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Asymmetric Baeyer–Villiger oxidation with Co(Salen) and H_2O_2 in water: striking supramolecular micelles effect on catalysis

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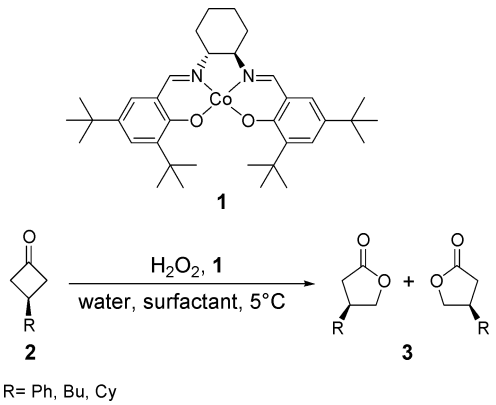
A micellar environment enables catalytic, diastereoselective and enantioselective Baeyer–Villiger oxidation of cyclobutanones (ee up to 90%) with H_2O_2 as oxidant using Co(Salen) catalyst 1, while the same catalytic system is inactive in organic solvents.

Nowadays catalysis, as the discipline devoted to the development of new species able to steer reactions activity and selectivity, has to face new challenges, including the ability to meet sustainability criteria which, once translated into chemical words, means the implementation of the twelve green chemistry principles.[1] Switching from chlorinated organic solvents to water[2] as reaction medium is a challenging task enabling avoidance of volatile toxic species, decreasing the overall E factor of the process[3] and increasing the selectivity thanks to the hydrophobic effect.[4] Despite limitations imparted by low solubility of organic substrates, synthesis and catalysis in water is a highly investigated field of research.[5,6]

Micellar catalysis represents a viable solution to solubilization problems; in fact, surfactant aggregation driven by the hydrophobic effect ensures the formation of apolar nanoenvironments where both substrates as well as catalysts can be efficiently dissolved and interact with high local concentrations. Moreover, this strategy allows the direct employment of catalysts developed for organic media without the need of chemical modification with water soluble tags that often negatively alter the performance of the catalysts.[7] Running asymmetric catalytic reactions in micelles often turns out to have positive effects on enantioselectivity due to stronger substrate–catalyst interactions arising once embedded in the palisade provided by the alignment of the alkyl chains of surfactant.[8,9a] This can be reasonably compared to performing chemical reactions in liquid crystals,[9,10] where enantioselective reactions were recently demonstrated to occur with higher enantioselectivity due to the highly anisotropically ordered medium.[11]

Oxidation reactions with hydrogen peroxide are intrinsically predisposed to be extended in pure water, and recent investigations underlined the positive effect of micellar catalysis in asymmetric oxidation reactions catalyzed by chiral Pt^{II} complexes.[12] In 2001 Katsuki reported Co^{III}(Salen) asymmetric Baeyer–Villiger (BV) oxidation of *meso* cyclobutanones[13] observing that (i) atropoisomeric Salen ligands bearing four carbon atom between N donors led to much more active catalysts compared to ligands derived by *trans*-1,2-diaminocyclohexane, (ii) electron poor ligands provided active and enantioselective catalysts while electron rich ones did not induce asymmetry in the lactones and (iii) polar organic solvents increased both catalytic activity and ee's.

Herein we report the remarkable effect induced by the employment of different surfactants in the asymmetric BV oxidation reaction[14] of four membered ring ketones with hydrogen peroxide as terminal oxidant in water mediated by Co(Salen) **1** catalyst bearing an electron rich chiral ligand characterized by a small spacer between N donors, as reported in Scheme 1.



Scheme 1 Enantioselective BV oxidation of cyclic ketones with H_2O_2 mediated by Co(Salen) catalyst **1** in water with surfactants.

As expected, on the basis of Katsuki's findings,[13] catalyst **1** was almost inactive and non enantioselective in the BV oxidation of *meso* cyclobutanones in chlorinated solvents, as reported in Table 1. Similar results were also obtained in methanol. Surprisingly, simply switching to water with surfactants as the reaction medium enabled the formation of the corresponding lactones, albeit in low yields but with a certain degree of enantioselectivity. In particular, SDS turned out to be the best surfactant for *meso* substrates.

