Pergamon

Tetrahedron: Asymmetry Vol. 6, No. 1, pp. 147-156, 1995
Elsevier Science Ltd
Printed in Great Britain
0957-4166/95 $9.50+0.00

0957-4166(94)00370-X

Enantioselective Allylic Oxidation in the Presence of the Cu(I)/Cu(II)-Proline Catalytic System

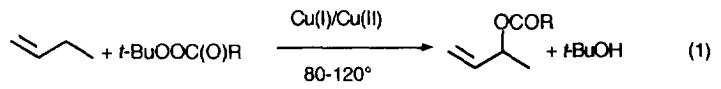
Aviva Levina[#] and Jacques Muzart*

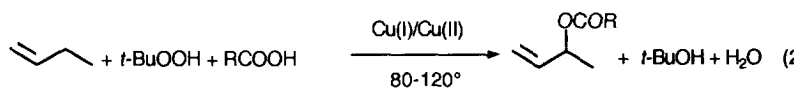
Unité "Réarrangements Thermiques et Photochimiques"Associée au CNRS
Université de Reims Champagne-Ardenne, B.P. 347, 51062 Reims Cedex, France.

Abstract: Optically active allylic esters have been obtained with *ee*'s up to 54% by acyloxylation of the corresponding alkenes with *t*-BuOOC(O)Ph or *t*-BuOOH + RCOOH in the presence of catalytic amounts of copper compounds and homochiral aminoacids ((*S*)- and (*R*)-prolines and their structural analogs). The influence of the nature of the alkene and acyl groups, the oxidant, solvent and chiral promotor on the enantioselectivity has been studied. A key role of CuL_2* (L* = aminoacid) in the enantioselective catalysis is suspected.

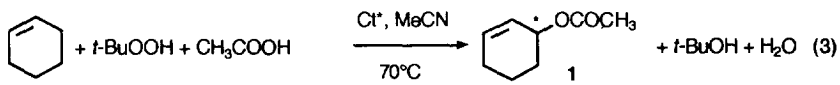
INTRODUCTION

The introduction of a stereogenic center into an achiral compound remains often a fastidious objective despite the large amount of work devoted to this subject. As part of current research programmes targeted towards metal-catalyzed oxidation reactions on the one hand[1] and the formation of stereogenic centers on the other,[2] we have been interested in the asymmetric allylic oxidation of alkenes. Indeed, chiral allylic alcohols have an important role as buiding blocks in the synthesis of biologically active compounds.[3] Possible approaches to such oxidations are based on the well known Kharash-Sosnovsky reactions: [4]





The allylic esters thus obtained in the processes (1) and (2) can be easily converted to the corresponding allylic alcohols by alkaline hydrolysis or by reduction with $LiAlH_4$. The first attempts to use chiral auxiliaries to obtain optically active products in processes (1)[5a] and (2)[5b] led to low enantioselectivities (*ee*'s up to 15%). More recently,[5c] (*S*)-2-cyclohexenyl-1-acetate **1** was obtained with an *ee* up to 30% using catalytic amounts of (*S*)-aminoacids as chiral promotors (process (3)):



Ct*: $Cu(OOCCH_3)_2$ or Cu_2O + Aminoacid*

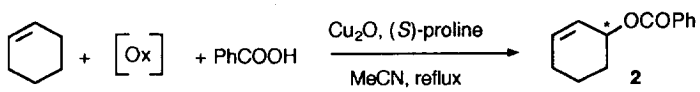
[#]On leave from Riga Technical University, Latvia.

In this last paper, the best enantioselectivity was achieved in the presence of (*S*)-proline. Despite of the rather low *ee*'s, process (3) is interesting because it requires only inexpensive commercial reagents and is simple to carry out. In the current work the scope and limitations of enantioselective variants of processes (1) and (2) have been studied in detail.

