete conversions after 24 hours in DMSO at 125 °C. In contrast, VMA was quantitatively reacted after 1 hour under similar conditions (entry 5).

Oxidation of Substituted Mandelic Acids

The strong influence of the substrate substitution on the oxidation rate and on the reaction products led us to examine the effect of the aromatic substituents on the reactivity and the selectivity of the decarboxylative oxidation in more detail.

Table 1. Oxidation of mandelic acid and VMA with different Bi^0 and Bi^{III} catalyst systems; general oxidation conditions: DMSO at 125 °C under O_2 (1 atm), substrate concentration of 0.4 M; Bi^0 or Bi^{III} 10 mol %

Entry	Substrate	Catalyst Conditions[a]	Reaction time / Temp.	Conversion	Yield of **b** + **c** [b]	Acid to aldehyde selectivity **b**/**c**
1	 **1a**	Bi(0) DMSO (A)	24 h 125 °C	54%	87%	**1b**/**1c** 93:7
2	**1a**	Bi(0) DMSO (B)	24 h 125 °C	24%	58%	**1b**/**1c** 99:1
3	**1a**	Bi(0) H_2O (A)	24 h 100 °C	< 5%	-	-
4	**1a**	Bi(III)[c] DMSO	24 h 125 °C	74%	75%	**1b**/**1c** 99:1
5	 **2a**	Bi(0) DMSO (A)	20 min 40 min. 125 °C	69% 97%	100% 98%	**2b**/**2c** 1:99 13:87
6	**2a**	Bi(0) DMF (A)	20 min. 125 °C	38%	100%	**2b**/**2c** 1:99
7	**2a**	Bi(III)[c] DMSO	24 h 125 °C	90%	78%	**2b**:**2c** 17:83

[a] Conditions (A): addition of aq. AcOH (50%), 1.5 equiv. with respect to the mandelic acid derivative; conditions (B): addition of aq. NaOH (50%), 1.5 equiv. with respect to the mandelic acid derivative. [b] Combined yield of carboxylic acid **b** and aldehyde **c**, calculated according to converted mandelic acid derivative. [c] Bi^{III}-phthalate[16] was used as the catalyst.

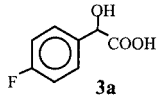
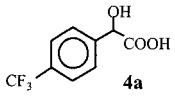
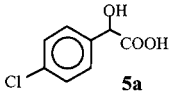
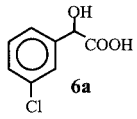
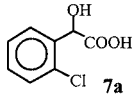
Oxidation of Mandelic Acid Derivatives with Electron-Withdrawing Substituents

The Bi^0-catalyzed oxidation of 4-fluoromandelic acid (**3a**) and 4-trifluoromethyl mandelic acid (**4a**) led selectively to the corresponding carboxylic acids **3b** and **4b** in good yields. The corresponding aldehydes **3c** and **4c** were obtained as trace compounds. Excellent selectivities **3b**:**3c** and **4b**:**4c** of 97−99% were attained with bismuth powder as the catalyst. The results are shown in Table 2.

The influence of the position of the substituent on the aromatic ring was examined in the case of 4-, 3- and 2-chloromandelic acids **5a**, **6a** and **7a**, respectively. In the presence of Bi^0, the oxidation mainly afforded the corresponding carboxylic acids **5b**−**7b**. The reactions were very selective for the 3- and 4-chloro derivatives, with **b**:**c** ratios higher than 97%.

2-Chloromandelic acid gave a lower conversion and a lower selectivity, with a **7b** to **7c** ratio of 71:29. Some deceleration due to the "*ortho*" effect could be operating in this case.

