### Mechanistic Aspects of the Bismuth-Catalysed Oxidation of Epoxides to α-Diketones

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The mechanism of the direct oxidation of 1,2-disubstituted epoxides to  $\alpha$ -diketones catalysed by Bi<sup>III</sup> derivatives was examined. The oxidation was carried out in DMSO under dioxygen. Experimental evidence for the various steps of the reaction was obtained from spectroscopic data, isolation of intermediate species, reactions with Bi<sup>0</sup>, reaction under dinitrogen rather than under dioxygen, measurement of the oxygen consumption, cyclic voltammetry, and oxidations performed in the presence of methyl phenyl sulfoxide. The

direct epoxide-to-diketone oxidation involves two main reaction steps: a first DMSO-mediated oxidative ring-opening of the oxirane ring, and a second Bi-catalysed oxidation to the  $\alpha$ -diketone by dioxygen. A catalytic cycle is proposed combining the different results. A new alternative preparation of Bi(OTf)<sub>3</sub> by oxidative dissolution of Bi<sup>0</sup> is also described.

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### Introduction

In the field of Bi-catalysed oxidation processes, we have described previously new synthetic methods involving bismuth derivatives under dioxygen. In particular, the oxidation of terminal aryl epoxides to carboxylic acids has been reported,<sup>[1,2]</sup> as well as that of  $\alpha$ -ketols<sup>[3,4]</sup> and  $\alpha$ hydroxy acids.<sup>[5]</sup> These reactions allow catalytic oxidative C-C bond cleavage through a new Bi<sup>III</sup>/Bi<sup>0</sup> redox couple under dioxygen.<sup>[6]</sup>

More recently, our interest has focused on the selective Bi-catalysed oxidation of internal epoxides to  $\alpha$ -diketones, involving the oxidative ring-opening of the oxirane without C–C bond cleavage.<sup>[7]</sup> A series of aliphatic and aromatic epoxides were converted into their corresponding  $\alpha$ -diketones in yields of 30–77% (Scheme 1). Bi<sup>0</sup> could be used as catalyst when combined with additives such as triflic acid (TfOH) or copper triflate.<sup>[8]</sup> This oxidation reaction constitutes the first direct transformation of an epoxide function



Scheme 1. Oxidation of epoxides to  $\alpha$ -diketones (R, R' are alkyl or aryl groups)

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In this paper, we provide some insights into the reaction mechanism of the oxidation of internal epoxides catalysed by the combination  $Bi^0/TfOH$ , based on several model reactions, <sup>1</sup>H NMR analysis and cyclic voltammetry. A catalytic cycle for the oxidation of internal epoxides to *a*-diketones is proposed. We also describe a novel alternative method for the preparation of bismuth triflate by oxidative dissolution of  $Bi^0$ .

### **Results and Discussion**

The Bi-catalysed oxidation of internal epoxides to  $\alpha$ -diketones was carried out at 100 °C in DMSO under O<sub>2</sub> (1 atm). Commercially available Bi<sup>0</sup> powder (5–10 mol %) was used in combination with 2–20 mol % of triflic acid. In this study, cyclohexene oxide (1) was taken as the model compound with 1,2-cyclohexanedione (2) being obtained in yields of around 50%. The main by-products were adipic acid, from the over-oxidation of 2, and *trans*-1,2-cyclohexanediol, formed by the non-oxidative ring-opening of the epoxide by water present in the reaction medium. Also, some mass loss was caused by the partial polymerisation of cyclohexene oxide under the reaction conditions used.

#### 1. In Situ Generation of the Catalyst from Bi<sup>0</sup>

The reaction of **1** with  $Bi^0$  (8 mol%) and TfOH (22 mol%) in DMSO under O<sub>2</sub> afforded 1,2-cyclohexanedione (**2**) in 49% yield. In the absence of either  $Bi^0$  or TfOH, no oxidation of **1** to **2** was observed.

