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Catalysis with Inorganic Cations. VI.[1] The Effect of Chiral Bis-Oxazoline-Magnesium Perchlorate Catalysts on Chemo- and Enantioselectivity of Intramolecular Hetero Diels-Alder and Ene Reaction

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Abstract (*E*)1-acetyl-[2-(3-methyl-2-butenyloxy)benzylidene]indolin-2-one (**1**) gives competition between the intramolecular Hetero Diels-Alder (HDA) (thermal conditions) and the intramolecular ene reaction (IER) (magnesium perchlorate - MP - catalyzed conditions). Several complexes derived from MP and chiral bis-oxazolines were found to be excellent chemo- and enantioselective catalysts with a different degree of selectivity depending on the substituents on the oxazoline ring. The most chemoselective oxazolinic ligand forced the reaction to give a ratio of [HDA] : [IER] products 5 : 95. The *trans*-(4,5-diphenyloxazoline) - MP complex is the best enantioselective catalyst and the product of the IER of **1** can be prepared in 75% yield and 88% e.e.. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

In the previous paper of this series[1] the reactivity of (*E*)1-acetyl-3-[2-(3-methyl-2-butenyloxy) benzylidene]indolin-2-one (**1**) was discussed. Magnesium perchlorate (MP) coordinates both carbonyl groups of this substrate and, in the presence of two equivalents of monocarbonyl ligand (or one equivalent of a β-dicarbonyl ligand) the chemoselectivity involving Hetero Diels-Alder (HDA) and intramolecular ene reaction (IER) is strongly influenced. Thus the ratio of [6a,13c]-*cis*- and *trans*-9-acetyl-7,7-dimethyl-6,6a,7,13c-tetrahydrochromeno[4',3':4,5]pyrano[2,3-*b*]indoles (**2a,b**) *vs* (3*S*,3'*R*,4'*S*) and (3*R*,3'*R*,4'*R*) 1-acetyl-3(3'-*iso*propenylchroman-4'-yl)oxindoles (**3a,b**), isomerized by silica gel into their (3*R*,3'*R*,4'*S*) and (3*S*,3'*R*,4'*R*) isomers (**4a,b**), ranges from 100 : 0 under thermal conditions to 50 : 50 when the reaction was run in the presence of MP and two equivalents of benzophenone at room temperature in CH_2Cl_2 (Scheme 1). Obviously all these products were racemic mixtures.