RESULTS AND DISCUSSION

Optimization of the model reaction

In the first stage of the work, optimization of reaction conditions has been undertaken with the aim of maximasing *ee*'s. We chose the oxidation of cyclohexene to 2-cyclohexenyl-1-benzoate **2** (process (4)) as a



[Ox] : 70% aqueous *t*-BuOOH or *t*-BuOOC(O)Ph)

model reaction since (i) the acyloxylations (1) and (2) of cyclohexene were more selective than for other alkenes, by-products being practically not formed;[4] (ii) the use of Cu_2O + *S*-proline as chiral catalyst and MeCN as solvent allowed us to achieve maximum *ee* in the process (3);[5c] (iii) the benzoate **2** is more convenient than the acetate **1** for purification by flash-chromatography, because of its low volatility and its ability to be detected on TLC by UV-light; (iv) anhydrous *t*-BuOOH solutions in organic solvents have been previously employed,[5c] but we havesubsequently observed that the use of commercial 70% aqueous *t*-BuOOH did not led to a decrease in the chemical yield or *ee* of **2**; (v) although it has been reported[4] that the processes (1) and (2) were inhibited by oxygen and therefore have to be carried out under an inert atmosphere, we have observed that at reflux of acetonitrile, results under argon atmosphere were similar to those achieved without any particular precaution.

For experimental optimization, both the variation of several parameters and the Sequential Simplex Method[6] have been used. The studied range of reaction conditions is shown in Table 1. The optical rotation of **2** was used as the main response function but chemical yields and reaction times were also taken into consideration.

Table 1. Range of experimental conditions used for the optimization of the process (4)

Parameter	Min.	Max.
Cyclohexene, mmol	5.0	80
t-BuOOH or *t*-BuOOC(O)Ph, mmol	1.0	8.0
PhCOOH[a], mmol	3.0	10.0
Cu_2O, mmol	0.06	0.20
S-proline, mmol	0.10	0.60
MeCN, mmol	0	220
Reaction time[b], h	1	10

[a]Some of the experiments with *t*-BuOOC(O)Ph have been done in the absence of PhCOOH. [b]The reaction was followed by iodometric titration and stopped when conversion of oxidant was ≥ 95%.

The optimization results (Fig. 1, curve 1a) show that the optical activity of **2** is determined mainly by the ratio "*S*-proline/Cu(I)" achieving the maximum value for 2. A small increase in the enantioselectivity was also observed when the ratio "substrate/oxidant" was increased (curve 1b). The chemical yield of **2** (related to the amount of *t*-BuOOH or *t*-BuOOC(O)Ph) was low (20-50%) in most experiments. It was found rather surprisingly that the

yield of **2** can be improved by increasing the initial amount of substrate both with and without decreasing the amount of MeCN (curve 2b). Nevertheless, a lower yield and *ee* were observed in the absence of MeCN. The increase of the amount of (*S*)-proline led to a drop in the yield of **2** (curve 2a). These facts allow us to deduce that the rather low yield of **2** in the process (4) is connected with the parallel decomposition of peroxide rather than with the formation of by-products. It seems that the decomposition of the peroxide is catalysed by the copper-proline complex and is greatly supressed by excesses of cyclohexene.

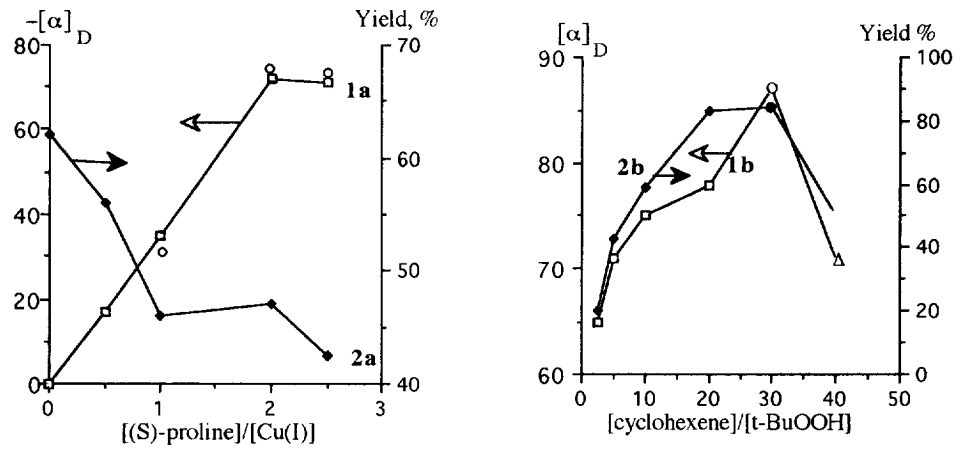


Fig. 1. Influence of reaction conditions on the optical purity (curves 1) and yield of product (curves 2) in process (4). (a) cyclohexene: 10 mmol, *t*-BuOOH: 2 mmol, PhCOOH: 5 mmol, Cu_2O: 0.1mmol (□,♦) or 0.2 mmol (o), MeCN: 96 mmol, 82°C. (b) *t*-BuOOH: 2 mmol, PhCOOH: 5 mmol, Cu_2O: 0.1 mmol, (*S*)-proline: 0.5 mmol, without solvent (Δ, ▲) or with MeCN: 150 mmol (□,♦) or 38 mmol (o,●), 82°C.