The enantioselective induction in BV reactions arises from the control of which C atom next to the carbonyl unit of the Criegee intermediate migrates to the oxygen. Small cyclobutanones are usually more reactive but less enantioselective compared to larger cyclic ketones.[12c] While **1** turned out to be inactive with *meso* cyclohexanones under micellar conditions, it performed much better with asymmetric chiral cyclobutanones.

In Table 2 are reported the results for the BV oxidation of (±)-**4** where two lactone products are possible, namely normal lactone **5** (NL) when migration involves the most substituted

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Table 1 Asymmetric BV oxidation of *meso* 3-substituted-cyclobutanones in water with H_2O_2 catalyzed by **1** in the presence of different surfactants

#	R	Medium	Yield (%)[a]	ee (%)[b]
1	Ph	CH_2Cl_2	2	0
2	Ph	H_2O/SDS[c]	20	13
3	Ph	H_2O/TritonX100[d]	12	13
4	Ph	H_2O/TritonX114[e]	15	11
5	Bu	CH_2Cl_2	1	0
6	Bu	H_2O/SDS[c]	12	26
7	Bu	H_2O/TritonX100[d]	6	20
8	Bu	H_2O/TritonX114[e]	5	15
9	Cy	CH_2Cl_2	2	0
10	Cy	H_2O/SDS[c]	24	14[f]
11	Cy	H_2O/TritonX100[d]	12	3[f]
12	Cy	H_2O/TritonX114[e]	2	4[f]

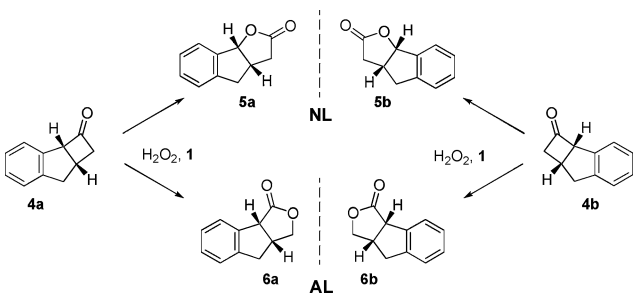
Experimental conditions: $[Sub]_0 = 0.5$ M; $[H_2O_2] = 0.5$ M; [**1**] = 1% mol, H_2O: 0.5 mL, $T = 5$ °C, 24 h.[a] Yield determined by GC analysis on HP-5 column. [b] ee determined on chiral GC column Lipodex B. [c] Sodium dodecylsulfate (75 mM). [d] Polyoxyethylene(10)isooctylphenyl ether (150 mM). [e] Polyoxyethylene(8)isooctyl cyclohexyl ether (150 mM). [f] ee determined on chiral GC column ASTEC γ-TA.

Table 2 Asymmetric BV oxidation of **4** in water with H_2O_2 catalyzed by **1** in the presence of different surfactants

#	Medium	Yield (%)[a]	dr **5**/**6**[a]	ee **5** (%)[b]	ee **6** (%)[b]
1	H_2O/SDS[c]	24	37	16	—
2	H_2O/SDBS[d]	42	13	6	20
3	H_2O/TritonX100[e]	44	31	22	—
4	H_2O/TritonX114[f]	30	28	3	—
5	H_2O/SPAN60[g]	26	11	0	46

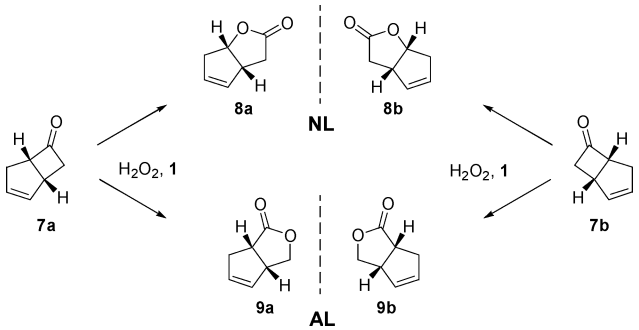
Experimental conditions: $[Sub]_0 = 0.5$ M; $[H_2O_2] = 0.5$ M; [**1**] = 1% mol, H_2O: 0.5 mL, $T = 5$ °C, 24 h.[a] Yield and dr determined by GC analysis on HP-5 column. [b] ee determined on chiral HPLC using Chiralcel OD-H column. ee% of **6** not reported if dr > 15. [c] Sodium dodecylsulfate (75 mM). [d] Sodium dodecylbenzensulfonate (75 mM). [e] X100 Polyoxyethylene(10)isooctylphenyl ether (150 mM). [f] X114 Polyoxyethylene(8)isooctyl cyclohexyl ether (150 mM). [g] Sorbitan monostearate (50 mM).