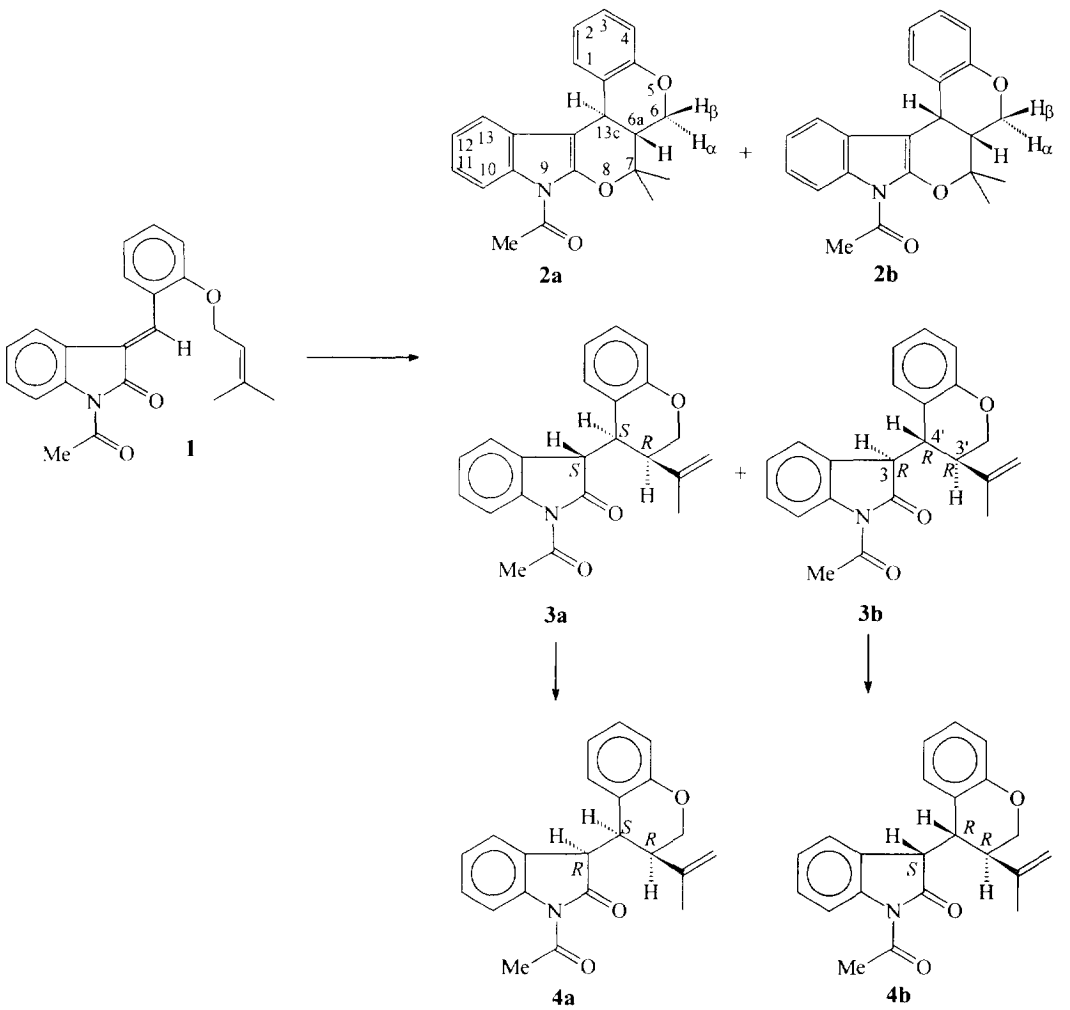
An attempt was made to use chiral ketones as auxiliary ligands coordinated to magnesium ion to induce enantioselectivity in the ring closure of **1**. The reaction run in the presence of two equivalents of (1*R*)-camphor gave **2** and **4** almost optically inactive.[1]

The hope to organize around Mg(II) the ligands and **1** in a supramolecolar device enantiotopically oriented, failed, but this was a potential route to catalyzed enantioselective intramolecular HDA and IERs.

Asymmetric catalysis in IER is a well known process in organic synthesis,[2] but Mg(II) was never used as the core of the catalyst. Asymmetric- catalyzed HDA (and its competition with ER) was studied when involving heterodienophiles.[2b,2c,3,4] Only two intramolecular examples involving α,β-unsaturated carbonyl-olefin cyclization have been reported,[5-7] both with a chiral titanium complex as catalyst, and good enantiomeric excesses were obtained in both reactions.

A development of the previous concepts was attempted by using a bidentate ligand, not necessarily having two carbonyl groups as the coordinating centers.

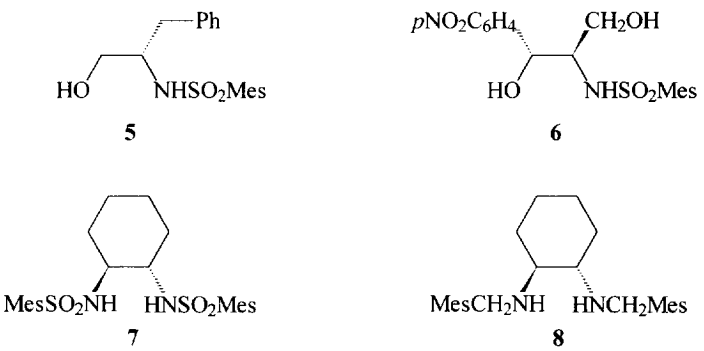
Scheme 1



RESULTS AND DISCUSSION

The first experiments were run with a variety of bi- and tridentate ligands with different degrees of symmetry. (*S*)-3-Phenyl-2-(2,4,6-trimethylbenzensulfonamido)-1-propanol (**5**), (*R,R*)-1-(4-nitrophenyl)-2-(2,4,,6-trimethylbenzensulphonamido)-1,3-propandiol (**6**), (*S,S*)-1,2-bis(2,4,6-trimethylbenzensulfonamido) cyclohexane (**7**), and (*S,S*)-1,2-bis(2,4,6-trimethylbenzylamino)cyclohexane (**8**) were synthetized, **7** and **8** being examples of C_2 symmetry ligands (Scheme 2 - Mes is 2,4,6-trimethylphenyl group).