As a conclusion for the optimization experiments, the best result (84% yield of **2**, $[\alpha]_D$= -87, which corresponds to 48% *ee* from the data of NMR in the presence of $Eu(hfc)_3$) has been achieved under the following conditions: 60 mmol of cyclohexene, 5.0 mmol of PhCOOH, 2.0 mmol of *t*-BuOOH, 0.1 mmol of Cu_2O, 0.5 mmol of (*S*)-proline, 38 mmol of MeCN, t = 82°C, reaction time: 4 h. However, these conditions, which require a great excess of alkene, cannot be recommended for more expensive or difficultly-available substrates. Therefore "model conditions" (Table 2) based on the optimization results, have been

Table 2. "Model conditions" used for the experiments with variation of substrate, RCOOH, chiral ligand and solvent.

Conditions	**A**	**B**
Substrate	10.0 mmol	10.0 mmol
Reagent	**A1**: 2.0 mmol *t*-BuOOC(O)Ph + 3.0 mmol PhCOOH **A2**: 2.0 mmol *t*-BuOOH + 5.0 mmol RCOOH	4.0 mmol *t*-BuOOC(O)Ph + 3.0 mmol PhCOOH
Catalyst	0.1 mmol Cu_2O + 0.5 mmol aminoacid*	0.2 mmol Cu_2O + 1.0 mmol aminoacid*
Solvent	5.0 ml	5.0 ml
Temperature	Reflux of solvent [a]	40°C
Atmosphere	Air	Ar

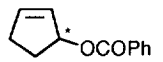
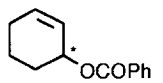
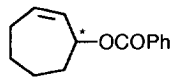
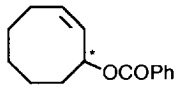
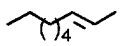
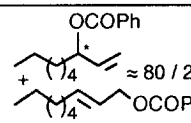
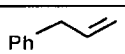
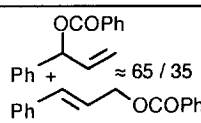
[a]in the case of sulfolane (b.p.: 283°C) the reactions were carried out at 80°C under an Ar atmosphere.

proposed for further work.

Use of various substrates

The results of application of the conditions of process (4) for the oxidation of various alkenes are enumerated in Table 3. The data of Table 3 show the strong tendency of enantioselectivities to decrease when the size of the alkene molecule was increased (runs 1, 2, 3a, 4a and 5a).

Table 3. Oxidation of various alkenes in the process (4)

Run	Substrate	Conditions[a]	Solvent	Time h	Product	Yield %[b]	$[\alpha]_D$ in $CHCl_3$	*ee* %[c] (*S*)[d]
1		B	MeCN	24[e]		39	-103	54
2		B	MeCN	24[e]		45	-70	39
3 a		A1	MeCN	2.0[f]		59	-67	37
3 b		A1	PhH	4.0[f]		59	-81	45
4 a		A1	MeCN	2.0[f]		27	-10.6	23
4 b		A1	PhH	5.0[f]		63	-1.3	4
5 a		A1	MeCN	5.0[f]		32	+3.1	4
5 b		A1	PhH	9.0[f]		34	+0.4	0.5
6 a		A1	MeCN	2.0[f]		23[g]	-2.0[g]	9
6 b		A1	PhH	5.0[f]		33[g]	-0.5[g]	2
7 a		A1	MeCN	5.5[f]		77[g]	0[g]	0
7 b		A1	PhH	2.0[f]		38[g]	0[g]	0

[a]see Table 2, chiral promotor: (*S*)-proline. [b]Isolated yield calculated on the reacted amount of *t*-BuOOC(O)Ph. [c]Determined by NMR in the presence of $Eu(hfc)_3$. [d]Determined by hydrolysis of esters and comparison of optical rotations of the alcohols obtained with literature data.[3,7] [e]Conversion of oxidant: 50%. [f]Conversion of oxidant ≥ 95%. [g]Data for the mixture of esters.

