Zn(II)-Catalyzed Desymmetrization of *meso*-Epoxides by Aromatic Amines in Water

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Dedicated to Professor Gianlorenzo Marino on the occasion of his 80th birthday

Abstract: The $Zn(OTf)_2$–SDS–bipyridine **1** system has proved to be an effective catalyst in water for the desymmetrization of epoxides **2a–d** by anilines **3a–d**. After obtaining comparable results by using Sc(III)–SDS and Zn(II)–SDS systems in the case of **2a** and **3a**, we have explored the enantioselective ring opening of small epoxides for which water has never been used as reaction medium. Up to date the 85% ee obtained in the case of cyclohexene oxide **2b** with amines **3a** and **3d** are very good results and are the highest values obtained in water as reaction medium.

Key words: aqueous medium, aminolysis, *meso*-epoxides, Zn(II)–SDS, desymmetrization

Water has proven to be an excellent reaction medium to realize environmentally friendly chemical processes reaching high chemically efficiency.[1–3] We have been investigating the use of water as a reaction medium for many years,[1a,2,3a,b,4] and more in detail, we have shown that aqueous medium is one of the most appropriate for the nucleophilic ring opening of epoxides.[2] We found that in the case of charged nucleophiles (such as N_3^-, Br^-, I^-) the best results are obtained by using Cu(II), Al(III), and In(III) salts not depending on their counterions.

Recently, the aminolysis of epoxides in water has been investigated[3,5] and excellent results have been accomplished.

We have contributed to the realization of this process and showed that: a) in water, by regulating appropriately the pH, amines readily react with epoxides,[3b] b) at pH 5.0 zirconium dodecyl sulfate [$Zr(DS)_4$] is one of the most effective catalysts but proved to promote poorly the desymmetrization of *cis*-stilbene oxide (**2a**) with aniline (**3a**).[3a]

Optically active β-amino alcohols are important molecules that find wide use as starting materials for the preparation of target molecules[6–8] and also as chiral auxiliary or ligands in asymmetric processes.[9] An elegant access route to this class of molecules in a catalytic and enantioselective manner is given by the asymmetric aminolysis of epoxides (i.e. desymmetrization and kinetic resolution).[5,10]

To realize this process many Lewis acid catalysts in combination with chiral ligands have been used,[10] and generally, the use of an organic reaction medium has been adopted to reach high level of enantioselectivity. Highly enantioselective processes in sole water are difficult to be realized and examples in this field are rare.[1,5]

Recently, in this context, excellent results have been accomplished by Kobayashi et al. by using $Sc(DS)_3$ as Lewis acid surfactant combined catalyst (LASC) and enantiomerically pure (*S*,*S*)-6,6′-bis(1-hydroxy-2,2-dimethyl propyl)-2,2′-bipyridine in water.[5] This protocol allowed to reach in the aminolysis of *meso*-epoxides by anilines, levels of enantioselectivity superior to those obtained by using organic solvents.[5] The higher efficiency found by using water has been justified by invoking hydrophobic interactions existing among the reactants and the LASC–bipyridine (**1**) complex.

Although the results achieved are brilliant, this work has been essentially focused on the aminolysis of *cis*-stilbene oxide (**2a**) and its derivatives and on the use of $Sc(DS)_3$.

We have decided to investigate this process in more detail by extending the study to more Lewis acids [other than Sc(III)] and to a wider range of *meso*-epoxides and amines.

Considering that hydrophobic interactions play a key role in the efficiency of this process,[3a,5] we intended to verify how the concentration of the reactants in water can influence the enantioselectivity of the aminolysis of *meso*-epoxides. We have focused our attention on inexpensive transition-metal catalysts [Zn(II), Cu(II), Ni(II), and Co(II), which are interesting biocatalysts generally used by nature to regulate catalytic processes[11]] combined with sodium dodecyl sulfate (SDS), to promote the aminolysis of *cis*-stilbene oxide (**2a**) with aniline (**3a**) in water by using (*R*,*R*)-bipyridine **1** as chiral ligand. The results obtained are illustrated in Table 1.