Scheme 2



The best conditions were found to be: equimolecular amounts of **1**, MP and ligand, at room temperature, in CH_2Cl_2 as solvent. After the time reported in Table 1, the composition of the reaction mixture was monitored by ^{1}H-nmr to determine the relative yields of **2a,b** and either **3a** and **3b** (if the kinetic products of the IER are stable under the experimental conditions) or **4a** and **4b** (if the isomerization at the C3 atom occurred). A column chromatography separated **2a,b** and the isomerized (by silica gel) **4a** and **4b**. Their enantiomeric excess was then determined following the protocol detailled in the experimental part.

All the above mentioned catalysts (**5-8**, entries A-D respectively) gave significant amounts of IER products (in the range 40-55%). From entries A-C, the kinetic products **3a,b** were formed, the diamine **8** (entry D) isomerized them to **4a,b**. The rotatory powers of all the isolated products corresponded to non-significant e.e. (< 5% - Table 2).

Chiral bis-oxazolines with C_2 symmetry have been reported to be excellent ligands for asymmetric catalysis of DA[8] and competing HDA-ERs.[4] Hence 2,2-bis{2-[4(*S*)-benzyl-, [4(*S*)-*iso*.propyl-, [4(*S*)-*tert*.butyl- (**9a-c**), [4(*R*)-phenyl- (**10**), and [4(*S*)-methyl-5(*R*)-phenyl-1,3-oxazolinyl]}propane (**11**) (Scheme 3) were tested as ligands with inorganic perchlorates as the cationic core of the catalysts. The bis-oxazolines **9c** and **10** are commercially available, **9a,b** were prepared following the known literature methods,[9,10] the synthesis of **11** was recently described by our group.[11]

Again the cation was found to be very important since the catalysts derived from **9a** and lithium, sodium or barium perchlorate were found to be inactive and, after 30 days at ambient temperature, nearly all starting product **1** was recovered unchanged. MP, on the contrary, was an excellent inorganic core for complexes with chiral bis-oxazolines as ligands.

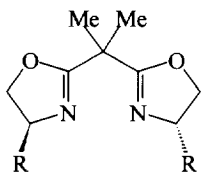
The starting product disappeared within three days and the reaction products were **2-4a,b** in the different ratios as determined by ^{1}H-nmr (Table 1).

Table 1. Chiral ligands, reaction conditions, yields, and product distribution of the intramolecular reaction of **1** at r.t. in CH_2Cl_2 with MP.

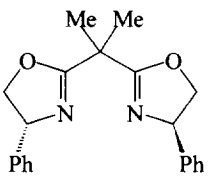
Entry	Ligand (L)	Ratio [1] : [L] : [MP]	time	Yield[a] %	Product distribution %[b] 2a	2b	3a	3b	4a	4b	[HDA] [IER]
A	**5**	1 : 1 : 1	36 h	quant.	51	6	13	30	c	c	57 : 43
B	**6**	1 : 1 : 1	24 h	quant.	55	5	16	24	c	c	60 : 40
C	**7**	1 : 1 : 1	24 h	quant.	53	5	14	28	---	---	58 : 42
D	**8**	1 : 1 : 1	24 h	quant.	42	4	c	c	19	35	46 : 54
E	**9a**	1 : 1 : 1	2 d	quant.	5	---	1	11	9	74	5 : 95
F	**9b**	1 : 1 : 1	3 d	quant.	11	c	c	6	13	70	11 : 89
G	**9c**	1 : 1 : 1	3 d	quant.	37	4	2	4	16	37	41 : 59
H	**10**	1 : 1 : 1	3 d	quant.	17	2	5	17	11	48	19 : 81
I	**10**	3 : 1 : 1	8 d	quant.	24	2	3	9	15	47	26 : 74
J	**11**	1 : 1 : 1	3 d	quant.	9	c	5	18	15	53	9 : 91
K	**11**	3 : 1 : 1	5 d	>95	10	c	2	8	20	60	10 : 90
L	**12**	1 : 1 : 1	3 d	quant.	24	2	3	7	15	43	26 : 74
M	**13**	1 : 1 : 1	3 d	quant.	10	c	2	13	13	62	11 : 89
N	**13**	3 : 1 : 1	6 d	85	11	1	3	7	12	65	12 : 88