Cyclopentene (run 1) was oxidized at 40°C because of its low boiling temperature (44°C). In this case, a satisfactory yield of product can be achieved only with doubled amounts of catalyst and oxidant (conditions B in Table 2; very low yields were obtained under A conditions). The relatively high *ee* observed in run 1 is not connected with a decrease of the reaction rate, because the oxidation of cyclohexene at both 40 and 82°C afforded **2** with similar *ee*'s (runs 2 and 3a). For the open-chain alkenes, 1-octene (runs 6) and allylbenzene (runs 7), and in agreement with the literature data,[4] a mixture of two esters was obtained, only one of them being potentially

optically active. However, the chiral oxidation product of allylbenzene, unlike that of 1-octene, did not show any optical activity.

Variation of the solvent

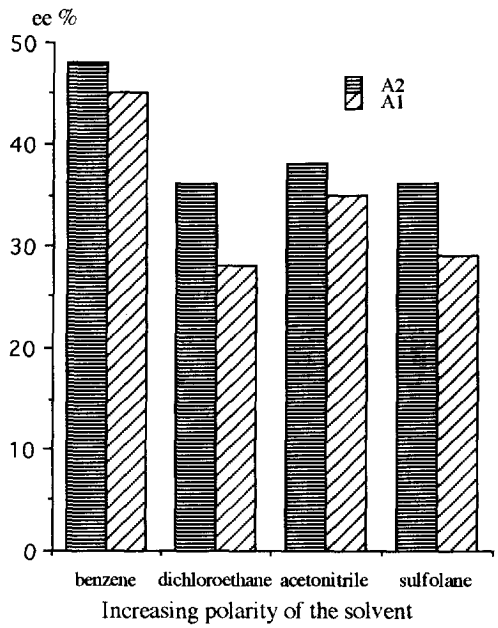
Ambiguous results have been obtained using benzene as solvent instead of acetonitrile in the process (4): *ee* is increased in the case of cyclohexene (run 3b in Table 3) and considerably decreased for the other alkenes (runs 4b, 5b, 6b). The chemical yield of ester is usually higher in benzene than in acetonitrile, except in the case of allylbenzene (run 7b).

The influence of the nature of the solvent on the enantioselectivity in the process (4) has been studied in more detail using cyclohexene as substrate. The number of useful solvents is very limited because they have to be (i) aprotic, (ii) non-oxidizable, (iii) with suitable boiling temperature, (iv) sufficiently polar to dissolve the components of the catalytic system.

Besides acetonitrile and benzene, 1,2-dichloroethane and sulfolane appeared to correspond to such conditions. The results of experiments with different solvents are shown in Fig 2. The solvents are shown on the X-axis according to their polarity which is the most common empiric characteristic of solvent properties (we followed the quantitative description of polarity proposed by Carlson et al.[6]).

Data of Fig. 2 show the absence of any correlation between solvent polarity and enantioselectivity of process (4). Nevertheless, similar dependences were observed using either *t*-BuOOC(O)Ph (conditions A1) or *t*-BuOOH (conditions A2) as oxidants.

Fig. 2. Enantioselectivity of process (4) in different solvents. Substrate: cyclohexene, chiral promotor: (*S*)-proline. A1 and A2 (R = Ph) conditions (see Table 2).

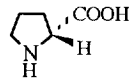
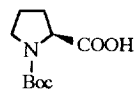
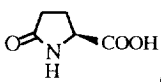
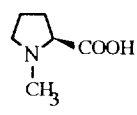
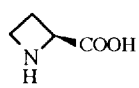
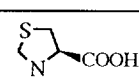
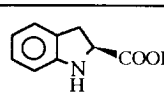
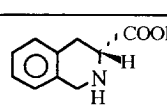
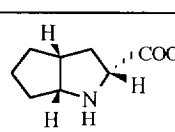
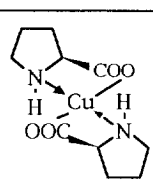


Variation of the chiral promotor

Various structural analogs of proline were tested as potential chiral promotors in the reaction (4) (Table 4). (*R*)-**2** can be obtained with the same enantioselectivity as (*S*)-**2** in using (*R*)-proline instead of (*S*)-proline (run 1, for comparison see run 3a in Table 3). In other cases, the conformity between absolute configurations of the chiral promotor and product was not observed (runs 8 and 9). Surprisingly, excess of (*R*)-**2** was obtained using (*S*)-

methylproline as chiral promotor (run 4). From all tested substances, (*S*)- and (*R*)-prolines allow us to achieve the best *ee*'s of **2** in the process (4).