In the reaction of **2a** with **3a** (1.0 M in water) at 30 °C and in the presence of 1 mol% of $Zn(OTf)_2$, 2 mol% of SDS, and 1.2 mol% of bipyridine **1**, after 30 hours the conversion to (*S*,*S*)-**4** was 20% only and with low ee (53%; Table 1, entry 1). It is noteworthy that by using Sc(III)–SDS system as catalyst the enantioselectivity of the reaction is opposite.[5a]

A better result was obtained when 5 mol% of $Zn(OTf)_2$ and **1** were used in the presence of 10 mol% of SDS, in

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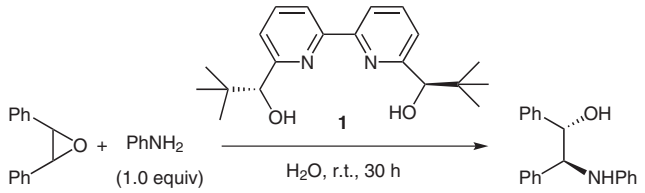
Table 1 Enantioselective Aminolysis of *cis*-Stilbene Oxide (**2a**) with Aniline (**3a**)



2a **3a** (+)-(*S*,*S*)-**4**

Entry	Catalyst (mol%)	SDS (mol%)	**1** (mol%)	Concentration (M)[a]	Conversion (%)[b]	ee (%)[c]
1	$Zn(OTf)_2$ (1)	2	1.2	1.0	20	53
2	$Zn(OTf)_2$ (5)	10	5	1.0	97	91[d]
3	$Zn(OTf)_2$ (5)	10	5	0.25	97	90
4	$Zn(OTf)_2$ (5)	5	5	0.25	97	90
5	$Zn(OTf)_2$ (5)	5	5	0.025	50	87
6	$Zn(OTf)_2$ (5)	–	5	0.25	–	–
7	$Zn(OTf)_2$ (5)	–	5[e]	0.25	54	80
8	$Cu(OTf)_2$ (5)	10	5	0.25	90	87
9	$CoCl_2$ (5)	10	5	0.25	15	51
10	$NiCl_2$ (5)	10	5	0.25	8	43

[a] Formal concentration calculated by considering that reactants are completely soluble.
[b] Conversion measured by GLC analyses, the remaining material was the unreacted **2a**.
[c] Enantiomeric excess measured by chiral HPLC analyses.
[d] Isolated yield: 93%.
[e] In CH_2Cl_2.

fact, β-amino alcohol (+)-(*S*,*S*)-**4** was isolated in 93% yield and 91% ee (Table 1, entry 2). When the concentration of **2a** and **3a** was reduced to 0.25 M similar results in terms of reaction rate and enantioselectivity were obtained both when 5 mol% or 10 mol% of SDS were used (Table 1, entries 3 and 4). When the concentration of **2a** and **3a** was reduced to 0.025 M the aminolysis slowed significantly, and also the enantioselectivity was slightly reduced (Table 1, entry 5).

The role of water and of SDS in this process is crucial. In fact, in aqueous medium and in the absence of SDS the conversion of **2a** to **4** was completely inhibited (entry 6) and when $Zn(OTf)_2$ and bipyridine **1** were used in dichloromethane this transformation was much slower and the enantiocontrol was less effective (Table 1, entry 7 vs. 4).

Copper triflate was only slightly less effective than $Zn(OTf)_2$ (Table 1, entry 8) while $CoCl_2$ and $NiCl_2$ gave unsatisfactory results in terms of reaction conversion and enantioselectivity (Table 1, entries 9 and 10).

These preliminary results showed that among the classic transition-metal Lewis acids – Zn(II), Cu(II), Co(II), and Ni(II) – only Zn(II) was truly effective and gave results quantitatively comparable but with opposite enantioselectivity to those obtained by using Sc(III).[5]

Considering that SDS alone can significantly promote the aminolysis of epoxides in water,[3a] it is important to reduce the amount of SDS used in the desymmetrization reactions in order to minimize the contribution of the not stereoselective reaction pathways. Therefore, we have considered the use of 5 mol% of $Zn(OTf)_2$–SDS–**1** in equimolar amounts at 0.5 M concentration (Table 1, entry 4) as the best catalytic conditions. Under these highly heterogeneous reaction conditions, the amount of $Zn(OTf)_2$, SDS, and bipyridine **1** that combine to form the true catalytic species are presumably significantly smaller than 5 mol%.

Zinc(II) has been recognized as one of the most important Lewis acid in metal-enzyme-catalyzed reactions in biological systems,[12] and we believe that Zn(II)–SDS system is a promising eco-friendly catalyst that merits to be further exploited in organic reactions in water.

