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Enantioselective epoxidations of alkenes catalyzed by (salen)Mn(III) in aqueous surfactant systems

Francesco P. Ballistreri [a], Lucia Brinchi [b], Raimondo Germani [b], Gianfranco Savelli [b], Gaetano A. Tomaselli [a,*], Rosa M. Toscano [a]

[a] *Dipartimento Scienze Chimiche, University of Catania, Viale A. Doria, 6-95125 Catania, Italy*
[b] *CEMIN, Centro di Eccellenza Materiali Innovativi Nanostrutturati, Dipartimento di Chimica, University of Perugia, Via Elce di Sotto, 8-06123 Perugia, Italy*

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ABSTRACT

An aqueous reaction medium, based on a surfactant solution of diethyltetradecylamine *N*-oxide (AOE-14), was developed for the enantioselective epoxidation of 1,2-dihydronaphthalene and of various *cis*-β-alkyl styrenes with increasing hydrophobicity, using bleach as oxidant and the Jacobsen chiral (salen)Mn(III) as catalyst. AOE-14 is able to both solubilize all reactants in water and bind the metal of the salen complex acting as coligand. Its use leads to good yields (>75%) and to ee values ranging from 75% up to 91% even in the case of *cis*-β-alkyl styrenes where lower cis/trans epoxide ratios are observed. The ratio of surfactant/substrate used is 1:1 or 4:1, much lower than those generally used in the literature.

1. Introduction

Asymmetric epoxidation of unfunctionalized olefins catalyzed by chiral (salen)Mn(III) complexes has proved to be one of the most useful reactions in organic synthesis. The chiral epoxides obtained contain two new stereocentres and can be easily transformed into a large variety of compounds,[1] including biologically active compounds, which are of wide use in the pharmaceutical and agricultural fields, as well as in the electronic industry. A typical protocol for this reaction makes use of commercial bleach as the oxygen source, and of a chiral salen in catalytic amount in a two-phase system (water and dichloromethane).[2] Difficulty of separation and recycling of the often expensive chiral catalyst, and the use of chlorinated solvents is the main drawback of this procedure. Recently, efforts have been made to 'heterogenize' the Jacobsen (salen)Mn(III) in order to recycle it, using mesoporous materials, (zeolites, poly-systems), but most of modified catalysts are less efficient than their corresponding unmodified ones,[3] and chlorinated solvents are always used. The search for new and improved synthetic procedures is growing, driven mostly by the need for higher selectivity and efficiency and by economic and environmental constraints. In the last few years particularly there has been a strong emphasis on so-called 'Green Chemistry' to protect the environment from pollutants.[4,5] Herein, we report a study on the asymmetric epoxidation reaction of model alkenes mediated by (salen)Mn(III) catalyst in aqueous surfactant media, avoiding chlorinated solvents.

Since the use of water as solvent is particularly attractive for developing mild, cheap and environmentally benign reaction conditions, there is a considerable interest in employing water as reaction medium.[6,7] Furthermore, aqueous association colloids are alternatives to the use of organic solvents, in that they provide reaction media distinct from bulk water in terms of polarity, and can provide acceleration of reaction and chemo-, regio- and stereoselectivity.[8,9] Starting from the observation reported by Jacobsen[10] that the addition of an amine oxide, able to bind the metal of the chiral catalyst, improved the reaction enantioselectivity, we selected some 'ad hoc' tailored surfactants, such as diethyltetradecylamine *N*-oxide (AEO-14), able to both solubilize all reactants in water, and at the same time act as coligand through the presence of an amine oxide group. In order to test both an increase in the amine oxide bulkiness and the introduction of an aromatic ring in the surfactant framework, we also employed dipropyltetradecylamine *N*-oxide (AOPr-14) and *p*-dodecyloxybenzyldimethylamine *N*-oxide (*p*DoAO), respectively. A comparison was also made with the cationic cetyltrimethylammonium

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* Corresponding author. Fax: +39 095 580138.
E-mail address: gtomaselli@unict.it (G.A. Tomaselli).

