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Bismuth(III)-catalyzed oxidative cleavage of aryl epoxides: substituent effects on the kinetics of the oxidation reaction

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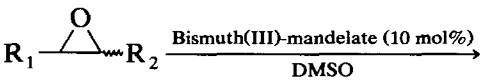
Abstract

Bismuth(III)mandelate catalyzes the oxidative C–C bond cleavage of a series of styrene epoxides in DMSO, to the corresponding aryl carboxylic acids. The reaction is accelerated in the presence of electron-donating groups substituting the phenyl ring. A good Hammet correlation of log k_{obs} *versus* σ has been obtained, with a ρ of -1.08.

Key words: Bismuth; Aryl epeoxide cleavage; Oxidation; Substituent effects; Bi(III) catalysis; Hammet correlation

1. Introduction

Epoxides are versatile building blocks in organic chemistry, and their ring opening by addition reactions has received considerable attention [1–3]. However, much less has been paid to epoxide oxidation. Oxidation of the oxirane function is reported to afford α-ketol derivatives [4–5]. We have recently found a new oxidation reaction, which directly transforms epoxides into carboxylic acids through the C–C cleavage of the oxirane ring (eqn. 1). This epoxide-carboxylic acid direct transformation, which is catalyzed by a bismuth(III)-carboxylate in dimethylsulfoxide (DMSO) [6], is unprecedented. Other bismuth salts, such as the acetate are much less effective as catalysis [6].



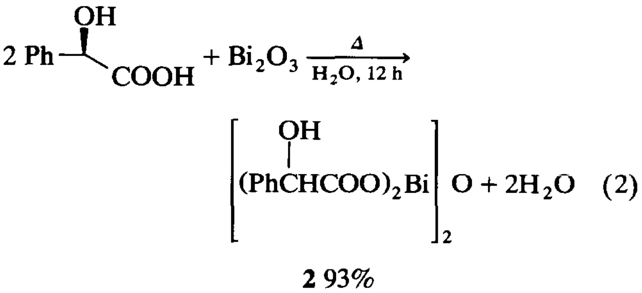
$$R_1COOH + R_2COOH \quad (1)$$

However, bismuth(V) compounds have been used as oxidants in stoichiometric organic transformations involving the Bi^{V}/Bi^{III} redox couple, essentially for the oxidation of alcohols [7], *gem*-diols [8], and phenols [9]. The Bi^{III}/Bi^{0} redox couple was shown as early as 1951 to oxidize acyloins efficiently, but this reaction seems not to have been developed [10]. Further, except for our recent report [6], there is only one example of bismuth(III) acting as a catalyst in an oxidation reaction [11]. This is the use of *N*-bromosuccinimide as the oxidant of $BiPh_3$, which promotes the catalytic cleavage of α-glycols. The Bi^{V}/Bi^{III} redox couple is also involved here [12].

We now extend our preliminary work on the bismuth(III)-catalyzed oxidation of epoxides to the reactivity of a series of terminal styrene epoxides, **1a–i**, in DMSO to kinetic and product studies.

2. Results and discussion

The catalyst, bismuth(III)mandelate (**2**) was prepared from Bi_2O_3 and (L)-mandelic acid, according to eqn. (2) [13], and used in a 5% molar ratio with respect to the epoxide throughout this work.



$$2\,Ph\overset{OH}{\overbrace{CH}}COOH + Bi_2O_3 \xrightarrow[H_2O,\ 12\ h]{\Delta} \left[(Ph\overset{OH}{\overset{|}{C}}HCOO)_2Bi\right]_2 O + 2H_2O \quad (2)$$

2 93%

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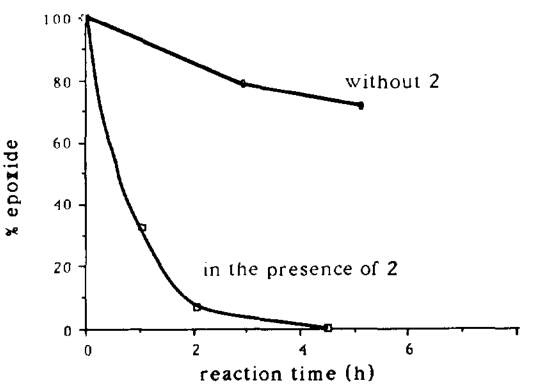
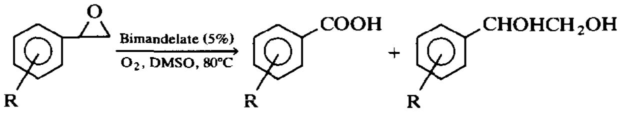


Fig. 1. Influence of the Bi catalyst **2** (5%) on the oxidation of styrene oxide (**1a**) in DMSO at 80°C.