However, the oxidation of **1** is also catalysed by Bi<sup>III</sup> derivatives. Thus, when Bi(OTf)<sub>3</sub> (5 mol %) was used as the catalyst instead of the Bi<sup>0</sup>/TfOH system, **1** was oxidized to **2** in 51% yield. If BiCl<sub>3</sub> or BiBr<sub>3</sub> were used in place of Bi-(OTf)<sub>3</sub>, the oxidation product **2** was formed in low yield (< 16%) and the main reaction products were *trans*-2-chloro- or *trans*-2-bromocyclohexanol, respectively, resulting from the non-oxidative epoxide ring-opening by the halides.

Furthermore, when the oxidation of **1** was carried out in the presence of  $Bi(OTf)_3$  but in the absence of  $O_2$ , under nitrogen, a low yield of **2** was obtained, and a black precipitate of  $Bi^0$  was formed. Under these conditions, the reduced bismuth species were not recycled and so the reaction was not catalytic.

These experiments indicate the strong influence of the Bi-<sup>III</sup> counterions on the efficiency of this reaction. They also suggest that the Bi<sup>III</sup> triflate catalyst can be generated in situ from metallic bismuth and TfOH and that the recycling of the active species requires the presence of dioxygen.

# 2. Preparation of Bismuth Triflate by Oxidative Dissolution of $\mathrm{Bi}^0$

When 1 equiv. of commercially available metallic bismuth, a black powder, was heated at 100 °C in anhydrous DMSO under  $O_2$  in the presence of 3 equiv. of triflic acid, the black powder slowly dissolved to form a light yellow homogeneous solution. The evaporation of DMSO by rectification in a bulb-to-bulb oven at reduced pressure allowed isolation of a white solid in a yield of 60-80% (Scheme 2).

### Bi + 3 TfOH + 3/4 O<sub>2</sub> $\longrightarrow$ Bi(OTf)<sub>3</sub>·7.8 DMSO + 3/2 H<sub>2</sub>O

Scheme 2. Oxidative dissolution of metallic bismuth in the reaction medium

The <sup>19</sup>F NMR spectrum of this solid dissolved in CDCl<sub>3</sub> contains a singlet at  $\delta = -79.6$  ppm. The <sup>19</sup>F NMR shift of TfOH in CDCl<sub>3</sub> appears at  $\delta = 76.44$  ppm,<sup>[9]</sup> and that of hydrated Bi(OTf)<sub>3</sub> has been reported at  $\delta = 0.84$  ppm relative to CF<sub>3</sub>COOH in [D<sub>6</sub>]acetone.<sup>[10]</sup> Moreover, the elemental analysis of the solid was consistent with the formation of bismuth(III) trifluoromethanesulfonate (bismuth triflate) solvated by DMSO (Scheme 2). Thus, Bi<sup>III</sup> can be obtained by the oxidative dissolution of Bi<sup>0</sup>.

Such a procedure for the preparation of metallic triflates has not been reported and constitutes an interesting and novel alternative, especially for the preparation of Bi(OTf)<sub>3</sub>.

The compound obtained is similar to the related solvate  $Bi(DMSO)_8(ClO_4)_3$ , which has been reported recently.<sup>[11]</sup> Bismuth triflate is a Lewis acid which has been widely described as a catalyst of various organic reactions.<sup>[12,13]</sup> Its preparation has been reported either from BiPh<sub>3</sub> <sup>[10]</sup> or Bi<sub>2</sub>O<sub>3</sub> <sup>[14]</sup> in the presence of TfOH. These procedures give Bi(OTf)<sub>3</sub> in a hydrated form, with 4–9 water molecules of solvation. Preparation of anhydrous bismuth triflate is difficult, and calcination is not suitable since decomposition of

the triflate moiety occurs upon heating of the salt above 100  $^{\circ}\text{C}.^{[15]}$ 

When  $Bi^0$  dissolution was attempted under nitrogen, no dissolution of the bismuth powder could be observed. This is consistent with Scheme 2, in which dioxygen is needed as the oxidant for the metal dissolution. The fact that the  $Bi^0$  dissolution takes place only under oxygen indicates that  $O_2$  is the oxidant for this process, and not the triflic acid.