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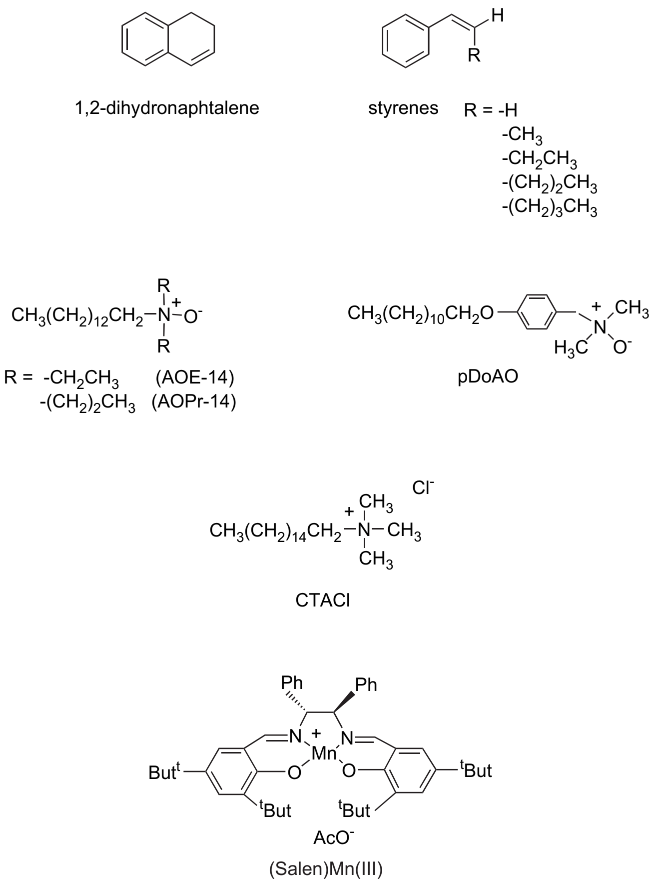

Figure 1. Alkenes, Mn(III)catalyst and surfactants with relative acronyms used in this work.

chloride (CTACl) surfactant, unable to bind the chiral catalyst. Structures of surfactants, the alkenes chosen (1,2-dihydronaphthalene and model *cis*-β-substituted styrenes, with substituents ranging from H to alkyl groups of increasing length up to *n*-butyl), and the (salen)Mn(III) employed as catalyst are shown in Figure 1.

2. Results and discussion

The epoxidation of 1,2-dihydronaphthalene, catalyzed by (salen)Mn(III) at 25 °C, was carried under different conditions and reaction media (Table 1).

The biphasic system water/dichloromethane, already employed by Jacobsen, was used as reference system (entries 1 and 2), and the reaction was carried out with and without the coligand amine oxide PPNO (4-phenyl-pyridine-*N*-oxide). We observed a 76% ee value after 90 min reaction time (entry 2), which matches with the 83% ee value observed by Jacobsen[11] for the same reaction time. In water, the amine oxide surfactant AEO-14 was initially used, and different concentrations of bleach and different reaction times were investigated (entries 3–6). The best result was obtained at [NaClO]=0.2 M (ee=91%) (entry 6), giving the reaction better ee values in aqueous solutions of AEO-14, and in shorter reaction time than in the biphasic system without (ee=56%) (entry 1) and with PPNO (ee=76%) (entry 2). It is interesting to observe that the ee values of the major epoxide, at higher concentrations of NaClO, increase with time (entries 4–6), suggesting that a secondary kinetic resolution process, previously observed by Jacobsen,[11] is occurring. In fact a one-pot tandem asymmetric epoxidation/kinetic resolution process, which leads to the 1*R*,2*S* epoxide in a highly enantiomerically enriched mixture is present at higher oxidant concentrations, consistent with the already reported in the literature asymmetric C–H benzylic bonds hydroxylation of the formed epoxide, which occurs slower with the major enantiomer epoxide ($k_{fast}/k_{slow}=4.8$).[11]

The AEO-14 seems to play three roles: it solubilizes reagents in water, it increases the rate, but it also acts as a coligand, similar to PPNO. Comparison of results obtained in AEO-14 with those in cationic CTACl, a surfactant, which is unable to bind the catalyst (entries 7–9), clearly shows the better role of AEO-14 probably due to its ability to work as coligand. In aqueous solutions of CTACl the ee values obtained increased with oxidant concentration, and the best results are more or less comparable with those observed in the biphasic system but without PPNO (entries 1 and 9). Furthermore, addition of PPNO to CTACl solutions increases the ee values (entry 7), supporting the observation that the presence of a coligand increases the selectivity. Another amine oxide surfactant was used, *p*DoAO, which in principle, having an aromatic moiety, could interact more deeply with the aromatic substrate giving better results. Data shown in Table 1 indicate that the surfactant *p*DoAO provides similar or better results than AOE-14 in similar conditions (compare entries 3 and 11), therefore acting also as a coligand. Unfortunately concentrations of surfactant cannot be varied widely with *p*DoAO, because of its tendency to form a gel in water.