Table 2. Bi^0-catalyzed oxidation of mandelic acids derivatives **3a**−**7a** containing electron-withdrawing substituents

Substrate	Conversion[a]	Yield of **b** + **c** [b]	Acid to aldehyde selectivity **b**/**c**
[c]  **3a**	72%	97%	**3b**/**3c** 97:3
[c]  **4a**	97%	99%	**4b**/**4c** 99:1
[c]  **5a**	56%	98%	**5b**/**5c** 98:2
 **6a**	95%	>98%	**6b**/**6c** 97:3
 **7a**	17%	>98%	**7b**/**7c** 71:29

[a] Oxidations catalyzed by metallic bismuth powder, run under the conditions (A) of Table 1; entry 1 at 125 °C during 24 h. [b] Combined yield of carboxylic acid **b** and aldehyde **c**, calculated according to converted **a**. [c] Results reported in ref.[13]

The oxidation rate with Bi^0 catalysis followed the decreasing order:

3-Cl > 4-Cl >> 2-Cl

These results suggested that with electron-withdrawing substituents on the aromatic ring, Bi^0 orientates the oxidation towards the corresponding carboxylic acids with excellent selectivities for the substitution at the 3- and 4-positions.

Oxidation of Methoxy-Substituted Mandelic Acids

4-, 3- and 2-Methoxymandelic acids (**8a**, **9a** and **10a**, respectively) were taken as model compounds to examine the influence of electron-donor substituents in the different aromatic positions. The results of Bi^0-catalyzed oxidations are reported in Table 3.

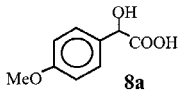
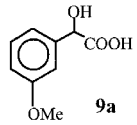
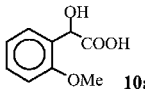
For oxidation by Bi^0, the rate of conversion decreases in the order:

4-OMe >> 3-OMe > 2-OMe

As for chloromandelic acid oxidation, the influence of the "*ortho*" effect for **10a** seems to significantly reduce its reaction rate.

The carboxylic acid was again the major reaction product in all the examples tested. However, the selectivities towards carboxylic acids varied from 62 to 85%, depending on the substitution pattern and the catalytic system. Substitution at the *ortho* and *para* positions afforded almost the same reaction selectivity. A methoxy substituent at the *meta* position, however, directed the reaction towards formation of the corresponding carboxylic acid more selectively.

Table 3. Bi^0-catalyzed oxidation of methoxy-substituted mandelic acids **8a**−**10a**

Substrate	Reaction time	Conversion[a]	Yield of **b** + **c**[b]	Acid to aldehyde selectivity **b**/**c**
 **8a**	6 h	77%	>98%	**8b**/**8c** 62:38
 **9a**	24 h	40%	>98%	**9b**/**9c** 85:15
 **10a**	24 h	17%	>98%	**10b**/**10c** 65:35

[a] Bi^0-catalyzed oxidations run under the conditions (A) of Table 1; entry 1 at 125 °C. [b] Combined yield of carboxylic acid **b** and aldehyde **c**, calculated according to converted **a**.

Oxidation of Hydroxy-Substituted Mandelic Acids

Several mandelic acids with the aromatic ring substituted by hydroxy groups were oxidized in the presence of Bi^0 under DMSO/O_2 conditions and the results are reported in Table 4.

The derivatives containing a hydroxy substituent on the aromatic ring showed higher rates of oxidation than derivatives possessing electron-withdrawing or electron-donating substituents, but without OH groups on the aromatic ring.

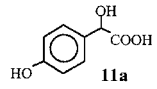
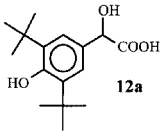
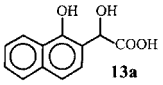
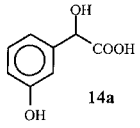
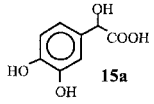
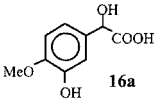
Mandelic acids with aromatic hydroxy substituents at the 2- or 4-positions, as in compounds **11a**, **12a**, **13a**, **15a** and **2a** (see Table 4 and Scheme 1) afforded the corresponding aldehyde derivatives as the major products in excellent yields and with aldehyde selectivities in the range of 77 to 99%.

The chemoselective formation of the aldehyde derivatives in the oxidation of hydroxy-substituted mandelic acids was taken to indicate that the presence of the OH group in the *ortho* or *para* positions of the aromatic ring was able to strongly control the reactivity and to selectively direct the reaction towards the formation of the corresponding aldehydes.