The oxidative dissolution of bismuth is efficient with DMSO as solvent. When the same reaction was carried out in DMF or acetonitrile (Scheme 2), no dissolution of the bismuth powder was observed even under oxygen. Therefore, DMSO is required as the solvent for this process.

#### 3. Role of DMSO: Oxidative Ring Opening of the Epoxide

In the oxidation reaction of epoxide 1 it was observed that the best yields of  $\alpha$ -diketone were obtained by heating a mixture of the appropriate amounts of metallic bismuth and triflic acid in DMSO at 100 °C under O<sub>2</sub>. After dissolution of the elemental bismuth (about 30 min), the epoxide 1 was introduced and the reaction was kept under O<sub>2</sub> for the required time (about 2 h). Bismuth triflate is considered as being the catalyst of the process, being generated in situ from bismuth powder and triflic acid (Scheme 3).



Scheme 3. Oxidation of internal epoxides to  $\alpha$ -diketones catalysed by bismuth and additives

The reaction of 1 in solvents other than DMSO, e.g. DMF or acetonitrile, did not result in formation of 2, neither with  $Bi^0/TfOH$  nor with  $Bi(OTf)_3$ . Therefore, DMSO is not only the solvent but it can be also considered as a potential oxidant in the reaction.

During monitoring of the progress of oxidation of epoxide 1 to  $\alpha$ -diketone 2 by GC analysis of aliquots, the formation and further consumption of a third intermediate species, 3, was observed. The analysis of the reaction mixture after 30 min, together with comparison with authentic samples, allowed the identification of 3 as the corresponding  $\alpha$ -ketol, 2-hydroxycyclohexan-1-one. The acid-catalysed oxidation of epoxides by DMSO has been already reported to afford  $\alpha$ -ketols in moderate yields.<sup>[16,17]</sup>

When oxidation of 1 was carried out using  $[D_6]DMSO$  as the solvent, the progress of the reaction could be followed by <sup>1</sup>H NMR spectroscopy. Data acquisition was performed at 100 °C in order to limit modification of the sample composition during handling and analysis. These experiments provided characteristic signals of the abovementioned organic compounds 1-3 accurately enough to

plot a kinetic curve of their relative proportion vs. reaction time (Figure 1).



Figure 1. Ratio of epoxide 1 (diamonds),  $\alpha$ -diketone 2 (triangles) and  $\alpha$ -ketol 3 (squares) in the reaction medium, as a function of time, according to <sup>1</sup>H NMR spectroscopy

The characteristic signals of each functional group were clearly resolved in the spectra. By comparison with the spectrum of an authentic sample of  $\alpha$ -ketol **3**, we identified this compound in the reaction medium after 20 and 40 min of reaction by the double-doublet signal at  $\delta = 4.07$  ppm.

Interestingly, another multiplet was observed, centred at  $\delta = 4.15$  ppm. This signal appeared only during the early stages of the reaction. We assume that it corresponds to a sulfonium intermediate, formed after the nucleophilic ring opening of the activated epoxide by DMSO, namely *trans*-2-[(dimethylsulfonio)oxy]cyclohexanolate. The presence of the sulfonium intermediate in the reaction mixture is consistent with previous studies on the acid-catalysed oxidation of epoxides by DMSO (Figure 2) described by Swern et al.,<sup>[16]</sup> and has also been reported in the solvolysis of triflates by DMSO.<sup>[18]</sup>

We consider that the reaction proceeds through a sequence of four consecutive steps: (i) the generation of the catalyst from bismuth powder and triflic acid, (ii) the DMSO-based ring-opening of the starting epoxide 1 to the oxysulfonium intermediate 4, (iii) the oxidation of 4 to the  $\alpha$ -ketol 3 and (iv) the oxidation of the  $\alpha$ -ketol 3 to the  $\alpha$ diketone 2 (Scheme 4).