[a]Isolated yields of **2a,b** and **4a,b**: the difference is recovered starting product **1**; [b]the product distribution, determined by nmr, is the average of at least three independent experiments; [c]yields less than 1% detected by nmr.

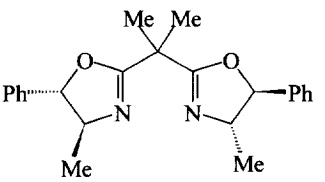
Scheme 3



9a: R = CH_2Ph
b: R = $CHMe_2$
c: R = CMe_3



10



11

Again **4a,b**, the thermodynamic IER products, are formed from **3a,b** under the experimental conditions. To prove this, a mixture of **2,3a,b** (prepared from **1** in MP - acetone - CH_2Cl_2, the conditions of entry F in ref. 1), stirred 3 days in CH_2Cl_2 with the catalyst derived from **10** and MP, gave **4a,b** and the ratios [**3a**]:[**4a**] and [**3b**]:[**4b**] were nearly identical to those obtained under the conditions described in this paper under entry H in Table 1.

The chemoselectivity was influenced by the substituents on the ligand and the ratio [HDA]:[IER] products ranges from 1:1 to 5:95, a significant result taking into account that, under thermal conditions, **1** gives HDA products only.[1]

The rotatory power of **4a** was always very low and it was impossible to correlate this to any specific e.e. since chiral europium reagents were found inactive in discriminating the enantiomers. The $[\alpha]_{546}$ of **2a** was negligible from the reaction with **9a-c**, low from reactions with **10** and **11**. The $[\alpha]_{546}$ of **4b**, the main reaction product, was unsatisfactory for samples deriving from the reactions catalyzed by **9a-c** and **10**, but was promising for the sample of **4b** derived from the reaction with ligand **11**. The product separated by the column chromatography had $[\alpha]_{546}$ = + 75° and chiral $Eu(cfc)_3$ gave an e.e. of 47% determined on the shift of the acetyl group. When this product was crystallized from pentane, a fraction separated having a strongly lower $[\alpha]_{546}$ value and from the mother liquors, by slow evaporations, nice needles of **4b** were isolated whose $[\alpha]_{546}$ was +158.6°. The $Eu(cfc)_3$ showed this was a single enantiomer, at least in the limit of the technique. These crystals were submitted to an x-ray structure determination whose results are shown in Figure 1.

The absolute configuration of (+)**4b** was not assigned, but the crystal packing showed it was a single enantiomeric species with a (3*S*,4'*R*,3'*R*) or (3*R*,4'*S*,3'*S*) configuration as previously supposed.[1] Thus, assuming $[\alpha]_{546}$ = +158.6° as the rotatory power of the pure dextrorotatory enantiomer, the e.e. of each sample of **4b** was easily determined by a simple polarimetric measure (Table 2).

Our attention was focussed on the results of **10** and **11**. The possibility of a short turn-over of the catalyst was tested in entries I and K where the ratio [**1**] : [ligand] : [MP] was 3 : 1 : 1. The results in terms of products distribution and enantioselectivity were very similar to those of the corresponding entries H and J. The sole difference was a longer reaction time required to accomplish the reaction.