In sharp contrast to these observations, the oxidation of **14a**, with the hydroxy substituent at the 3-position, afforded mainly the corresponding carboxylic acid **14b** with an acid to aldehyde selectivity **14b**:**14c** of 81:19. Polymeric by-products were formed in this case and the combined yield of products **14b** and **14c** was only 50%.

The presence of an OH substituent at the *meta* position of the aromatic ring induced the opposite carboxylic acid to aldehyde selectivity, when compared to the effect of *ortho* or *para* substitution.

Table 4. Bi^0-catalyzed oxidation of hydroxy-substituted mandelic acids

Substrate	Reaction time	Conversion[a]	Yield of **b** +**c**[b]	Acid to aldehyde selectivity **b**/**c**
 **11a**	6 h	100%	>98%	**11b/11c** 23:77
 **12a**	8 h	100%	80%	**12b/12c** 5:95
 **13a**	1 h	100%	38%[c]	**13b/13c** 1:99
 **14a**	3 h	41%	50%	**14b/14c** 81:19
 **15a**	1 h	94%	>98%	**15b/15c** 6:94
 **16a**	4 h	82%	>98%	**16b/16c** 22:78

[a] Bi^0-catalyzed oxidations run under the conditions (A) of Table 1; entry 1 at 125 °C. [b] Combined yield of carboxylic acid **b** and aldehyde **c**, calculated according to converted **a**. [c] The remaining yield corresponds to the naphthalen-1,2-(α-hydroxy-γ-butyrolactone) that was isolated in this case.

When two hydroxy groups were present simultaneously in the *para* and *meta* positions, as in 3,4-dihydroxymandelic acid (**15a**), the aldehyde **15c** was obtained in high yield and with an excellent selectivity (94%). This result indicated that the OH at the *para* position influences the reactivity of the substrate more strongly than the OH at the 3-position. The product selectivity was also mainly directed by the presence of the hydroxy substituent at the *para* position.

Relating the results of Table 3 and 4 to the oxidation of VMA (**2a**; Scheme 1, Table 1), one can consider the combined effect of a hydroxy group at the *para* position for VMA oxidation, which should favor the formation of aldehyde **3b**, and the opposite effect of the methoxy substituent at the *meta* position, which alone was shown to favor carboxylic acid formation. The combined effect of both functional groups in the oxidation of **2a** afforded a **2b**:**2c** ratio of 25:75. This acid to aldehyde ratio is similar to that obtained in the oxidation of 4-hydroxy mandelic acid **11a** (**11b**:**11c** of 23:77). Again, the influence of the OH at the 4-position affects the chemical outcome of the process more strongly.

However, the hydroxy-directing rule could not be applied to the oxidation of 3-hydroxy-4-methoxymandelic acid (**16a**). The Bi^0-catalyzed oxidation of **16a** led to 82% conversion after 4 hours, with formation of the carboxylic acid **16b** and the benzaldehyde **16c** in a 22:78 ratio. The aldehyde product was the major product even though oxidation of both 4-methoxy- and 3-hydroxymandelic acids leads mainly to the corresponding carboxylic acids.

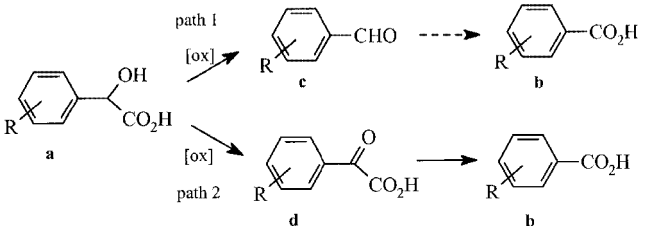
Mechanistic Aspects of Mandelic Acid Oxidation

The strong change in selectivity observed in the different reactions suggests the possibility that different mechanisms are operating for the oxidation of mandelic acids, and that these mechanisms depend strongly, amongst other features, on the nature of the substrate substitution.

We examined some mechanistic aspects in the case of the oxidation by Bi^0. Two main substrate types should be considered according to the results obtained on the product distribution: type I, substrates without hydroxy substituents on the aromatic ring, and type II, substrates containing OH substituents.