A further experiment was carried out in order to determine the role of DMSO as an oxidant and its quantitative conversion into dimethyl sulfide. The oxidation reactions carried out with **1** produced dimethyl sulfide, which is difficult to quantify. The oxidation of **1** was thus performed in the presence of methyl phenyl sulfoxide instead of DMSO. The reaction was carried out at 100 °C with toluene as cosolvent (1:1, v/v). The  $\alpha$ -ketol **3**, together with thioanisole (the reduced product of the sulfoxide), were formed in an



Figure 2. <sup>1</sup>H NMR spectrum showing the characteristic signals of commercial  $\alpha$ -ketol 3 (left) and of the reaction mixture after 40 min (right) in the same chemical shift range



Scheme 4. Comprehensive reaction sequence from (i) to (iv)

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approx. 1:1 ratio. This experiment demonstrates that DMSO acts as the exclusive oxygen donor to the epoxide. It also plays the role of solvent, being polar enough to allow the dissolution of the Bi-chelated species. The role of DMSO as solvent is also especially important for the in situ catalyst preparation by oxidative dissolution of  $Bi^0$ .

#### 3. Oxidation of the $\alpha$ -Ketol 3 to the $\alpha$ -Diketone 2

Several reactions were carried out on the  $\alpha$ -ketol/ $\alpha$ -diketone oxidation step. The oxidation of commercially available  $\alpha$ -ketol **3** in DMSO by Bi(OTf)<sub>3</sub> under O<sub>2</sub> afforded the  $\alpha$ -diketone **2** in 39% yield. The same process catalysed by Bi<sup>0</sup>/TfOH led to **2** in 45% yield as the main isolated product (Scheme 5).



Scheme 5. Oxidation of  $\alpha$ -ketol 3 to  $\alpha$ -diketone 2 by molecular bismuth and triflic acid

The Bi(OTf)<sub>3</sub>-catalysed reaction of **3** can also be performed in DMF or acetonitrile under  $O_2$ . Therefore, DMSO is not necessary as the oxidant in this step. On the other hand, the oxidation of **3** in the absence of  $O_2$ , resulted in only a limited conversion of the ketol.

In the absence of bismuth triflate or of other sources of bismuth(III), the oxidation of **3** to the  $\alpha$ -diketone **2** did not proceed, even under O<sub>2</sub>, and so the  $\alpha$ -ketol **3** was not consumed.

Thus, the combination of the  $Bi^{III}$  catalyst and  $O_2$  as the oxidant is required for the oxidation of **3** to **2**.

It is worth noting that when the reaction of **3** was performed under nitrogen in the presence of a stoichiometric amount of bismuth(III) triflate, a black precipitate of metallic bismuth slowly appeared. This stoichiometric process was monitored by <sup>1</sup>H NMR spectroscopy, with particular attention paid to the characteristic signals of  $\alpha$ -ketol **3** and  $\alpha$ -diketone **2**. In the absence of dioxygen, the oxidation of **3** to **2** was concomitant with the reduction of the active Bi<sup>III</sup> species. Bi<sup>III</sup> was consumed stoichiometrically during the  $\alpha$ ketol oxidation, being reduced to Bi<sup>0</sup>. In the catalytic reaction (under O<sub>2</sub>) no precipitation of black Bi<sup>0</sup> was observed and the reduced bismuth species were recycled following oxidation by O<sub>2</sub>.

#### 4. Role of Molecular Oxygen

In light of the different experimental results, we conclude that molecular oxygen plays a double role in this oxidation.