TABLE 1. Bismuth(III)-catalyzed oxidation of terminal styrene epoxides **1**

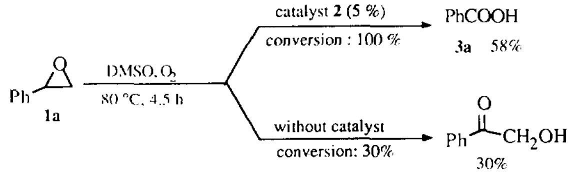


1a–i **3a–i** **4a–i**

Epoxide	R	time (h)	Carboxylic Acids 3 (% isolated yield)	Diol 4
1a	H	4.5	C_6H_5COOH (58%)	11%
1b	4-Me	2.3	$4\text{-}MeC_6H_4COOH$ (46%)	14%
1c	3-Me	2.5	$3\text{-}MeC_6H_4COOH$ (42%)	17%
1d	4-Cl	7	$4\text{-}ClC_6H_4COOH$ (53%)	21%
1e	2-Cl	9	$2\text{-}ClC_6H_4COOH$ (64%)	18%
1f	4-AcO	4.3	$4\text{-}AcOC_6H_4COOH$ (4%) $4\text{-}HOC_6H_4COOH$ (61%)	17%
1g	3-Br	23	$3\text{-}BrC_6H_4COOH$ (47%)	13%
1h	$3\text{-}NO_2$	24	$3\text{-}NO_2C_6H_4COOH$ (50%)	-
1i	2-Naphth	2.3	2-Naphth-COOH (54%)	25%

Our preliminary Bi-catalyzed epoxide oxidations had been carried out in air [6]. Taking styrene oxide (**1a**) as a model compound to optimize the reaction conditions, we found that the reaction was very sensitive to the atmosphere. The reaction was not only faster under dioxygen, but yielded a different product distribution. Thus, under O_2 (1 atm), consumption of **1a** was complete in 4.5 h at 80°C, and benzoic acid was isolated in 58% yield. In contrast, in the same conditions but under dinitrogen atm, benzoic acid was obtained only in 8% yield, the major product being phenacyl alcohol, 28% yield and the epoxide conversion was incomplete (87%). The major product, phenacyl alcohol, is the product from the DMSO oxidation in the presence of acid [4–5]. Thus, dioxygen appears to be necessary in the catalytic oxidative C–C cleavage of **1a** to give benzoic acid.

The catalytic effect of bismuth(III)mandelate is shown in Fig. 1 and Scheme 1. In the absence of the catalyst, no benzoic acid was formed in the reaction of **1a** under dioxygen. The observed 30% conversion of **1a** after 4.5 h afforded the α-ketol as the main product (Scheme 1). In the presence of 5% of **2**, the reaction of **1a** resulted in benzoic acid (58%) with complete conversion under the same conditions. Thus, the presence of the bismuth catalyst **2** not only enhanced the reactivity of **1a** but most important, forced the process through a different pathway, leading to a more completely oxidized product. The effect of the temperature was examined in reactions of **1a** at 65, 80, and 120°C, and the best results with respect to yield, selectivity, and catalyst stability were obtained at 80°C. DMSO as the solvent was important for the chemoselectivity of the oxidation because in DMF, the C–C bond cleavage of the epoxide is negligible.



Scheme 1.

The reaction conditions optimized for **1a** were then applied to a series of terminal aryl epoxides, **1a–i**. These reacted in the presence of **2** (5%) as the catalyst, in DMSO at 80°C under dioxygen (1 atm) and the results are reported in Table 1.

Styrene epoxides **1a–h**, as well as 2-naphthyl epoxide (**1i**) afforded the corresponding carboxylic acid derivatives **3a–i** in fair-to-good yields (45–65%), as shown in Table 1. Byproducts were essentially the 1,2-diols (**4**) resulting from epoxide hydrolysis, together with some sulfur-containing derivatives.