The behaviour of AOE-14 as coligand was furtherly investigated, studying the effects of AOE-14 concentration changes on the ee values. The ee values improve with increasing concentration, reaching a plateau at [AOE-14]=0.6 M (Fig. 2).

Table 1
Enantioselective epoxidation of 1,2-dihydronaphthalene (salen)Mn(III) catalyzed in various aqueous reaction media at 25 °C[a]

Exp	Reaction medium	10^2[Surfactants] (M)	10^2[NaClO] (M)	Time (min)	Conv.[b] (%)	ee[b,c] (%)
1	Water/CH_2Cl_2	—	20.0	150	100	56
2	Water/CH_2Cl_2[d]	—	20.0	90	100	76[e]
3	AEO-14	5	3.8	1	55	17
				15	83	17
				30	83	17
4		5	5.9	1	54	29
				15	89	30
				45	90	34
5		5	11.1	1	61	42
				20	100	88
6		5	20.0	1	72	50
				15	100	91
7	CTACl	5	3.8	20	55	14
				45	67	14
				70	72	13
				20	95	30[d]
8		20	3.8	20	51	16
				45	70	14
				70	70	21
9		5	20.0	20	48	28
				90	100	44
10	*p*DoAO	1.3	3.8	20	67	14
				45	76	17
				150	78	16
11		5	3.8	1	34	31
				20	74	30
				45	76	32
12		1.3	20.0	1	44	28
				20	100	50

[a] In all experiments [alkene]=0.05 M, [salen]=2×10^{-3} M.

[b] Determined by GC on chiral column.

[c] The absolute configuration of the epoxide in excess was determined to be (1*R*,2*S*) by measuring the optical rotation.

[d] [4-PPNO]=2×10^{-2} M.

[e] For this reaction, under the same conditions, after 90 min a 83% ee value is reported by Jacobsen (Ref. 11).

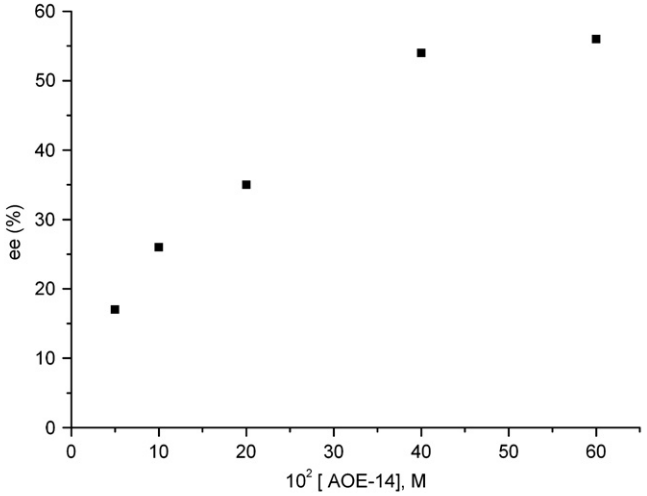

Figure 2. Effects of surfactant concentration variation on the ee values in the (salen)Mn(III) enantioselective epoxidation of 1,2-dihydronaphthalene in water at 25 °C ([alkene]=0.05 M, [salen]=2×10^{-3} M, [NaClO]=0.04 M).

Table 2
Effects of the reaction medium on the enantioselective epoxidation of styrene (salen)Mn(III) catalyzed at 25 °C[a]

Exp	Reaction medium	10^2[Surfactants] (M)	Time (min)	Conv.[b] (%)	Yield[b] (%)	ee[b,c] (%)
13	H_2O/CH_2Cl_2	—	300	100	94	8
14	H_2O/CH_2Cl_2[d]	—	60	90	95	43
15	AOE-14	2.5	15	100	93	7
16		5.0	15	100	95	16
17		10	15	100	91	23
18		20	15	100	95	34
19		40	15	100	98	41
20	*p*DoAO	1.3	20	100	94	21
21	CTACl	5.0	30	90	91	5
22		10	30	90	97	10

[a] In all experiments [alkene]=0.05 M, [salen]=2×10^{-3} M, [NaClO]=0.2 M.
[b] Determined by GC on chiral column.
[c] The absolute configuration of the epoxide in excess was determined to be (*R*) by comparison with an authentic sample.
[d] In the biphasic system with [4-PPNO]=2×10^{-2} M.