Firstly, dioxygen is the oxidant in the Bi<sup>III</sup>-catalysed step of  $\alpha$ -ketol to  $\alpha$ -diketone. In this oxidation the Bi<sup>III</sup> species are reduced either to Bi<sup>I</sup> or to Bi<sup>0</sup>, and O<sub>2</sub> is also responsible for their re-oxidation to Bi<sup>III</sup>. As Bi<sup>0</sup> was not detected during the course of catalytic reactions, we suggest that a redox couple  $Bi^{III}$  / $Bi^{I}$  operates in this system. However, efforts to isolate or characterise the intermediate  $Bi^{I}$  or  $Bi^{0}$  species have not been successful. The generation of  $Bi^{I}$  species has been reported previously.<sup>[13]</sup>

As  $O_2$  was required for the Bi<sup>III</sup>-catalysed oxidation of **3**, we measured its consumption during the reaction catalysed by metallic bismuth in combination with triflic acid. We found that the consumption of  $O_2$  was 1.67 mmol per 1.52 mmol of  $\alpha$ -diketone **2** formed, corresponding to 1.1 equiv. of  $O_2$  per  $\alpha$ -diketone. As the oxidation of **3** to **2** requires 0.5 mol of  $O_2$  per mol of **3**, this result indicates that this excess  $O_2$  consumption could account for the over-oxidation of **2** to adipic acid.

Secondly, the presence of  $O_2$  is necessary to generate the active catalytic species, a Bi(OTf)<sub>3</sub> complex, from Bi<sup>0</sup> and TfOH. The possibility of performing the oxidation starting from stable Bi<sup>0</sup> powder, after the in situ generation of the catalyst, interested us because the reagents are available and the reaction can be run using a limited amount of water. The presence of water in the reaction medium lowers the yield of **2** and favours the formation of *trans*-1,2-cyclohexanediol by the ring-opening of the epoxide.

#### 5. Cyclic Voltammetry

Cyclic voltammetry was used to monitor the presence of  $Bi^{III}$  species during the course of the oxidation of epoxide 1. Analysis of a model sample of bismuth(III) triflate in dry acetonitrile gave a reduction wave at -0.5 V (vs. Ag/AgCl) (Figure 3).



Figure 3. Cyclic voltammetry of bismuth triflate (12 mM in acetonitrile, nitrogen-flushed, 100 mV/s, reference Ag/AgCl)

The oxidative dissolution of metallic bismuth in the presence of triflic acid in DMSO/O<sub>2</sub> was carried out as described above, and analysed by cyclic voltammetry in acetonitrile solution. A reduction wave was observed at -0.35 V (vs. Ag/AgCl) (Figure 4, curve a). After addition of epoxide 1 to the solution (10 equiv. per Bi), the reduction peak at -0.35 V disappeared and was not observed again during the oxidation of epoxide 1 to  $\alpha$ -diketone 2 (curve b). After 4 h, this reduction wave had returned (curve c). These

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experiments illustrate the formation of bismuth(III) triflate during the oxidative dissolution of metallic bismuth, as well as the regeneration of the Bi<sup>III</sup> species after completion of the catalytic reaction.



Figure 4. Cyclic voltammetry of an acetonitrile solution under nitrogen (100 mV/s, reference Ag/AgCl) containing: curve a: bismuth (15 mM) and triflic acid (35 mM); curve b: solution of curve 1 after addition of the epoxide 1 (0.15 M); curve c: solution of curve b after 4 h of reaction

#### 6. Proposed Catalytic Cycle

With the support of the results from various experiments carried out on the oxidation of epoxide **1**, we propose the catalytic cycle shown in Scheme 6. For simplicity, the catalytic cycle starts with  $Bi(OTf)_3$  and does not include the preliminary formation of bismuth(III) triflate from  $Bi^0$ .