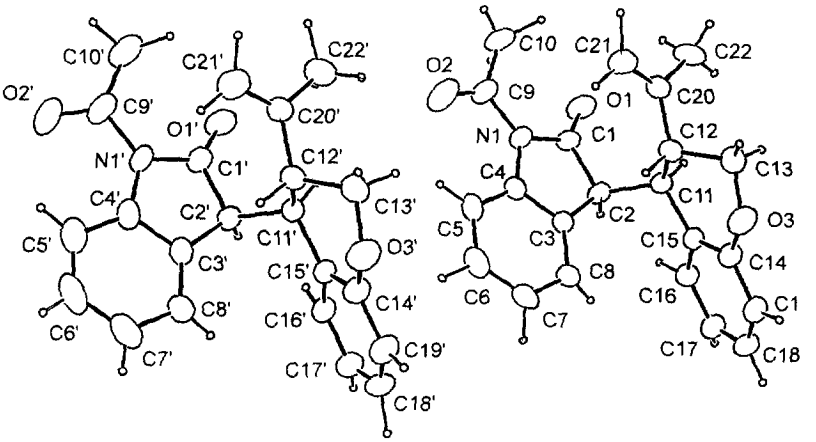
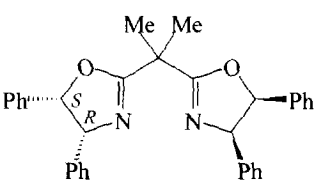


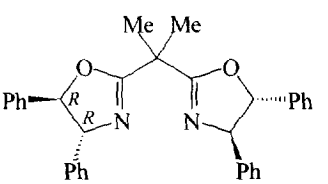
Figure 1. ORTEP II drawing of the asymmetric unit of **4b**.

The important result was the effect of a 4(*R*)-phenyl group on the oxazoline ligand (**10**) that gave (–)**4b** in about 30% e.e., whereas a 5(*S*)-phenyl group (ligand **11**) gave (+)**4b** in 47% e.e.. This means the phenyl groups in 4- and 5- on the same face of the ring give rise to opposite e.e. of **4b** and suggests that a worse result in terms of enantioslelectivity should be obtained from a *cis*-(4,5)-diphenyl oxazolinic ligand than from its *trans* diastereoisomer. The ligands **12** and **13** (Scheme 4) were tested, the former prepared in accordance to the patented Masamune protocol,[12] the latter following the synthesis recently described by our group.[11]

Scheme 4



12



13

The *cis* isomer **12** (entry L) was less chemo- and enantioselective than the *trans* isomer **13**, either with this in a ratio 1 : 1 or 1 : 3 with **1** (entries M and N respectively). The chemoselectivity with **12** and **13** gave ratios [HDA] : [IER] of 1 : 4 and 1 : 9 respectively. The enantioselectivity with **12** and **13** resulted in the formation of (–)**4b** as the main isomer for both catalysts, and the e.e. was 51% and 88% respectively. This is an appreciable result, taking into account that the reactivity of **1** requires the reaction to be run at room temperature.

Table 2. Isolated yields and enantiomeric excess of products from the intramolecular HDA and ER of **1** under the catalytic conditions in Table 1.

Entry	Ligand	**2a**[a]		**4a**	**4b**	
		yield %	e.e %[b,c]	yield %	yield %	e.e %[b,c]
A	**5**	50	d	15	27	2(+)
B	**6**	42	4(−)	12	20	d
C	**7**	49	5(−)	10	25	d
D	**8**	40	d	15	30	d
E	**9a**	5	--	10	75	12(−)
F	**9b**	7	--	12	65	15(+)
G	**9c**	42	3(−)	15	40	29(+)
H	**10**	15	14(−)	16	61	30(−)
I	**10**	20	9(−)	15	53	29(−)
J	**11**	8	5(+)	18	63	47(+)
K	**11**	8	4(+)	23	69	46(+)
L	**12**	21	11(−)	16	48	51(−)
M	**13**	8	5(−)	11	75	88(−)
N	**13**	9	5(−)	11	70	81(−)

[a]Isolated in admixture with the corresponding amount of **2b**. [b]The sign of the optical rotation of the main isomer is reported in parenthesis. [c]Determined as reported in the experimental section. [d]Nearly 0% e.e..