Table 4. Oxidation of cyclohexene using various chiral promotors under the process (4) conditions[a]

Run	Aminoacid	Time h[b]	Yield of **2**[c] %	$[\alpha]_D$ in $CHCl_3$	*ee* %,[d] (abs. config.)
1	 (*R*)	2.0	62	+66	36 (*R*)
2	 (*S*)	4.0	62	0	0
3	 (*S*)	6.5	55	0	0
4	 (*S*)	4.0	62	+27	15 (*R*)
5	 (*S*)	2.0	70	-49	27 (*S*)
6	 (*R*)	1.0	65	-6.8	< 5 (*S*)
7	 (*S*)	3.0	52	-5.5	< 5 (*S*)
8	 (*R*)	10[e]	80	-10.3	5.5 (*S*)
9	 (*R*)	4.0	60	-9.1	5.0 (*S*)
10[f]	 (*S*)	2.0[g]	71	-69	38 (*S*)

[a]Conditions A1 from Table 2, solvent: MeCN. [b]Conversion of *t*-BuOOC(O)Ph ≥ 95%. [c]Isolated yield (estimated to reacted amount of *t*-BuOOC(O)Ph). [d]See notes (c and d) in Table 3. [e]Conversion of *t*-BuOOC(O)Ph: 17%. [f]0.2 mmol di-((*S*)-prolinato)Cu(II) in the absence of Cu_2O. [g]Conversion of *t*-BuOOC(O)Ph: 50%.

Structure of chiral catalyst

The green colour of the reaction mixture (λ_{max}= 690 nm) for the non-enantioselective processes (1) and (2) has been related to the formation of Cu(II) acylates.[9] In contrast, we have observed a deep blue coloration of the reaction mixture (λ_{max} = 610 nm) for the process (4) carried out in the presence of proline or its analogs. This color change evokes the formation of stable CuL_2* chelates (L*:aminoacid).[10] The strong dependence between the blue color of reaction mixtures and the formation of optically active products was shown for the process (4). The use of N-Boc-(*S*)-proline or (*S*)-pyroglutamic acid as chiral auxiliaries (runs 2 and 3 in Table 4) has led to green-coloured reaction mixtures (λ_{max}= 690 nm) and to racemic products. Obviously, these two aminoacids are unable to form chelates with Cu(II) because of the withdrawing electron pair fixed to the nitrogen atom.
When allylbenzene was oxidized in the presence of (*S*)-proline (run 7 in Table 3), the reaction mixture was brown-colored (λ_{max} < 400 nm). In this case, we suppose a strong complexation between allylbenzene or its oxidation products and Cu(II), which lead to displacement of the chiral auxillary from the reaction sphere.
From the data described above, the formation of CuL_2* complex can be assumed to be the reason for enantioselectivity in the process (4).[11] The following observations are in agreement with this assumption: (i) the maximum enantioselectivity was achieved with the ratio (*S*)-proline/Cu(I) = 2 independently of the total amounts of Cu and aminoacid (see Fig. 1), (ii) the use of di-(*S*-prolinato)-Cu(II) as a chiral calalyst instead of the Cu_2O/(*S*)-proline mixture led to the same enantioselectivity (run 10 in Table 4).

Variation of the acyl group

Since only *t*-BuOOC(O)Ph and *t*-BuOOC(O)Me are commercially available, only allylic benzoates and acetates have been usually obtained in process (1).[4] On the contrary, very different carboxylic acids can be used in process (2). Thus, an additional degree of freedom appears for the enantioselective variant of the process (2) in comparison with (1). One can suppose that the modification of R in the process (2) will lead to differences in the transition state geometries and hence to different enantioselectivities. The results of experiments with various cyclohexene/ *t*-BuOOH/RCOOH systems are summarized in Table 5. These data do not show any clear dependence between the enantioselectivity and the nature of R, except a weak increase in *ee* for aliphatic acids (runs 3-6) relatively to aromatic ones (runs 7-10). The esters of the strongest carboxylic acids cannot be obtained under the present reaction conditions (runs 1, 2).