Table 1 reveals that electron-releasing substituents such as 4-Me or 3-Me accelerate the oxidation, whereas electron-attracting groups retard it. For the 2-chloro-epoxide (**1e**) conversion was slower than that of the 4-chloro-isomer (**1d**) possibly due to the steric hindrance by the *ortho*-substituent to the approach of the Bi/DMSO complex. Surprisingly, with the 4-acetoxystyrene oxide (**1f**) 4-hydroxybenzoic acid was the main product, obtained in 61% yield. Further, the reaction rate was much faster than we would have expected for an electron-attracting group such as acetoxy. We have shown using GC-MS, that **1f** can be oxidized directly and slowly to 4-acetoxybenzoic acid (4% after 4.3 h) but that it can also first suffer an acetate bond cleavage in a bismuth-catalyzed ester hydrolysis to give an intermediate phenol-epoxide,

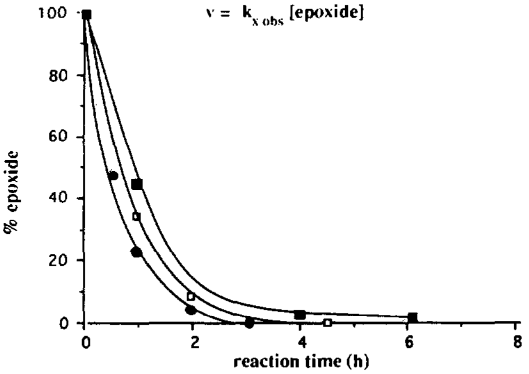


Fig. 2. Kinetics of epoxide transformation in the bismuth(III)-catalyzed oxidation in DMSO at 80°C. □ **1a**, ● **1b**, ■ **1c**.

which, through the Bi-catalyzed oxidative cleavage of the oxirane ring, gives 4-hydroxybenzoic acid.

Presumably the phenyl group is an electron-donating group in epoxide **1a**, since its reaction rate was higher than that of 1-decyl epoxide with bismuth(III)-mandelate [6].

Figure 2 displays the epoxide consumption with time, in the bismuth(III)-catalyzed oxidation in DMSO. The rate was determined by monitoring the epoxide concentration by GC in the presence of an internal standard. The decrease in epoxide concentration for a series of 4- and 3-substituted styrene epoxides obeys a first-order rate law, and the oxidation rate constants, $k_{x\,obs}$ were calculated (Table 2). The $k_{x\,obs}$ data could also be obtained from the $t_{1/2}$ in Fig. 2, corresponding to 50% of epoxide consumption.

The Hammet equation (eqn. 3) relates the $k_{x\,obs}$ of the different epoxides to the σ values for each substituent.

$$\log(k_{x\,obs}/k_{H\,obs}) = \rho\sigma_x \tag{3}$$

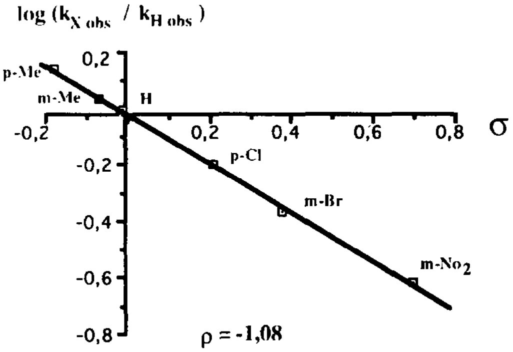


Fig. 3. Hammet-type correlation for the bismuth(III)-catalyzed oxidation of epoxides.

The plot depicted in Fig. 3 shows that the rate of epoxide consumption is linearly related to the Hammet σ constants, with a slope $\rho = -1.08$ and a correlation coefficient of 0.998. The electron density at the reaction centre is clearly affected by the nature of the substituent. To our knowledge, this is the first example where a Hammet-type linear correlation was found for oxirane oxidative C–C bond cleavage.

TABLE 2. Rates of bismuth(III)-catalyzed oxidation of various epoxides [a]

Epoxide	$k_{x\,obs} \times 10^{-4}$ (s^{-1})	$A = k_{x\,obs}/k_{H\,obs}$	log(A)	σ from [16]
1a	3.8	1.00	0	0
1b	5.25	1.38	0.14	−0.17
1c	4.1	1.08	0.035	−0.06
1d	2.4	0.63	−0.2	+0.22
1g	1.6	0.42	−0.37	+0.39
1h	0.9	0.23	−0.62	+0.71

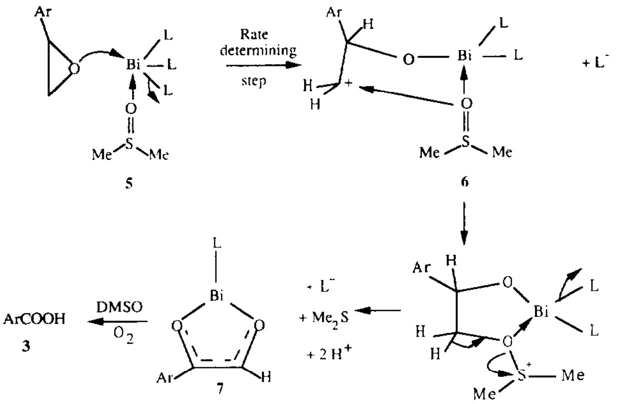
[a] Reaction conditions as described in Experimental details. The rates and the progress of the oxidation were determined by GC analysis (in the presence of decane as internal standard) of samples withdrawn from the reaction mixture.