This behaviour seems to support the presence of the following equilibrium:

$$L + Cat \leftrightarrows L{-}Cat \qquad (1)$$

L=AOE-14; where the catalyst L−Cat, bearing the coligand L, is more efficient than the catalyst Cat without coligand. An increased concentration of L−Cat with higher amount of added L leads to better ee values.

In conclusion, AEO-14 seems to be a good choice to carry out epoxidation of 1,2-dihydronaphthalene in the conditions used, as it is able to make all reactants soluble in water, and to act as coligand towards the metal of the salen. This improves the selectivity and doesn't introduce any practical complication, such as gel formation (as *p*DoAO does) or emulsion formation during work-up, as often happens.[9b–d] One more interesting aspect deriving from AOE-14 use is the low ratio of surfactant/substrate 1/1 (both surfactant and substrate are 0.05 M) required to obtain the best results, which is at variance with many reports in the literature in which much higher ratios surfactant/substrate are employed. The use of low ratio surfactant/substrate is often not possible, as solubilization isn't high, and because the good results obtained with higher ratios are not always maintained with lower ratios.[9b,d] In fact, efforts are often made to reduce surfactant/substrate ratios, because their reduction implies a lower environmental impact of the reaction medium.[9,12]

The best reaction conditions found for 1,2-dihydronaphthalene (entry 6 in Table 1) were extended to other alkenes, and the results for the epoxidation of styrene and some *cis*-β-alkyl styrenes in various surfactant solutions, and also in the biphasic system, are reported in Tables 2 and 3. In these cases no kinetic resolution is observed, and data are collected at only one reaction time. For styrene, the results of the epoxidation reaction, obtained in aqueous solutions of the 2-amine oxide surfactant AEO-14 (entries 15–19, Table 2), both in terms of yield and ee values, are much better than those obtained in the biphasic medium without the coligand PPNO (entry 13) but similar to those observed in the biphasic medium in the presence of the coligand PPNO (entry 14).

Also in this case AOE-14 works as coligand, as shown by the increased ee values on increasing AOE-14 concentration. This is further supported by the scarce ee values obtained with a surfactant such as CTACl (entry 21), which is not able to bind the catalyst metal site, and whose behaviour is comparable to that observed in the biphasic system without addition of PPNO (entry 13).[13] A similar situation was found for the slightly more hydrophobic substrate *cis*-β-methyl styrene, i.e., reactions in the biphasic system in the presence of PPNO (entry 24) and in aqueous surfactant solutions give similar results when amine oxide surfactants are used, with almost complete reaction and a value of ee around 75% (Table 3, entries 25–27), even if the reactions now are slower in the aqueous system than in the biphasic medium.

Indeed, if cis/trans ratios are taken into consideration, the reaction in the AOE-14 medium is less selective than that in the biphasic system in the presence of PPNO (cis/trans ratios 4 versus 8, respectively). Analogous lower cis/trans ratios are observed with the other amine oxide AOPr-14 and *p*DoAO (Table 3, entries 26 and 27). According to Jacobsen,[15] epoxidation reaction occurs through the irreversible formation of a radical intermediate, which can collapse to yield the cis epoxide or can undergo rotation followed by collapse to give the isomer trans epoxide. The lower cis/trans ratios observed in surfactant media than in the biphasic system might find a rationale if we assume that the radical intermediate, bearing the surfactant bound to the metal, is longer lived than the

Table 3
Effects of the nature of the alkene on the enantioselective epoxidation (salen)Mn(III) catalyzed in various aqueous reaction media at 25 °C[a]