Table 5. Variation of RCOOH in the process (4).[a]

Run	R	Time h[b]	Yield of ester, % [c]	$[\alpha]_D$ in $CHCl_3$	*ee* % (*S*)[d]
1	CF_3-	3.0	0[e]	-	-
2	CCl_3-	5.0	0[e]	-	-
3	$ClCH_2$-	5.0	43	-62	38
4	CH_3-	7.0	44	-57	41
5	$(CH_3)_3C$-	18	6.5	-51	52
6	*c*-C_6H_{11}-	30	37	-50	43
7	Ph-	9.0	36	-71	39
8[f]	Ph-	5.0	53	-56	31
9		20[g]	38,5	-32	32
10		10	21	-26	25

[a]Conditions A2/Table 2 with cyclohexene in MeCN. [b]*t*-BuOOH conversion ≥90%. [c]Isolated yield estimated from reacted *t*-BuOOH. [d]See notes (c) and (d) in Table 3. [e]Unidentified products are formed. [f]98% $PhCMe_2OOH$ is used instead of *t*-BuOOH. [g]*t*-BuOOH conversion: 17%

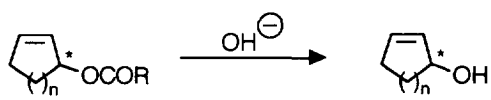
Variation of the oxidant

For the conversion of cyclohexene to (*S*)-2-cyclohexenyl-1-benzoate in the presence of (*S*)-proline as chiral promotor and MeCN as solvent, the enantioselectivity slightly decreases using the following range of oxidants: *tert*-butylhydroperoxide ≈*tert*-butylperbenzoate > cumylhydroperoxide (see run 3a in Table 3 and runs 7, 8 in Table 5).

Hydrolysis of opticaly active allylic esters

Alkaline hydrolysis (0.4 M KOH solution in MeOH) was used as method to obtain corresponding allylic alcohols from allylic esters. Typical results are shown in Table 6. Although not optimized, this method appears to be useful independently of the nature of the alkene and acyl groups. The *ee*'s for allylic alcohols obtained (calculated from previously reported $[\alpha]_D$)[3,7,12] are in good agreement with those of the corresponding esters determined by NMR in the presence of $Eu(hfc)_3$.

Table 6.



Run	Ester n	R	$[\alpha]_D$ in $CHCl_3$	*ee*[a]	Conditions of hydrolysis[b]	Alcohol Yield %[c]	$[\alpha]_D$ in $CHCl_3$	*ee*[d]
1	2	Ph	-49	27 (*S*)	3 h at 20°C or 12 h at 5°C	58	-28	21 (*S*)
2	2	Ph	+66	36 (*R*)	12 h at 5°C	50	+38	29 (*R*)
3	2	CH_2Cl	-62	38 (*S*)	10 min at 20°C	50	-43	33 (*S*)
4	1	Ph	-103	54 (*S*)	3h at 20°C	30	-54	46 (*S*)
5	3	Ph	-10.6	23 (*S*)	3h at 20°C	51	-6.3	24 (*S*)
6	4	Ph	+3.1	3.5 (*S*)	12 h at 5°C	71	+1.6	3.0 (*S*)

[a]Determined by NMR with $Eu(hfc)_3$. [b]5 ml of 0.4 M KOH in MeOH was added to 0.5-1.0 mmol of allylic ester. [c]Isolated yield. Losses of the alcohols during purification are significant because of their solubility in water and rather low boiling temperature. [d]Calculated from $[\alpha]_D$ values reported for optically pure substances: (*R*)-2-cyclopenten-1-ol: +116.6 (c= 0.64, $CHCl_3$), (*R*)-2-cyclohexen-1-ol: +130.6 (c= 1.21, $CHCl_3$), (*R*)-2-cyclohepten-1-ol: +26.1 (c= 1.27, $CHCl_3$),[3,12] (*S*)-2-cycloocten-1-ol: +51.2 (c= 6.52, CH_2Cl_2).[7b]

CONCLUSION

Chiral (*S*) and (*R*)-allylic esters and alcohols can be obtained with low to moderate *ee*'s by a simple procedure from the corresponding alkenes using catalytic amounts of (*S*) or (*R*)-proline as the chiral source. The enantioselectivity of the process is determined mainly by the nature of both the alkene and chiral auxiliary and is less dependent on the nature of the acyl group.

EXPERIMENTAL PART

Materials and equipment. Most reagents were commercially available. Di-((*S*)-prolinato)-copper(II) and N-Boc-(*S*)-proline have been synthesized by standard procedures [10,13]. Structural analogs of proline (used for runs 5 to 9 in Table 4) have been obtained from Pr. J. Martens' laboratory.[14] Alkenes and solvents have been distilled from CaH_2 before use. Perkin-Elmer-241 automatic polarimeter has been used for optical rotation measurements. ^1H NMR spectra were recorded using a Bruker AC 250 spectrometer. $Eu(hfc)_3$ was used as chiral shift agent. UV-VIS spectra were recorded with an UVICON 941 spectrometer.