Scheme 6. Proposed catalytic cycle for the Bi-catalysed oxidation of epoxides to  $\alpha\text{-diketones}$ 

As illustrated in Scheme 6, the different steps of the cycle include: (a) Coordination of the bismuth(III) catalyst to the epoxide, with Bi<sup>III</sup> acting as a Lewis acid. (b) Nucleophilic ring-opening of the epoxide by DMSO, favored by the activation of the oxirane ring by Bi<sup>III</sup>, leading to the sulfonium intermediate **4**. (c) Formation of the  $\alpha$ -ketol **3** as a Bi<sup>III</sup> keto

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hydroxylate intermediate by a redox reaction involving the loss of dimethyl sulfide, and the liberation of 1 equiv. of acid; the keto hydroxylate **3** may be represented under its enediolate form. (d) Redox reaction with the oxidation of the enediolate of **3** to the  $\alpha$ -diketone **2**, with the concomitant reduction of Bi<sup>III</sup> to a proposed Bi<sup>I</sup> intermediate species.<sup>[19]</sup> (e) Re-oxidation of reduced bismuth species by O<sub>2</sub> in the presence of protons leading to the regeneration of the bismuth(III) catalyst, with the formation of one water molecule.

The proposed catalytic cycle is consistent with several experimental observations. Thus, step (b), in which DMSO attacks the activated oxirane ring, is in competition with the attack of other nucleophilic species present in the reaction medium. For example, this was the case when bismuth(III) halides were used as the source of bismuth, where the resulting halohydrin was formed from the oxirane ring-opening by the halides present in the reaction medium. The presence of water in the reaction medium is also responsible for the formation of the  $\alpha$ -diol, in competition with the attack by DMSO.

The reaction step (c) introduces the  $\alpha$ -ketol to the reaction medium, coordinated with a bismuth(III) species, and the formation of dimethyl sulfide. Following the DMSObased oxidative ring-opening, the  $\alpha$ -ketol remains in its basic form, as a Bi<sup>III</sup> keto hydroxylate or a Bi<sup>III</sup> enediolate. Therefore, when the reaction step (d) was carried out with commercial  $\alpha$ -ketol as the starting material, a 45% yield of the corresponding  $\alpha$ -diketone was obtained compared to a 51% yield from the two-step reaction of the epoxide. In its protonated form, the  $\alpha$ -ketol is slightly less reactive towards Bi<sup>III</sup> oxidation than its in situ generated enediolate form from the DMSO-based oxidation. Additionally, the quantitative formation of the sulfide byproduct was confirmed by the presence of methyl phenyl sulfide in the reaction mixture when methyl phenyl sulfoxide was used as the primary oxidant.

The redox step (d), together with the re-oxidation of the reduced bismuth species step (e), constitute the key processes of this oxidation reaction. The  $Bi^{III}/Bi^{I}$  redox step and the possibility of recycling of the  $Bi^{III}$  catalytic species by dioxygen under mild conditions, confer a particular interest to the system because of the limited number of efficient metal-based catalytic systems able to function under  $O_2$ . Further insight into the mechanism of this system may be obtained from the identification of the different intermediate species responsible for the activation and reduction of dioxygen.

#### Conclusions

The mechanism of the Bi-catalysed oxidation of epoxides to  $\alpha$ -diketones in DMSO/O<sub>2</sub> was studied in detail. We have described the mechanism of the oxidation in several steps involving an initial acid-catalysed oxidative ring opening of the epoxide affected by DMSO, followed by a redox process involving the in situ generated  $\alpha$ -ketol intermediate and a

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then re-oxidised to the  $+^{iii}$  oxidation state by  $O_2$  in the presence of protons. Under nitrogen, stoichiometric consumption of the initial bismuth(III) salt and gradual formation of a black bismuth(0) precipitate occurs, probably after a dismutation reaction of a bismuth(I) intermediate species.[20]

### **Experimental Section**

Materials: Cyclohexene oxide (1), 1,2-cyclohexanedione (2), 2hydroxycyclohexanone (3), Bi<sup>0</sup> powder, triflic acid, bismuth(III) chloride, bismuth(III) bromide and the solvents used in this study were purchased from Aldrich. Bismuth(III) triflate was prepared according to a literature procedure.[10]