Exp	Substrate	Reaction medium	Time (min)	Conv.[b] (%)	Yield[c] (%)	ee[b,d] (%)	cis/trans[b] ratio
23	*cis*-β-methyl styrene	H_2O/CH_2Cl_2	1440	50	90	73	4
24		H_2O/CH_2Cl_2[e]	30	100	90	80	8
25		AOE-14 (0.2 M)	300	80	89	74	4
26		AOPr-14 (0.2 M)	360	71	95	73	3
27		*p*DoAO (0.013 M)	120	80	89	72	3
28	*cis*-β-ethyl-styrene	H_2O/CH_2Cl_2	480	56	62	71	3
29		H_2O/CH_2Cl_2[e]	60	90	89	83	11
30		AOE-14 (0.2 M)	180	88	80	79	2
31	*cis*-β-propyl-styrene	H_2O/CH_2Cl_2	480	58	75	74	5
32		H_2O/CH_2Cl_2[e]	180	95	82	86	10
33		AOE-14 (0.2 M)	180	90	75	80	4
34	*cis*-β-butyl-styrene	H_2O/CH_2Cl_2	480	45	83	72	3
35		H_2O/CH_2Cl_2[e]	60	90	85	89	7
36		AOE-14 (0.2 M)	180	85	90	75	4

[a] In all experiments [alkene]=0.05 M, [salen]=2×10^{-3} M, [NaClO]=0.2 M.
[b] Determined by GC on chiral columns.
[c] Yield by weight of the isolated product.
[d] Enantiomeric excess (ee) values are referred to the major cis epoxide (ee_{cis}). In the case of *cis*-β-methyl styrene the absolute configuration of the major cis epoxide was determined to be (1*R*,2*S*) by measuring the optical rotation.
[e] In the biphasic system with [4-PPNO]=2×10^{-2} M.

corresponding radical intermediate bearing the PPNO bound to the metal. However, higher reaction times and lower cis/trans ratios might be a price to pay to avoid the use of toxic, volatile and environmentally non-friendly dichloromethane. With the more hydrophobic *cis*-β-methyl styrene, the ratio surfactant/substrate is a bit higher (4) than in the case of 1,2-dihydronapthalene, but still very low, and in every case lower than that usually used in the literature.

Other alkenes of increasing hydrophobicity were investigated, and the results obtained in the biphasic systems and in AEO-14 media are reported in Table 3 (entries 28–36). There is no effect of the alkene hydrophobicity although, in principle, an increase of it could affect the akene–surfactant interaction and, maybe, the yield or the ee values. As in the case of *cis*-β-methyl styrene in the biphasic system, the addition of PPNO has a small effect on ee values but a more significant effect on the rate of reaction and on the cis/trans ratios. As was also observed previously with *cis*-β-methyl styrene, the use of AOE-14 determines lower cis/trans ratios with the other *cis*-β-alkyl styrenes. At any rate, the use of aqueous surfactant solutions as reaction media for the epoxidation of various styrenes gives results almost comparable to those obtained in the biphasic system with PPNO added, apart from the case of the most hydrophobic alkene, i.e., *cis*-β-butyl styrene, where the ee is 75% in aqueous surfactant and 89% in the biphasic system containing PPNO.

3. Conclusion

An aqueous reaction medium, based on surfactant solutions of diethyltetradecylamine *N*-oxide (AOE-14), has been developed for the enantioselective epoxidation of 1,2-dihydronaphthalene and various *cis*-β-alkyl styrenes with increasing hydrophobicity, using bleach as oxidant and the Jacobsen chiral (salen)Mn(III) as catalyst. The amine oxide surfactant AOE-14 carries out enantioselective epoxidation in water very well, because it is able to make all reactants soluble in water and to act as coligand towards the metal of the salen. Its use doesn't introduce any practical complication, such as emulsion formation, and leads to good yields (>75%) and to ee values ranging from 75% up to 91%. The used surfactant/alkene ratios are 1/1 or 4/1, lower than those generally used in the literature.[9] Results are much better than those obtained in the biphasic system H_2O/CH_2Cl_2, but comparable with those of the biphasic system H_2O/CH_2Cl_2 containing PPNO as coligand, except for a slower reaction rate for more hydrophobic *cis*-β-alkyl styrenes. The lower cis/trans ratios observed for *cis*-β-alkyl styrenes in aqueous AOE-14 than in the biphasic system with added PPNO are largely counterbalanced by the elimination of toxic solvents such as dichloromethane.