There are some implications in the catalytic effect of complexes between bis-oxazolines and MP. The *iso*-propyl, *tert*-butyl and phenyl groups in position 4 with the same (*R*) configuration (consider **10** and the enantiomers of **9b** and **9c**), give (−)**4b** as main enantiomer. This suggests that the approach of the enic fragment to the *Si* face of the enophile is prevented by the steric hindrance of the substituents. If this is true, (−)**4b** could have a (3*R*,4'*S*,3'*S*) configuration.

A 5-phenyl group in the (*R*) configuration (consider **13** and the enantiomer of **11**) increases the formation of (−)**4b**. Hence the approach of the ene to the *Re* face of the enophile must be favoured, even if steric hindrance should disfavour this.

In conclusion, a synergism between the phenyl groups in the positions 4 and 5 both with the (*R*) configuration, makes the *trans* isomer **13** (and not the *cis* one **12**) a ligand suitably designed for the enantioselective intramolecular ene reaction of **1**.

EXPERIMENTAL SECTION

Melting points were determined by the capillary method and are uncorrected. Elemental analyses were made on C. Erba CHN analyzer mod. 1106. ^{1}H-Nmr (TMS as standard) were recorded on a Bruker AC 300 spectrometer, ir spectra (nujol mulls) on a Perkin Elmer 881 spectrophotometer; optical rotation at room temperature on a Perkin Elmer 241 polarimeter with 1 dm cell. Column chromatography: silica gel 230-400 mesh.

*(E)-1-Acetyl-3-[2-(3-methyl-2-butenyloxy)benzylidene]-2-oxindole (**1**)* was prepared as previously described.[1]

*(S)-3-Phenyl-2-(2,4,6-trimethylbenzensulfonamido)-1-propanol (**5**).* (L)-Phenylalanilol (1.0 g - 6.6 mmol) was added to a stirred solution of 2,4,6-trimethylbenzensulfonyl-chloride (1.45 g - 6.6 mmol) in triethylamine (6.6 mmol) and dichloromethane (35 mL). The work-up of the mixture and a column chromatography (cyclohexane-ethyl acetate 70:30 as eluant) gave pure **5** (1.55 g - 71%), m.p. 56-8 °C from *n*-hexane. I.r.: $\nu_{OH,NH}$ = 3500, 3320 cm^{-1}. ^{1}H-Nmr (DMSO-d_6), δ: 7.45 (1H, d, NH), 7.07 (3H, m, aromatic protons), 6.95 (2H, m, aromatic protons), 6.87 (2H, s, aromatic protons), 4.80 (1H, t, OH), 3.36 (1H, m, CH), 3.20 (2H, m, OCH_2), 2.84 and 2.47 (1H + 1H, dd + dd, CH_2Ph), 2.43 (6H, s, 2 CH_3), 2.23 (3H, s, CH_3). Elem. anal.; calc. for $C_{18}H_{23}NO_3S$: C, 64.9; H, 7.0; N, 4.2. Found: C, 64.9; H, 6.9; N, 4.2%. $[\alpha]_D$ = -32.3° (c = 1, chloroform).

*(R,R)-1-(4-nitrophenyl)-2-(2,4,6-trimethylbenzensulfonamido)-1,3-propaandiol (**6**).* From (*R,R*)-2-amino-1-(*p*.nitrophenyl)-1,3-propandiol and 2,4,6-trimethylbenzensulfonylchloride, following the method reported for **5**, **6** was obtained in 82% yield, m.p. 246-7 °C from ethanol. I.r.: $\nu_{OH,NH}$ = 3570, 3525, 3455, and 3262 cm^{-1}. ^{1}H-Nmr (DMSO-d_6), δ: 7.80 and 7.32 (2H + 2H, d + d, *p*.nitrophenyl aromatic protons), 7.28 (1H, d, *J* = 6.5 Hz, 1-OH), 6.64 (2H, s, mesityl aromatic protons), 5.68 (1H, d, *J* = 5.3 Hz, NH), 4.99 (1H, dd, *J* = 6.5 and 1.7 Hz, H-1), 5.00 (1H, dd, *J* = 6.8and 4.3 Hz, 3-OH), 3.63 (2H, ~dt, *J* = 6.8, 10.0, and 10.5 Hz, H_3), 3.50 (1H, ~dt, *J* = 4.3, 5.0, and 10.5 Hz, $H_{3'}$), 3.34 (1H, m, *J* = 1.7, 5.0, 10.0, and 6.5 Hz, H_2), 2.30 (6H, s, 2 CH_3 mesityl), 2.09 (3H, s, CH_3 mesityl). Elem. anal.; calc. for $C_{18}H_{22}N_2O_6S$: C, 54.8; H, 5.6; N, 7.1. Found: C, 54.6; H, 5.7; N, 7.2%. $[\alpha]_D$ = -57.3° (c = 0.8, chloroform-DMSO 5:1).

