Enantioselective Oxidation of Chiral Titanium Enolates Derived from Propiophenone by Dimethyldioxirane or 3-Phenyl-2-phenylsulfonyloxazirdine☆

Waldemar Adam* and Frank Prechtl

Institut für Organische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

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The stereoselective oxidation of the optically active titanium enolate complexes **2** of propiophenone by dimethyldioxirane (**3**) (as acetone solution) and 3-phenyl-2-phenylsulfonyloxaziridine (**4**) has been investigated. The chiral titanium enolates **2** were synthesized by the reaction of the lithium enolate of propiophenone and the respective optically active chlorotitanate complexes **1**. For **3** as oxidant, the stereoselectivity of the α hydroxylation strongly depends on the substitution pattern at the central titanium atom and reached for the best case, namely **2e**, an enantiomeric excess (ee) of 63%. Solvent and temperature exhibited only small effects on the stereoselectivity. Compound **4** as oxidant gave lower enantiomeric excesses than **3**.

The optically active α-hydroxy carbonyl structural unit is widespread in natural products and has during the last years been frequently used as convenient building block in organic synthesis[1]. Their preparation has mainly employed electrophilic hydroxylation of enolates. This was achieved by fixing of the carbonyl compound in form of its enolate to an optically active organic auxiliary, followed by oxidation of the corresponding enolate and liberation of the acyloins[2]. Alternatively, prochiral enolates have been directly oxidized by optically active electrophilic oxidants, e.g. chiral oxaziridines[3]. Our approach to this challenging synthetic problem is based on the oxidation of optically active transition-metal complexes to which the prochiral enolate is coordinated. As promising chiral auxiliary, the chloro(η^5-cyclopentadienyl)[(4*R*,5*R*)-α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanolato]titanium complexes were chosen, which had been already utilized by Duthaler[4] for highly enantioselective C–C bond formation reactions. Dimethyldioxirane[5] has served as oxidant, which – besides its general applications in organic synthesis[6] – has already succesfully used for the hydroxylation of lithium[7a], sodium[7b] and titanium enolates[7c] and for the oxidation of the ligand sphere of organometallic complexes[8]. Also racemic 3-phenyl-2-phenylsulfonyloxaziridine[9] was used as oxygen transfer agent to compare its reactivity and stereoselectivity in oxygen transfer processes with those of dimethyldioxirane.

Results and Discussion

The chlorotitanium complexes **1a**, **b**, **d**, **e** were synthesized according to the published procedure (cf. Experimental) by reaction of the chiral diol ligand with the respective titanium complex [Eq. (1)]. In contrast to Duthaler[4a], who isolated the (4*S*,5*S*) enantiomer of complex **1d** as a 4:1 mixture of the two diastereomers and reported its use as a stock solution in diethyl ether, in our hands, complex (4*R*,5*R*)-**1d** precipitated from diethyl ether and, after recrystallization of the $Et_3N \cdot HCl$/**1d** precipitate from boiling toluene, was obtained in 45% yield as a 81:19 mixture of the two diastereomers. Further recrystallization did not change this isomer ratio; however, complex **1e** could not be isolated in crystalline form and was used as stock solution in ether.

The titanium complex **1c** was obtained according to the procedure published by Seebach[10]. Thus, exchange of two isopropoxy ligands in $(i\text{PrO})_3\text{TiCl}$ by the chiral diol and subsequent removal of 2-propanol by azeotropic distillation afforded the complex **1c** in nearly quantitative yield.

The titanium enolates were prepared by a transmetalation reaction of the lithium enolate of propiophenone, generated by reaction with lithium diisopropylamide at −78°C, with the corresponding chiral titanium complexes **1a–e** [Eq. (2)]. For stereoselective oxygen transfer to be successful, a stereochemically uniform double-bond geometry at the titanium enolate is required. To ensure that this prerequisite was fulfilled for the complexes employed herein, after transmetalation with the titanium complex **1a**, all volatile materials were removed under vacuum at 0°C/0.1 Torr, and the residue was investigated by NMR spectroscopy. Only one enolate complex could be observed, which exhibited the characteristic signals in the ^{1}H-NMR spectrum for the olefinic proton at δ = 5.30 (q) and in the ^{13}C-NMR spectrum for the enolate carbon atoms at δ = 99.8 (d) and 162.5 (s). Unfortunately, it was not possible to determine the enolate geometry by NOE experiments because of severe overlap of the signals for the phenyl group of the enolate and ligand moiety. However, in analogy to the titanium enolate derived from transmetalation between the lithium en-

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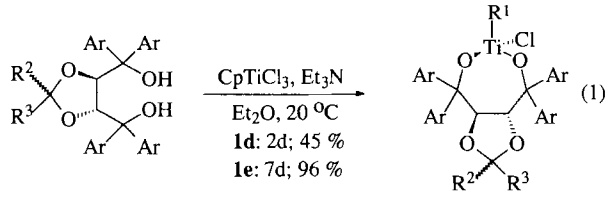
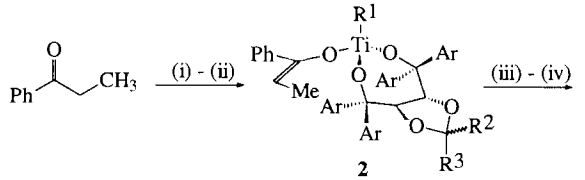
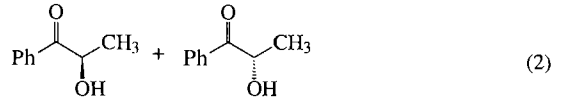
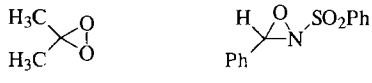