(*S*)-2-Cyclohexenyl-1-benzoate 2 (representative procedure for obtaining allylic esters)

A1 conditions. A mixture of Cu_2O (14.3 mg, 0.1 mmol), (*S*)-proline (57.7 mg, 0.5 mmol), PhCOOH (366 mg, 3.0 mmol) and cyclohexene (1.0 ml, 10 mmol) was dissolved by stirring and heating (82°C) in 5.0 ml (96 mmol) of anhydrous MeCN. Addition of *t*-BuOOC(O)Ph (98%, 0.39 ml, 2.0 mmol) to the resulting colorless solution led immediately to a deep blue coloration. The resulting mixture was refluxed for 2 h. After this time, the blue color changed to green and iodometric titration showed the virtual absence of peroxides (conversion of oxidant ≈ 97%). The reaction mixture was cooled to room temperature, diluted with 50 ml of saturated $NaHCO_3$ aqueous solution and extracted with 2 x 15 ml of Et_2O. The ether layer was washed with water and dried over $MgSO_4$. Column chromatography (SiO_2, petroleum ether/EtOAc = 95/5) gave 232 mg (1.15 mmol, 59% to reacted *t*- BuOOC(O)Ph) of **2**, $[\alpha]_D$= -67 (c= 4.64, $CHCl_3$).

A2 conditions. The procedure was as described above except that 5.0 mmol (611 mg) of PhCOOH and 2.0 mmol (0.27 ml) of 70% aqueous *t*-BuOOH were used instead of *t*-BuOOC(O)Ph. After heating for 9 h, iodometric titration showed the high conversion of peroxides (> 95%). The purification led to **2** (137 mg, 0.68 mmol, 36% to reacted *t*-BuOOH), $[\alpha]_D$= -71 (c= 2.74, $CHCl_3$).

These procedures were used for varying the alkene, RCOOH, solvent and chiral auxillary. For the oxidation of 1-octene and allylbenzene, the mixture of esters obtained by column chromatography were then separated by preparative TLC (SiO_2, petroleum ether/EtOAc = 95/5). The structure and purity of substances obtained were confirmed by ^1H NMR data.

(*R*)-2-cyclohexen-1-ol (representative procedure for obtaining allylic alcohols)

5.0 ml of 0.4 M KOH solution in MeOH was added to 133 mg (0.66 mmol) of (*R*)-2-cyclohehenyl-1-benzoate ($[\alpha]_D$= +66, *ee* = 36%). The mixture was kept in the fridge (≈ 5°C) for 12 h. After this time, TLC showed the complete dissappearance of the benzoate. MeOH was removed under reduced pressure and the resulting mixture extracted with Et_2O. The ether layer was washed with minimal amounts of 1M HCl and brine, then dried over $MgSO_4$. Column chromatography (SiO_2, pentane/acetone = 80/20) gave 32 mg (0.33 mmol, 50%) of (*R*)-2-cyclohexen-1-ol ($[\alpha]_D$= +38, *ee* = 29%).

Iodometric titration. The standard procedure[15] was used for titration of *t*-BuOOH. Before titration, *t*-BuOOC(O)Ph was converted to *t*-BuOOH by alkaline hydrolysis (0.4 M KOH in MeOH, 20°C, 2 min).[16]

Optical rotation measurements. $[\alpha]_D$ values were measured at 20°C in $CHCl_3$ solutions with concentrations c= 0.2-8.0 g/100 ml. The independence of $[\alpha]_D$ values and concentrations (error < 3%) has been determined under the conditions used.

Acknowledgements: We are grateful to "Ministère de la Recherche et de la Technologie" for a post-doc fellowship to A.L. We acknowledge Pr. J. Martens, Mrs W. Trentmann and J. Wilken (Oldenburg University, Germany) for providing large samples of aminoacids. We also thank Mr. H. Baillia (Reims University) for help

in NMR spectroscopy, Pr A. Pfaltz (Basel University) for sending us unpublished results (section of the thesis of U. Leutenegger, Zürich, 1990, N° 9091) and Dr. G. Bird (ZENECA Pharma, Reims) for checking English of the manuscript.