*(S,S)-1,2-bis(2,4,6-trimethylbenzensulfonamido)cyclohexane (**7**).* It was prepared as described in the literature.[13]

*(S,S)-1,2-bis(2,4,6-trimethylbenzylamino)cyclohexane (**8**).* The synthesis of **8** was accomplished by heating (*S,S*)-1,2-diaminocyclohexane with 2.2 equivalents of mesitaldehyde following essentially the preparation reported in the literature for a similar product,[14] except the reduction of the isolated Schiff base (m.p. 122-3 °C from ethanol) that was made with sodium borohydride in ethanol-toluene 10:1 solution. **8** was purified by column chromatography (eluant: cyclohexane-ethyl acetate 85:15), m.p. 167-8 °C (from ligroin). I.r.: ν_{NH} = 3300 cm^{-1}. ^{1}H-Nmr ($CDCl_3$), δ: 6.81 (2H, s, aromatic protons), 3.85 and 3.48 (1H + 1H, d + d, *J* =

10 Hz, $ArCH_2$), 2.30 (6H, s, 2 CH_3), 2.27 (3H, s, CH_3). Elem. anal.; calc. for $C_{26}H_{38}N_2$: C, 82.5; H, 10.1; N, 7.4. Found: C, 82.6; H, 10.3; N, 7.4%. $[\alpha]_D$ = -98.2° (c = 0.9, chloroform).

*2,2-Bis{2-[4(S)-benzyl- or 4(S)-isopropyl-1,3-oxazolinyl]}propanes (**9a,b**).* These were prepared according to the procedures described for bis(oxazolines) from the corresponding aminoalcohols and dimethyl malonyl dichloride.[15]

9a. The intermediate hydroxyamides and chloroamide had the m.p. and ^{1}H-nmr spectra identical to those reported in the literature.[9] The bis-oxazoline **9a** was isolated in 51% yield after chromatographic purification (eluant: cyclohexane-ethyl acetate 1:1 first, then with ethyl acetate). The oil was crystallized from diisopropyl ether, m.p. 61-2 °C (Lit.[9] 52-3 °C). ^{1}H-nmr spectra was identical to that reported in the literature. $[\alpha]_D$ = -42.7° (c = 0.95, chloroform).

9b. The preparation of this bis-oxazoline is reported by Evans and coworkers[16] in the supplementary material of the paper in the reference.

*2,2-Bis{2-[4(S)-tert.butyl- or 4(R)-phenyl-1,3-oxazolinyl]}propanes (**9c,10**).* These are commercially available by Aldrich.

*2,2-Bis{2-[4(S)-methyl-5(R)-phenyl-, (4R,5S)-diphenyl-, and (4R,5R)-diphenyl-1,3-oxazolinyl]}propanes (**11-13**)* were prepared as desciribed in the literature.[11,12]