4. Experimental section

4.1. General methods and materials

NMR spectra were carried on a 500 MHz Varian Unity Inova spectrometer (^{1}H at 499.88 MHz, ^{13}C NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tunable 5 mm inverse detection probe (ID-PFG), and on a 200 MHz Bruker. The chemical shifts (ppm) were referenced to TMS (^{1}H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.0 ppm). ESI mass spectra were obtained by employing an ES-MS spectrometer equipped with an ion trap analyzer. GC–MS analyses of reaction mixtures were performed on a gas chromatograph (using an HP-1 dimethyl-polysiloxane 25 m capillary column) equipped with a MS computerized system. The absolute configuration of (1*R*,2*S*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene and (1*R*,2*S*)-1,2-epoxy-1-phenylpropane was determined by measuring the optical rotation with a polarimeter. 1-Phenyl-1-propyne, 1-phenyl-1-butyne, 1-phenyl-1-pentyne, 1-phenyl-1-hexyne, Lindlar catalyst, (1*R*,2*R*)-(+)-1,2-diphenylethylendiamine, 3,5-di-*tert*-butyl-salicylaldehyde, manganese(III) acetate dihydrate, 1,2-dihydronaphthalene, styrene, (*R*)-(+)-styrene oxide, (*S*)-(−)-styrene oxide, (1*R*,2*R*)-(+)-1,2-epoxy-1-phenylpropane, 3-chloperoxybenzoic acid, sodium hypoclorite and CTACl were commercially available reagent-grade materials.

4.2. Preparation of alkenes

cis-1-Phenyl-1-(propene, butene, pentene and hexene) were obtained from the corresponding commercial alkyne by hydrogenation with the Lindlar catalyst in cyclohexane according to the following procedure.[16] In a 100 mL three-necked flask, equipped with a stirring bar, containing a solution of alkyne (0.15 mol) in cyclohexane (50 mL) and the Lindlar catalyst (10%), H_2 was bubbled for 8 h at room temperature. The catalyst was filtered off and the cyclohexane was removed by distillation on a rotary evaporator. The residue was column chromatographed (SiO_2, eluent *n*-hexane) to afford *cis*-1-phenyl-1-propene (80% yield), *cis*-1-phenyl-1-butene (76% yield), *cis*-1-phenyl-1-pentene (78% yield) and *cis*-1-phenyl-1-hexene (82% yield), respectively. ^{1}H NMR spectra of all products correspond to those reported in the literature.[17]

4.3. Preparation of surfactants

All surfactants were prepared as reported previously.[18]

4.3.1. *Synthesis of diethyltetradecylamine N-oxide (AOE-14)*

In a 500 mL round-bottom flask diethyltetradecylamine (0.16 mol) and 35% hydrogen peroxide (0.50 mol) were dissolved in ethanol (200 mL), and the mixture was kept to reflux for 10 h. After cooling at room temperature, the mixture was treated with solid MnO_2 to destroy the excess hydrogen peroxide, filtered and evaporated to dryness to yield the desired *N*-oxide as a white solid (yield 95%). ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.88 (3H, t, CH_3), 1.33 (22H, m, CH_2), 1.45 (6H, t, $2CH_3$), 1,70–1.90 (2H, m, CH_2), 3.18 (2H, t, CH_3), 3.28 (4H, q, $2CH_2$).

4.3.2. *Synthesis of dipropyltetradecylamine N-oxide (AOPr-14)*

AOPr-14 was obtained following the same procedure adopted for AOE-14, starting from dipropyltetradecylamine (yield 90%). ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.88 (3H, t, CH_3), 0,95 (6H, t, $2CH_3$), 1.29 (22H, m, CH_2), 1.70–1.90 (6H, m, $4CH_2$), 3.13–3.01 (6H, m, $3CH_2$).[18]

4.3.3. *Synthesis of p-dodecyloxybenzyldimethylamine N-oxide (pDoAO)*

*p*DoAO was obtained following the procedure adopted for AOE-14, starting from *p*-dodecyloxybenzyldimethylamine (0.021 mol) and 35% H_2O_2 (0.063 mol) in ethanol (15 mL) in a 100 mL flask. After work up, the yellow oil obtained was treated 3–4 times with ethyl ether and evaporated until a white solid was obtained. The solid was dispersed in ethyl ether, sonicated, cooled at 0 °C, filtered, rinsed with cold ethyl ether and dried over P_2O_5 under vacuum (yield 90%). The ^{1}H NMR spectrum is identical to that already reported.[18]