Considering the results obtained with *cis*-stilbene oxide (**2a**) with **3a** we have decided to develop a complementary study and to extend the use of Zn(II)–SDS system in the aminolysis of rarely studied *meso*-epoxides and for which the enantioselectivity is generally low.

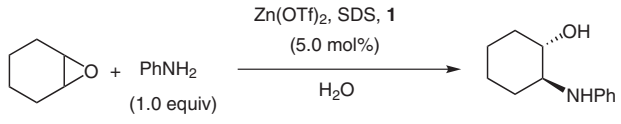
We have studied the aminolysis of epoxides **2b**–**d** with anilines **3a**–**d** and the results obtained are reported in Tables 2–4. Only the aminolysis of **2b**–**d** with **3a** has been previously studied in an organic solvent and with generally low enantioselectivity, while all these processes have never been investigated in water.

Initially, we have taken under consideration the aminolysis of cyclohexene oxide (**2b**) with aniline (**3a**) (Table 2).

A significant influence of the temperature has been found, in fact by lowering the reaction temperature from 30 °C to 4 °C, the enantiomeric excess goes from 34% to 52% (Table 2, entry 1 vs. 2). Moreover, the concentration effect is impressive and by varying from 0.125 M to 0.50 M the concentration of epoxide **2b** and aniline (**3a**), β-amino alcohol **5** is obtained in 52% and 85% ee, respectively (Table 2, entries 2 and 3). By further increasing the concentration to 1.50 M and 2.50 M, the enantiomeric excess was 80% and 77%, respectively (Table 2, entries 4 and 5).

From these data it is clear that there is an optimal concentration where the invoked hydrophobic interactions existing between the $Zn(OTf)_2$–SDS–bipyridine **1** complex and the reactants are more effective in increasing the reaction rate and maximizing the transfer of the chiral message.

Table 2 Enantioselective Aminolysis of Cyclohexene Oxide (**2b**) with Aniline (**3a**)



2b **3a** (+)-(*S*,*S*)-**5**

Entry	Concentration (M)[a]	T (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	0.125	30	20	90	34
2	0.125	4	65	50	52
3	0.50	4	50	90	85
4	1.50	4	25	90	80
5	2.50	4	18	90	77

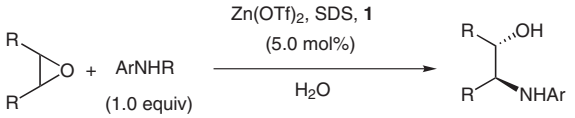
[a] Formal concentration calculated by considering that reactants are completely soluble.
[b] Isolated yield.
[c] Enantiomeric excess measured by chiral HPLC analyses.

A similar study was then extended to anilines **3a**–**c** and also to epoxides **2c**–**d**. Those substrates display a hydrophilicity roughly similar to that of **2b** and **3a** and the best enantioselectivity results were achieved at a 0.5 M formal concentration of the reactants. The results are summarized in Table 3.

On this basis we have considered that by using a highly hydrophobic amine, such as α-naphthylamine (**3d**), good enantioselectivity in the desymmetrization of 'small' epoxides such as **2b**–**d** could be obtained.

The data illustrated in Table 4 support this hypothesis. The enantioselective aminolysis of **2b** with α-naphthylamine (**3d**) confirmed the close dependency of the enantiocontrol of the process on the concentration of the reactants. The best efficiency was achieved with a formal concentration of **2b** and **3d** of 0.125 M and in the presence of 10 mol% of $Zn(OTf)_2$–SDS–**1** catalytic system (Table 4, entry 2 vs. 1 and 3). Under these reaction conditions, the rate of the process is acceptable and the corresponding β-amino alcohol **14** has been obtained in a very

Table 3 Enantioselective Aminolysis of Epoxides **2b**–**d** with anilines **3a**–**c** at 0.50 M Concentration in Water at 4 °C[a]

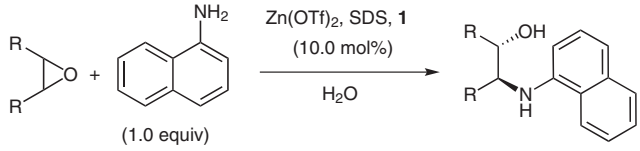


2b–d **3** (+)-(*S*,*S*)