REFERENCES AND NOTES

1. a) Muzart, J. *Bull. Soc. Chim. Fr.* **1986**, 65. b) Muzart, J. *Chem. Rev.* **1992**, *92*, 113. c) Muzart, J. *Synthesis* **1993**, 11. d) Muzart, J.; N'Ait Ajjou, A.; Ait-Mohand, S. *Tetrahedron Lett.* **1994**, *35*, 1989.
2. a) Mortezaei, R.; Hénin, F.; Muzart, J.; Pète, J.P. *Tetrahedron Lett.* **1985**, *26*, 6079. b) Muzart, J.; Hénin, F.; Pète, J.P.; M'Boungou-M'Passi, A. *Tetrahedron: Asymmetry* **1993**, *4*, 2531. c) Hénin, F.; M'Boungou-M'Passi, A.; Muzart, J.; Pète, J.P. *Tetrahedron* **1994**, *50*, 2849. d) Jamal Aboulhoda, S.; Hénin, F.; Muzart, J.; Thorey, C.; Behnen, W.; Martens, J.; Mehler, T. *Tetrahedron: Asymmetry* **1994**, *5*, 1321.
3. Fukazawa, T.; Hashimoto, T. *Tetrahedron: Asymmetry* **1993**, *4*, 2323.
4. Rawlinson, D.J.; Sosnovsky, G. *Synthesis* **1972**, 1.
5. a) Araki, M.; Nagase, T. *Ger. Offen. 26 25 030*, **1976**; *Chem. Abstr.* **1977**, *86*, 120886r. b) Denney, D.B.; Napier, R.; Cammarata, A. *J. Org. Chem.* **1958**, *30*, 3151. c) Muzart, J. *J. Mol. Catal.* **1991**, *64*, 381.
6. The method was described for the first time by Spendley, W; Hext, G.R.; Hinsworth, F. *Technometrics*, **1962**, *4*, 441. For a summary of the method and its application to chemistry, see for example: Berridge, J.C. *J. Chromatogr.* **1989**, *485*, 3.
7. a) Sato, T; Gotoh, Y.; Wakabayashi, Y.; Fujisawa, T. *Tetrahedron Lett.* **1983**, *24*, 4123. b) Whitesell, J.K.; Carpenter, J.F.; Yaser, H.K.; Machajewski, T. *J. Am. Chem. Soc.* **1990**, *112*, 7653. c) Jeromin, G.E.; Scheidt, A. *Tetrahedron Lett.* **1991**, *32*, 7021.
8. Carlson, R.; Lundstedt, T.; Albano, C. *Acta Chem. Scand.* **1985**, *B39*, 79.
9. a) Kochi, J.K. *J. Am. Chem. Soc.* **1962**, *84*, 3271. b) Kochi, J.K.; Bemis, A. *Tetrahedron* **1968**, *24*, 5099.
10. Greenstein, J.P.; Winitz, M. *Chemistry of the amino acids* Wiley: New York, 1961, Vol. 1, p. 1312.
11. Concerning the mechanism of the acyloxy transfer, see: Beckwith, A.L.J.; Zavitsas, A.A. *J. Am. Chem. Soc.* **1986**, *108*, 8230.
12. We are aware of the confusions concerning the optical rotation value of 2-cyclohexen-1-ol enantiomers (Bhuniya, D.; Singh, V.K. *Synth. Commun.* **1994**, *24*, 375) and retained $[\alpha]_D$= +130.6 for pure (*R*)-isomer accordingly to ref. 3 and Asami, M.; Ishizaki, T.; Inoue, S. *Tetrahedron: Asymmetry* **1994**, *5*, 793. Similarly, we chose the more recent $[\alpha]_D$ value[3] ascribed to (*R*)-2-cyclopenten-1-ol rather than an older one from Wahhab, A.; Tavares, D.F.; Rauk, A. *Can. J. Chem.* **1990**, *68*, 1559.
13. Greene, T.W.; Wuts, P.G.M. *Protection groups in organic synthesis* (2nd ed.) Wiley: New York, 1991.
14. For the synthesis of these compounds, see: Mehler, T.; Behnen, W; Wilken, J.; Martens, J. *Tetrahedron: Asymmetry* **1994**, *5*, 185 and references therein.
15. Sharpless, K.B.; Verhoeven, T.R. *Aldrichimica Acta*, **1979**, *12*, 63.
16. Antonovsky, V.L.; Buzlanova, M.M. *Analytical chemistry of organic peroxide compounds* Khimia: Moscow, 1978 (Russian), p. 30.

(*Received in UK* 15 *September* 1994)