*Reaction of **1** catalyzed by MP-chiral ligands (Entries A-N). General procedure.* Anhydrous magnesium perchlorate (223 mg - 1 mmol) was added to a stirred solution of chiral organic ligands (**5-13** - 1 mmol) in anhydrous CH_2Cl_2 (1.0-3.0 mL, the minor volume is required for bis-oxazolines) and within one hour the inorganic salt in general dissolved and a nearly limpid solution is obtained. For entries I, K,, and N the above amounts are reduced to one third. **1** (347 mg - 1 mmol) is added and stirring is continued at room temperature for the time reported in Table 1. The reaction mixture, when **1** disappeared, was decomposed in water and extracted with CH_2Cl_2. A portion of the crude reaction mixture was monitored by ^{1}H-nmr and the ratios of **2a,b**, **3a,b**, and **4a,b** were determined. The reaction mixture was column chromatographed over siliga gel. The eluant, cyclohexane-ethyl acetate 97:3, was suitable to separate **4a**, **4b**, and **2a,b** in the order, and the chiral ligands were recovered unchanged, suitable to be recycled. The $[\alpha]_D$ and $[\alpha]_{546}$ of **2a** (in admixture with **2b** in a ratio of about 10:1), **4a** (whose values were always very low), and **4b** were measured in acetone at the following concentrations: **2a** (c = 0.3) except entries J, K, M, and L where the rotatory powers were measured at c = 0.1; **4a** (c = 0.15-0.20); **4b** (c = 1.0). The e.e. of **2a** reported in Table 2 are derived from a relationship observed between $[\alpha]_{546}$, measured as above, and the e.e. measured with chiral $Eu(cfc)_3$ that splitted the signals of the methyl groups at 1.52 and 1.58 δ and that of the acetyl group at 2.63 δ. The e.e. of **4b** reported in Table 2 are referred to a sample of pure (+)-**4b** whose $[\alpha]_{546}$ = + 158.6° was taken as the reference and whose structure was determined by X-ray analysis.

Table 3. Crystal and refinement data.

Formula	$C_{22}H_{21}NO_3$
Mw	347.42
Crystal Colour	colourless
Crystal Size	0.48 × 0.12 × 0.10 mm
System	monoclinic
Space Group	$P2_1$
a	9.650(3) Å
b	10.246(1) Å
c	18.497(6) Å
α, β, γ	90, 99.70(1), 90°
V	1802.8(8)
Z	4
D_{calc}	1.28 Mg × m^{-3}
Radiation	Cu K_α (λ = 1.54184 Å) graphite monochromated
μ	0.646 mm^{-1}
T	293(3) °K
θ range	2 - 70 °
Scan Type	ω - 2θ
Reflection Measured	-11 < h < 11 ; 0 < k < 12 ; 0 <l < 22 and Friedel's pairs
Transmission Coeff.	Tmin 0.658 ; Tmax 0.994
Tot. Reflections Meas.	7342
Unique Reflections	3559
R_{int}	0.031
Obs. Refls [I > σ(I)]	3384
[a]R	0.061
G.O.F.	1.334
[b]Rw (w = 1)	0.067
Refined Parameters	469

[a] $R = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$ [b] $Rw = [\Sigma w(|Fo|-|Fc|)^2 / \Sigma w(Fo)^2]^{1/2}$

*Crystal data and single crystal structure refinement of (+)-**4b**.* The crystal structure was determined on a sample of **4b** whose $[\alpha]_{546}$ was +158.6° (c = 1.0, acetone). The asymetric unit contains two indipendent molecules which show significative differences in the acetyl group orientation. Unit cell parameters and intensity data were obtained on Enraf-Nonius CAD-4 diffractometer. Calculations were performed with the MOIEN software[17] on a MicroVax 3100 computer.

The cell dimensions were determined by least-squares fitting of 25 centred reflections monitored in the range $29<\theta<33°$. Correction for Lp and empirical absorption[18] were applied. The structure was solved by direct methods (SIR88).[19] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

All the hydrogen atoms were found in the difference Fourier map, inserted with an overal atomic displacement parameter equal to 5.0 $Å^2$ but not refined.

Secondary extinction[20] were applied. Atomic scattering factors were taken from ref. 21.

In order to establish the absolute chirality of the structure, the pairs of Friedel-related reflections were measured but without any results: the least-squared refinements of both alternative models converged to the same R value, while the refinement of the η parameter[22] gave ambiguous answers. The enatiomer reported here it has been chosen on the basis of chemical considerations.

Diagrams of the molecular structure were performed by ORTEP program,[23] and the pertinent experimental details are given in Table 3.

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