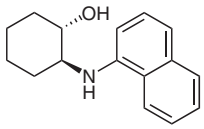
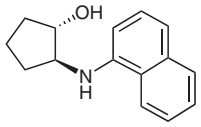
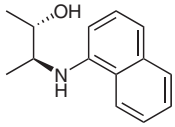
Entry	Epoxide	Aniline	Time (h)	Product	Yield (%)[b]	ee (%)[c]
1	**2b**	**3b**	70	(+)-(*S*,*S*)-**6**	90	66
2	**2b**	**3c**	62	(+)-(*S*,*S*)-**7**	90	68
3	**2c**	**3a**	160	(+)-(*S*,*S*)-**8**	85	52
4	**2c**	**3b**	120	(+)-(*S*,*S*)-**9**	88	46
5	**2c**	**3c**	120	(+)-(*S*,*S*)-**10**	81	55
6	**2d**	**3a**	70	(+)-(*S*,*S*)-**11**	90	51
7	**2d**	**3b**	160	(+)-(*S*,*S*)-**12**	89	48
8	**2d**	**3c**	160	(+)-(*S*,*S*)-**13**	79	59

[a] Formal concentration calculated by considering that reactants are completely soluble.
[b] Isolated yield.
[c] Enantiomeric excess measured by chiral HPLC analyses.

Table 4 Enantioselective Aminolysis of Epoxides **2b–d** with α-Naphthylamine (**3d**) in Water at 4 °C



2b–d **3d** (+)-(*S*,*S*)

Entry	Epoxide	Concentration (M)[a]	Time (h)	Product	Yield (%)[b]	ee (%)[c]
1		0.50	48		91	76
2	**2b**	0.125	50		92	85
3		0.025	114		90	77
				(+)-(*S*,*S*)-**14**		
4	**2c**	0.125	160		90	71
				(+)-(*S*,*S*)-**15**		
5	**2d**	0.125	180		90	70
				(+)-(*S*,*S*)-**16**		

[a] Formal concentration calculated by considering that reactants are completely soluble.
[b] Isolated yield.
[c] Enantiomeric excess measured by chiral HPLC analyses.

good yield and enantiomeric excess (92% and 85%, respectively).

The same reaction conditions were extended to the reactions of **2c** and **2d** with **3d**, and the corresponding β-amino alcohols **15** and **16** were isolated in satisfactory yield and enantiomeric excess (Table 4, entries 4 and 5).

In conclusion, Zn(II)–SDS system combined with bipyridine **1** has proved to be an effective catalyst in water for the desymmetrization of *meso*-epoxides. In this study we have explored the desymmetrization by aminolysis with anilines **3a–d** by focusing our attention on substrates **2b–d**, for which generally rare and poor results have been reported, never by using water as reaction medium. Up to date the 85% ee obtained in the case of cyclohexene oxide (**2b**) and aniline (**3a**) is a very good result and is the highest value obtained in water as reaction medium.

The chiral bipyridine ligand **1** was prepared according to the reported procedure.[13] β-Amino alcohols **4–9**, **11**, **12**, **14**, and **15** are known compounds while β-amino alcohols **10**, **13**, **16** are new compounds and their characterization data are reported below.

Zn(II)-Catalyzed Desymmetrization of *meso*-Epoxides – Typical Procedure for the Aminolysis of 2d with 3c

In a screw-capped vial equipped with a magnetic stirrer, $Zn(OTf)_2$ (0.025 mmol), SDS (0.025 mmol), and chiral bipyridine ligand **1** (0.025 mmol) were stirred in H_2O (1 mL) for 5 min at r.t. 2-Fluoroaniline (**3c**, 0.5 mmol) was added and, after a few minutes, 2,3-epoxybutane (**2d**, 0.5 mmol) was added at 0 °C. The reaction mixture was stirred for 160 h at 4 °C, then basified with aq 5 M NaOH to pH 10 and extracted with EtOAc (3 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, the solvent was evaporated and the crude product was charged on a Et_3N pretreated SiO_2 column chromatography [Et_2O–PE (1:2); SiO_2–sample (30:1)]. Pure (2*S*,3*S*)-3-(2′-Fluoro-phenylamino)butan-2-ol (**13**) was isolated as a colourless oil (79% yield, 59% ee).