4.4. Preparation of *p*-dodecyloxybenzyldimethylamine

p-Dodecyloxy benzylbromide (0.052 mol), prepared as already reported,[19] was dissolved in 60 mL ethanol/ethyl ether 1:1 and treated with a solution of $NHMe_2$ (0.234 mol) in ethanol under magnetic stirring at room temperature, and the reaction was carried on for 4 h. At the end of the reaction a 10% NaOH aqueous solution was added and, after extraction with ethyl ether, the organic phase was washed with water until neutrality and evaporated. The pale yellow oil obtained was separated from a fine white solid impurity by filtration on a short neutral alumina column by elution with petroleum ether. The ^{1}H NMR spectrum is identical to that already reported.[18]

4.5. Preparation of (1*R*,2*R*)-(*N*,*N'*)-bis(3,5-di-*tert*-butylsalicylaldehyde)-1,2-diphenylethylendiamino (salen)

The salen ligand was prepared according to the Jacobsen procedure.[2] ^{1}H NMR spectrum (CDCl$_3$, 500 MHz): δ=13.57 (s, 2H, OH) 8.39 (s, 2H, *CH*=N), 7.31 (d, 2H, *J*=2.5 Hz, ArH), 7.22–7.16 (m, 10H, ArH), 6.97 (d, 2H, *J*=2.5 Hz, ArH), 4.72 (s, 2H, Ph*CH*N), 1.42 (s, 18H, *t*-Bu), 1.22 (s, 18H, *t*-Bu). The epoxidation catalyst was prepared as follows: 0.62 mmol of $Mn(AcO)_3\cdot 2H_2O$ and 0.62 mmol of the salen ligand were dissolved in EtOH and the solution was allowed to stir at room temperature. When the reaction was complete (TLC, petroleum ether/CH_2Cl_2 4:1, v/v) (6 h), the mixture was concentrated in vacuum to give a residue, which was dissolved in CH_2Cl_2, filtered and concentrated to yield the Mn(III) catalyst quantitatively. (ESI-MS *m/z* 698 M$^+$).

4.6. Product analysis

Gas chromatographic analyses of the reaction mixtures were carried out on a gas chromatograph equipped with a flame ionization detector and program capability. The ee, yields and conversions values were determined employing the chiral column DMePeBETACDX (25 m×0.25 mm ID×0.25 μm film; MEGA) for styrene (column conditions: 100 °C (5 min) to 118 °C (1 min) at 3 °C/min), and for 1,2-dihydronaphthalene (isotherm 150 °C), the chiral column DMeTButiSililBETA (25 m×0.25 mm ID×0.25 μm film; MEGA) for *cis*-β-methyl styrene (column conditions: 50 °C (0 min) to 120 °C (1 min) at 2 °C/min), the chiral column DiAc-TBuSililBETA-ov 1701 (25 m×0.25 mm ID×0.25 μm film; MEGA) for *cis*-β-(ethyl, propyl, butyl)-styrene (column condition: 50 °C to 180 °C (1 min) at 2 °C/min). The injector and detector temperatures were maintained at 250 °C for all columns, *n*-decane was used as an internal standard throughout. In order to determine the absolute configuration of the major enantiomer cis epoxide, 1,2-epoxy-1,2,3,4-tetrahydronaphthalene and 1,2-epoxy-1-phenylpropane were isolated from the reaction mixture by preparative PLC (SiO_2) using cyclohexane/EtOAc (15:1, v/v) and cyclohexane, respectively, as reported.

4.7. Epoxidation reactions in surfactant solutions

In a typical run, olefin (0.1 mmol) was added to a stirred solution of surfactant (0.1–0.4 mmol) and catalyst (0.004 mmol) in distilled water (2 mL); the mixture, limpid, was kept in a round-bottom flask and maintained at 25 °C in a thermostatic bath; buffered bleach (0.4 mmol, buffered to pH=11.2 with 0.05 M Na_2HPO_4) was added at the end. After a certain reaction time, the internal standard was added to the reaction mixture, and the aqueous solution was extracted with Et_2O (2×5 mL). Combined organic extracts were dried over anhydrous $MgSO_4$, reduced to a small volume, and analyzed by GC as described above. The products in the organic phase were isolated by PLC (SiO_2, cyclohexane/EtOAc 15:1 for 1,2-epoxy-1,2,3,4-tetrahydronaphthalene and cyclohexane for 1,2-epoxy-1-phenylpropane, 1,2-epoxy-1-phenylbutane, 1,2-epoxy-1-phenylpentane, 1,2-epoxy-1-phenylhexane), weighted and characterized as reported previously.[20]

Epoxidation reactions in the biphasic water/dichloromethane system were carried out according to the procedure already reported.[20]

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References and notes

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