C atom, and abnormal lactone **6** (AL) when the less substituted C atom is the migrating one. Overall the reaction is a double parallel kinetic resolution BV reaction, and the concomitant competition for NL and AL allows high ee's of products also at high conversions (Scheme 2). Micellar conditions in this case allowed catalyst **1** to oxidize the chiral substrate with good diastereoselectivity and with enantioselective induction up to 46% when the neutral surfactant SPAN60 was employed.



Scheme 2 Enantioselective BV oxidation of chiral racemic cyclobutanone (±)-1,2A,7,7A-tetrahydro-cyclobuta(a)inden-2-one **4** with H_2O_2 mediated by Co(Salen) catalyst **1** in water with surfactants.

Yields were limited by the low solubility of the apolar substrate in the medium, in fact by switching to a more polar substrate like **7** bearing the same cyclobutanone moiety, much better results were observed (Scheme 3). Under identical experimental conditions, substrate **7** turned out to be much more reactive leading to formation of the corresponding lactones in moderate to good yields, with rather high diastereoselectivity and moderate to good ee's.



Scheme 3 Enantioselective BV oxidation of (±)-*cis*-bicyclo(3.2.0)hept-2-en-6-one **7** with H_2O_2 mediated by Co(Salen) catalyst **1** in water with surfactants.

It is worth noting that a remarkable surfactant effect was observed comparing anionic with neutral surfactants, in fact the latter enabled much higher preference for the NL with dr **8**/**9** up to 86 : 1. This suggested the use of half the equivalent of oxidant to ensure high ee of product **8**.

In Table 3 (entries 7–14) are reported the results of these experiments together with the effect of surfactant concentration. While for TritonX100 the increase of concentration favored catalytic activity and ee but decreased slightly the dr, with TritonX114 the lower concentration employed was the best, ensuring a dr up to 70 : 1 and ee up to 90%.

In conclusion, we have demonstrated that it is possible to teach old catalysts new tricks; in fact, commercially available chiral

Table 3 Asymmetric BV oxidation of **7** in water with H_2O_2 catalyzed by **1** in the presence of different surfactants

#	Medium	Yield (%)[a]	dr **8**/**9**[a]	ee **8** (%)[b]	ee **9** (%)[b]
1	CH_2Cl_2	15	34	0	—
2	H_2O/SDS (75 mM)	75	14	4	45
3	H_2O/SDBS (75 mM)	83	15	8	—
4	H_2O/CTABr[c] (75 mM)	68	52	15	—
5	H_2O/TritonX100 (150 mM)	65	86	45	—
6	H_2O/TritonX114 (150 mM)	81	73	68	—
7	H_2O/SDS (75 mM)	60[d]	17	13	—
8	H_2O/SDBS (75 mM)	52[d]	10	6	13
9	H_2O/TritonX100 (75 mM)	48[d]	74	51	—
10	H_2O/TritonX100 (125 mM)	54[d]	58	52	—
11	H_2O/TritonX100 (190 mM)	68[d]	56	60	—
12	H_2O/TritonX114 (75 mM)	60[d]	70	90	—
13	H_2O/TritonX114 (125 mM)	98[d]	41	74	—
14	H_2O/TritonX114 (190 mM)	80[d]	55	88	—

Experimental conditions: $[Sub]_0 = 0.5$ M; $[H_2O_2] = 0.5$ M; [**1**] = 1% mol, H_2O: 0.5 mL, $T = 5$ °C, 24 h.[a] Yield and dr determined by GC analysis on HP-5 column. [b] ee determined on chiral HPLC using Chiralcel OD-H column, absolute configuration not assigned, ee% of **9** not reported if dr > 15. [c] Hexadecyltrimethyl ammonium bromide. [d] $[H_2O_2] = 0.25$ M.