(1*S*,2*S*)-2-(2′-Fluorophenylamino)-1-cyclopentanol (10)

Isolated in 81% yield; colorless oil; chromatography on SiO_2, eluent: Et_2O–PE (1:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35–1.50 (m, 1 H), 1.55–1.70 (m, 1 H), 1.70–1.90 (m, 2 H), 1.90–2.05 (m, 1 H), 2.05–2.20 (m, 1 H), 2.20–2.35 (m, 1 H), 3.55–3.65 (m, 1 H), 3.70–3.95 (br s, 1 H), 4.05–4.10 (m, 1 H), 6.55–6.65 (m, 1 H), 6.82 (t, *J* = 8.3 Hz, 1 H), 6.90–7.00 (m, 2 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 151.4, 136.2, 124.6, 116.7, 114.4, 112.9, 78.2, 61.7, 32.9, 31.1, 21.0. GC-MS (EI): *m/z* (%) = 195 (51) [M^+], 151 (13), 150 (100), 137 (13), 136 (10), 130 (11), 124 (52), 122 (18), 111 (24), 109 (10), 95 (10). Anal. Calcd for $C_{11}H_{14}FNO$: C, 67.67; H, 7.23; F, 9.73; N, 7.17. Found: C, 67.30; H, 7.01; F, 9.76; N, 7.20. The ee was determined by HPLC using a Daicel Chiralpak OD-H column [hexane–*i*-PrOH (95:5); flow rate 0.5 mL/min; λ = 254 nm, t_R (1*R*,2*R*) = 26.3 min, t_R (1*S*,2*S*) = 30.7 min]; ee = 55%. $[\alpha]_D^{21}$ +11.1 (*c* 0.86, CH_2Cl_2).

(2*S*,3*S*)-3-(2′-Fluorophenylamino)butan-2-ol (13)

Isolated in 79% yield; colorless oil; chromatography on SiO_2, eluent: Et_2O–PE (1:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 6.4 Hz, 3 H), 1.26 (d, *J* = 6.2 Hz, 3 H), 2.45–2.80 (br s, 1 H), 3.34 (quint, *J* = 6.3 Hz, 1 H), 3.60–3.80 (br s, 1 H), 3.70 (quint, *J* = 6.2 Hz, 1 H), 6.60–6.70 (m, 1 H), 6.79 (t, *J* = 8.4 Hz, 1 H), 6.90–7.05 (m, 2 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 152.2, 136.1, 124.6, 117.4, 114.7, 113.6, 71.2, 55.6, 19.4, 17.3. GC-MS (EI): *m/z* (%) = 183 (22) [M^+], 139 (17), 138 (100), 91 (13). Anal. Calcd for $C_{10}H_{14}FNO$: C, 65.55; H, 7.70; F, 10.37; N, 7.64. Found: C, 65.87;

H, 7.72; F, 10.32; N, 7.66. The ee was determined by HPLC using a Daicel Chiralpak AD-H column [hexane–*i*-PrOH (95:5; flow rate 1.0 mL/min; λ = 254 nm, t_R (2*R*,3*R*) = 9.4 min, t_R (2*S*,3*S*) = 11.4 min]; ee = 59%. $[\alpha]_D^{21}$ +55.5 (*c* 0.57, CH_2Cl_2).

(2*S*,3*S*)-3-(Naphth-1′-ylamino)butan-2-ol (16)

Isolated in 90% yield; colorless oil; chromatography on SiO_2, eluent: Et_2O–PE (1:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25–1.30 (br s, 2 H), 1.27 (d, *J* = 6.4 Hz, 3 H), 1.34 (d, *J* = 6.2 Hz, 3 H), 3.58 (quint, *J* = 6.4 Hz, 1 H), 3.88 (quint, *J* = 6.2 Hz, 1 H), 6.80 (d, *J* = 7.3 Hz, 1 H), 7.27–7.40 (m, 2 H), 7.40–7.50 (m, 2 H), 7.75–7.85 (m, 1 H), 7.85–7.90 (m, 1 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 142.1, 134.5, 128.7, 126.4, 125.8, 125.0, 124.1, 120.0, 118.5, 106.8, 71.3, 55.9, 19.8, 16.9. GC-MS (EI): *m/z* (%) = 215 (24) [M^+], 171 (15), 170 (100), 155 (13), 154 (15), 129 (13), 128 (15), 127 (15). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.71; H, 7.99; N, 6.48. The ee was determined by HPLC using a Daicel Chiralpak AD-H column [hexane–*i*-PrOH (95/5); flow rate 1.0 mL/min; λ = 254 nm, t_R (2*S*,3*S*) = 10.2 min, t_R (3*R*,3*R*) = 11.6 min]; ee = 70%. $[\alpha]_D^{21}$ +77.0 (*c* 0.58, CH_2Cl_2).

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