With type I substrates, we could establish that aldehyde **1c** is not an intermediate in the formation of carboxylic acid **1b**. When **1c** was reacted with Bi^0/O_2/DMSO under the standard reaction conditions (Table 1, entry 1), the aldehyde could be recovered in 85% yield after 24 hours and only 15% of carboxylic acid **1b** was formed. This result was taken to indicate that in the oxidation of mandelic acid with Bi^0, the mechanism involving the formation of benzaldehyde with a further oxidation to benzoic acid could be ruled out as the main reaction pathway.

The selective formation of the carboxylic acid derivatives can be considered to proceed through an alternative mechanism, via the α-keto acid, **d**,[21,22] as shown in path 2 of Scheme 2.



Scheme 2. Aldehyde and α-keto acid intermediates in the oxidation of mandelic acid derivatives

The oxidation of phenylglyoxylic acid (**1d**) by Bi^0 afforded benzoic acid exclusively, with 85% conversion after 24 hours. The rate of keto acid oxidation was higher than that of mandelic acid. Keto acid **1d** was therefore not formed from the oxidation of **1a**, and **1d** could be a plausible intermediate in the oxidation of **1a** to **1b**.

The oxidation of type II substrates with OH substituents on the aromatic ring afforded essentially the corresponding aldehydes (with the exception of *meta*-substituted **14a**). For these mandelic acid derivatives, a mechanism involving the participation of the phenolic OH group should be operating. More mechanistic studies need to be undertaken on the oxidation of these compounds, presumably involving the participation of the phenolic hydroxy group in quinoid-type

intermediates that further evolve towards the selective aldehyde formation.[23]

Conclusions

The oxidation of mandelic acid derivatives can be carried out by a novel catalytic system based on the use of metallic bismuth in DMSO/O_2 systems. We have shown that that the nature of the substituents on the aromatic ring may very strongly determine the chemoselectivity of the process as well as the reaction rate.

With the Bi^0 catalytic system, the formation of benzaldehyde derivatives is highly favoured with substrates bearing hydroxyl substituents at the 2- or 4-positions of the aromatic ring. The presence of an OH group at these positions has a much stronger directing effect than the other substituents.

The oxidation of mandelic acids with electron-withdrawing substituents allows the clean and selective preparation of the corresponding benzoic acids. The reaction is proposed to take place through the intermediate formation of α-keto acids.

Electron-donor groups as substituents on the aromatic ring of mandelic acid, such as methoxy, direct the oxidation reaction towards less selective mixtures of aldehyde and carboxylic acid.

More mechanistic insight is needed for a more complete understanding of the factors controlling the selectivity of this oxidation reaction.

Experimental Section

The commercially available products were used without further purification.

HPLC analysis was effected with a Waters Millipore apparatus. The eluent was a mixture of H_2O and MeOH (80:20) with H_3PO_4 (0.5%). The elution was made at 1 mL/min in an isocratic mode. The products were detected by UV at $\lambda = 220$ nm. The HPLC column was a μ-Bondapack C18 Waters 9 μm (30 cm × 3.9 mm).

The reactions were carried out under atmospheric pressure of molecular oxygen. Mandelic acid or its derivatives (**1−16a**) (2 mmol), was dissolved in DMSO (5 mL) in the presence of Bi^0 powder (0.2 mmol). The mixture was stirred at 125 °C until consumption of the starting material, which was followed by HPLC and/or ^{1}H NMR spectroscopy. The crude reaction mixture was hydrolysed with 5 mL of an aqueous 1 M HCl solution saturated with NaCl, and extracted with ethyl acetate (5 × 10 mL). The organic phases were collected and washed twice with an aqueous 0.1 M HCl solution saturated with NaCl, dried over $MgSO_4$ and filtered off. The products were analysed and quantified by HPLC and by ^{1}H NMR spectroscopy, and their spectroscopic data compared to those of authentic samples. Compounds **1a−16a**, **1b−11b**, **14b−16b**, **1c−11c** and **14c−16c** are commercially available. The other compounds are reported in the literature: **13b**,[24] **13c**,[25] naphthalen-1,2-(α-hydroxy-γ-butyrolactone),[26] 3,5-di-*tert*-butyl-4-hydroxybenzoic acid,[27] 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde.[28]

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