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Co(Salen) **1** complex is almost inactive and non enantioselective in the BV oxidation of cyclobutanones in organic media but, once dissolved in water with the aid of surfactants, moderate catalytic activity, high diastereoselectivity and enantioselectivity were generally observed, along with excellent results with one chiral substrate. Micellar media represent viable environments for enantioselective reactions; surfactant type and concentration being further variables deserving optimization since each substrate/catalyst/surfactant combination is a unique catalytic system.[12c] Despite this extra work, favorable effects on catalytic activity and selectivity are often possible.

Experimental

Reagents and materials

General. The chiral catalyst (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino-cobalt(II) **1** and cyclobutanone (±)-*cis*-bicyclo[3.2.0]hept-2-en-6-one **7**, hydrogen peroxide (35%) and all surfactants employed are all commercial products (Aldrich) and were used as received. *meso* Cyclobutanones **2** and (±)-1,2A,7,7A-tetrahydro-cyclobuta(a)inden-2-one **4** were prepared following procedures reported in the literature.[15] Lactone products were confirmed by ^{1}H NMR analysis in comparison with reported assignments.[12,14] GLC measurements were taken on a Hewlett-Packard 5890A. ^{1}H NMR spectra were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 MHz, δ values in ppm are relative to $SiMe_4$. GLC measurement were taken on a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector (carrier gas He). All reactions progress were monitored by GC.

Catalytic studies. General procedure for asymmetric BV oxidation of cyclobutanones with H_2O_2 catalyzed by **1**: in a vial equipped with a screw capped septum the cyclic ketones (0.25 mmol) were dissolved in water (0.5 mL) with the aid of the proper amount of surfactant. Complex **1** was added (1% mol) to this solution and the vial was thermostatted at 5 °C. 35% H_2O_2 (1 eq. or 0.5 eq., checked iodometrically prior to use) was then added in one portion and the resulting mixture was vigorously stirred. After 24 h reaction time 2 ml of H_2O and 2 ml of AcOEt were added, the mixture stirred for 10 min, followed by phase separation. The organic layer was concentrated under vacuum, and yield and dr were determined by GC analysis on a HP-5 column 1.0 mL min^{-1} carrier He.

Enantiomeric excess determination. Enantiomeric excess of five membered ring lactones derived by *meso* cyclobutanones was analyzed by GC: 4-phenyldihydrofuran-2(3*H*)-one **3a**: chiral GC column Lipodex B, 170 °C isotherm analysis, carrier He 1.0 mL min^{-1}, t_R = 24.8 min, 25.5 min; 4-butyldihydrofuran-2(3*H*)-one **3b**: chiral GC column ASTEC γ-TA, He 1.0 mL min^{-1}, 120 °C X 5 min, 5 °C min^{-1} up to 200 °C, t_R = 19.3 min, 19.6 min; 4-cyclohexyldihydrofuran-2(3*H*)-one **3c**: chiral GC column Lipodex B, 170 °C isotherm analysis, carrier He 1.0 mL min^{-1}, t_R = 25.6 min, 26.6 min. Enantiomeric excess of five membered ring lactones from chiral cyclobutanones was determined after preparative TLC chromatography with hexane–AcOEt 4 : 6 on the AcOEt extracted organic phase. **5** and **6**: chiral HPLC analysis on a Chiralcel OD-H column, hexane/*i*PrOH 99/1 from 0 to 15 min, then up to hexane/*i*PrOH 96.5/3.5 at 20 min with constant composition until 60 min, flow 1.2 mL min^{-1}, (+)-(1*R*,5*S*)-**5a** t_R=29.1 min, (−)-(1*S*,5*R*)-**5b** t_R = 34.3 min; (−)-(1*R*,5*R*)-**6a** t_R = 28.0 min, (+)-(1*S*,5*S*)-**6b** t_R = 31.1 min. **8** and **9**: chiral HPLC analysis on a Chiralcel OD-H column, hexane/*i*PrOH 99/1 from 0 to 30 min, then up to hexane/*i*PrOH 98.5/1.5 at 35 min with constant composition until 60 min, flow 1.0 mL min^{-1}, (+)-(1*R*,5*S*)-**8a** t_R=23.8 min, (−)-(1*S*,5*R*)-**8b** t_R = 26.4 min; (−)-(1*R*,5*R*)-**9a** t_R = 21.7 min, (+)-(1*S*,5*S*)-**9b** t_R=22.4 min.

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