Equipment: GC analyses were carried out using a Varian CP 3380 gas chromatograph with an FID detector, under the following operating conditions: vector gas N<sub>2</sub>; injector and detector temperatures 250 °C; split ratio 1:50; constant flow 1 mL/min; Chrompack column WCOT fused silica (25 m  $\times$  0.20 mm i.d., film thickness 0.25 µm). GC-MS analyses were performed using an HP 5890 gas chromatograph (conditions: carrier gas He; injector and detector temperatures 250 °C; injected volume 0.5 µL; split ratio 1:100; pressure 180 kPa; HP1 column polydimethylsiloxane (50 m  $\times$ 0.20 mm i.d., film thickness 0.33 µm); coupled to an HP 5970A mass-selective detector. Mass spectra were obtained by electron ionisation at 70 eV, m/z = 35-400, source temperature 250 °C. <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra were recorded with a Bruker AC 200 FT spectrometer at 20 °C in CDCl<sub>3</sub> with TMS as internal standard. Analyses at 100 °C were recorded with a Bruker Avance 500 spectrometer equipped with a thermostat. Cyclic voltammetry curves were obtained with a Potentiostat/Galvanostat EG&G Princeton Applied Research, model 273 A (electrodes: graphite, platinum; reference Ag/AgCl).

General Procedure for the Oxidation Catalysed by Bi/O2 in the Presence of Triflic Acid: A mixture of the appropriate amount of bismuth(0) (0.25 to 0.50 mmol) and the additive (CAUTION: triflic acid is highly corrosive!), or bismuth triflate (0.25 to 0.50 mmol), in freshly distilled DMSO (15 mL) was heated at 100 °C under O2 (1 atm). The substrate (5 mmol) in DMSO (5 mL) was introduced through a serum cap and the mixture was stirred at this temperature until completion (monitored by GC). The reaction mixture was then hydrolysed with brine (50 mL) and extracted with diethyl ether (3  $\times$  50 mL). The combined organic layers were dried with MgSO<sub>4</sub> and the solvents evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with a gradient pentane/dichloromethane as the eluent. Fiveand six-membered ring  $\alpha$ -diketones were only observed in their enol form under analytical conditions. All compounds were characterised by comparison with authentic samples.

Preparation of Bi(OTf)<sub>3</sub> by Oxidative Dissolution of Bi<sup>0</sup>: Metallic bismuth powder (10 mmol, 2.1 g) was placed in a 25-mL roundbottomed flask. After flushing with nitrogen, freshly distilled DMSO (10 mL) was added. The flask was then cooled in an icebath and kept cool during the addition of triflic acid (30 mmol, 4.5 g) (CAUTION!) in three aliquots. The flask was then connected to a condenser capped with an oxygen bag, and the mixture was heated to 100 °C with stirring. Reaction progress was monitored by observation of the slow dissolution of the black bismuth powder. After completion, DMSO was removed by rectification using a bulb-to-bulb oven (100 °C, 0.1-1 mbar). The white solid obtained was washed with a small volume of cold dichloromethane under nitrogen and stored under nitrogen. <sup>19</sup>F NMR (200 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta = -79.6$  (s) ppm. Bi(OTf)<sub>3</sub>·7.8DMSO  $(C_{18.6}H_{46.8}BiF_9O_{16.8}S_{10.8};\,1455.63):\,calcd.\ C$ 17.6, H 3.7, Bi 16.5, F 13.5, S 27.4; found: C 17.5, H 3.7, Bi 16.2, F 13.2, S 27.7.

Measurement of Oxygen Consumption During Oxidation Reactions: The procedure was identical to the one presented above except that the O<sub>2</sub> source bag is also connected through a silica gel trap to an open graduated U-shaped cylinder containing water. Direct observation of the change of the water level in the graduated tube allows calculation of the amount of gas consumed during the reaction.

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