The negative ρ value indicates that some positive charge is developed at the α or β aryl carbon atom at the transition state. Consistently, the reaction should be accelerated by electron-donating substituents that stabilize this positive charge, and slowed down by electron-withdrawing groups. The value of ρ obtained in the bismuth(III)-catalyzed oxidation and therefore its sensitivity to the electronic effects of the aromatic substituents is lower than the $\rho = -4.1$ reported for the acid-catalyzed methanolysis of a series of substituted styrene oxides [14], or the value of $\rho^+ = -4.2$ reported for the reactivity of 4-substituted styrene oxides towards hydronium-ion catalyzed hydrolysis [15]. In our case, the susceptibility of the reaction to electronic substituent effects is comparable to that obtained for the dissociation reaction of aromatic carboxylic acids in aqueous solution ($\rho = 1.0$) [16].

The relative low value found for ρ in the bismuth(III)-catalyzed oxidation of substituted styrene oxides may arise from the creation of a positive charge on the epoxidic carbon atom in the β rather than the α position with respect to the aryl ring [16]. It might also result from a solvent contribution in the activation process [17].

Our kinetic data are consistent with a mechanism involving a rate-determining step involving the epoxide (the rate is first order in epoxide concentration) and Bi^{III}. This is illustrated in Scheme 2.

The bismuth(III)mandelate complex dissolves slowly in DMSO, probably with formation of a solvate of type **5**. Coordination of the oxirane oxygen atom to Bi^{III} in **5** and simultaneous opening of the three-membered ring would then be the rate-determining step in the



Scheme 2.

reaction, and form the cationic intermediate species **6**. Consistent with our rate data, the positive charge in **6** should be located on the β carbon atom. After H^+ and dimethylsulfide formation, intermediate **6** could be converted to the ketal, compound **7**. Research is in progress to seek a better understanding of the reaction steps, the role of dioxygen, and the intermediates in the sequence **5**–**3** (Scheme 2).

3. Experimental details

3.1. Products and instrumentation

DMSO was distilled under vacuum from CaH_2. Epoxides **1b**–**i** were prepared from the corresponding styrene derivatives by oxidation with 3-chloroperbenzoic acid [18]. Bismuth(III)-mandelate was prepared from Bi_2O_3 and (L)-mandelic acid, according to ref. [13]. The other products were used as supplied.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer. Mass spectra were obtained with a Finnigan MAT INCOS 500E spectrometer (GC/MS). The GC analysis were obtained on a DELSI-300 chromatograph (column SE30, 10%, 3 m × 3/8″) and on a Varian-3400 chromatograph (capillary column DB-1, 25 m).

3.2. General procedure for the oxidation of epoxides

Anhydrous DMSO (5 ml) was stirred in the presence of bismuth(III)mandelate (**2**) (156 mg, 0.15 mmol) at 80°C for 30 min under oxygen (1 atm), followed by the addition of the epoxide, **1a**–**i** (3 mmol). The reaction was followed by GC until consumption of the substrate was complete. Acidic hydrolysis by aqueous 0.1N HCl solution, ether extraction, treatment of the organic layer by aqueous 0.1N NaOH solution until pH = 12–13 and ether re-extraction gave the neutral products of the reaction, the diols **4**. Acidification of the basic aqueous phase with 1N HCl solution to pH 1–2 followed by a final ether extraction afforded the carboxylic acids **3a**–**i**, which were precipitated from ether-pentane mixtures and filtered off. The products were analyzed by GC, ^1H, and ^{13}C NMR, mass spectra and their spectral data compared to those of authentic samples.

3.3. Kinetic measurements

The epoxide consumption was measured by GC during the oxidation of a series of 4- and 3- substituted styrene epoxides in DMSO, following the general oxidation procedure, in the presence of decane (3 mmol) as internal standard. The epoxide concentration was measured with aliquots regularly taken from the reaction medium. The aliquots were hydrolyzed, extracted with pentane, and analyzed by GC. The plot of ln([epoxide]/[epoxide°]) *versus* time gave a straight line with a slope corresponding to $k_{x\ obs}$. The experimental curve of epoxide concentration *versus* time (see Fig. 2), enables one to determine $t_{1/2}$ values. With the $t_{1/2}$ values, the $k_{x\ obs}$ can be calculated according to the equation $k_{x\ obs} = \ln 2/t_{1/2}$. Both methods gave concordant results. The average values of $k_{x\ obs}$ for all substituents are given in Table 2.

Acknowledgement

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