	R^1	R^2	R^3	Ar
a	Cp	Me	Me	Ph
b	$C_5H_4SiMe_3$	Me	Me	Ph
c	O*i*Pr	Me	Me	Ph
d	Cp	H	*t*Bu	Ph
e	Cp	Me	Me	1-Naphthyl

(i) LDA, THF, −78°C, 30 min; (ii) L_3TiCl (**1**), 3 h; (iii) Oxidant **3** or **4**; (iv) NH_4F, H_2O, 12 h



3 **4**

olate of propiophenone and Cp_2TiCl_2, the (*Z*) configuration for the enolate structure seems likely[7c].

There complexes were oxidized by acetone solutions of dimethyldioxirane (**3**), which reacted spontaneously with the metal enolates. Alternatively, the oxidations were carried out with 3-phenyl-2-phenylsulfonyloxaziridine (**4**), which was allowed to react for 30 min as described for the corresponding lithium enolates[3c]. After quenching of the reaction mixture with aqueous NH_4F solution at −78°C, 2-hydroxy-1-phenyl-1-propanone (**5**) was obtained as the only product. The reaction conditions for the transmetalation and oxidation reactions, yields (%) and enantiomeric excesses (% ee) are summarized in Table 1. The enantiomeric purity of the hydroxylated product **5** was determined by using a chiral HPLC column, while the absolute configuration was established by optical measurements and comparison with the reported values[3c].

As displayed in Table 1 (Entries 1−3), the enantioselectivity increases when the transmetalation was conducted at higher temperatures. For example, transmetalation at −78°C led to 13% ee (Entry 1), which increased to 17% ee (Entry 2) on transmetalation at −30°C, while a maximum value of 40% ee (Entry 3) was reached at 0°C; all oxidations were carried out at −78°C. Further rise of the metalation

Table 1. Oxidation of chiral titanium enolates with dimethyldioxirane[a] (**3**) and 3-phenyl-2-phenylsulfonyloxaziridine (**4**)

Entry	L_3TiCl	Titanation temp.[b] [°C]	Oxidation Reagent	Oxidation Temp. [°C]	Oxidation Time [min]	Conv. [%][c]	Yield [%]	ee [%][d]
1	**1a**	-78	**3**	-78	1	43	93	13 (R)
2	**1a**	-30	**3**	-78	1	44	96	17 (R)
3	**1a**	-78 to 0	**3**	-78	1	67	95	40 (R)
4	**1a**	-78 to 0	**3**	0	1	40	97	37 (R)
5	**1a**	-78 to 0	**3**[e]	-78	1	39	96	43 (R)
6	**1a**	-78 to 0	**4**	-78	30	35	92	14 (R)
7	**1b**	-78 to 0	**3**	-78	1	41	96	38 (R)
8	**1b**	-78 to 0	**4**	-78	30	25	93	12 (S)
9	**1c**	-78 to 0	**3**	-78	1	24	~100	5 (S)
10	**1d**	-78 to 0	**3**	-78	1	39	93	13 (R)
11	**1d**	-78 to 0	**4**	-78	30	25	92	3 (R)
12	**1e**[f]	-78 to 0	**3**	-78	1	20	92	63 (R)

[a] As ca. 0.08−0.1 M acetone solution. − [b] Longer transmetalation times (>3 h) did not increase the enantioselectivity, however, resulted after the oxidation in lower conversions and yields, through partial decomposition of the − under these reaction conditions − unstable titanium enolate complex. − [c] Based on reisolated starting material. − [d] The enantiomeric excess (% ee) was determined by HPLC on a chiral column, error ±1%; the absolute configuration is given in parentheses and was assessed from optical measurements. − [e] All volatile materials were removed under vacuum (ca. 20°C/0.1 Torr), and the residue was dissolved in 20 ml of toluene. − [f] As a stock solution in Et_2O.

temperature but maintainance of the oxidation temperature at −78°C did not alter the stereoselectivity. Presumably, the transmetalation reaction between the lithium enolate of propiophenone and the titanium complex **1a** requires higher temperatures than reported for similar esters[4e].

In contrast, the stereoselective oxygen transfer with dimethyldioxirane was not sensitive to the temperature at which the oxidation was performed since at −78°C (Entry 3) about the same enantioselectivity (ca. 40% ee) as at 0°C (Entry 4) was obtained. Moreover, replacement of THF (Entry 3) by toluene (Entry 5) as solvent gave also the same enantioselectivity (43% ee) in the hydroxylation of the titanate **2a** by dimethyldioxirane, which indicates that the solvent polarity plays an insignificant role in the stereocontrol.

The selectivity of the oxygen transfer strongly depended on the ligands coordinated to the titanium atom, as examplified by the simple variation of the ligand sphere of the complex **2**. For example, while incorporation of a trimethylsilyl group in the cyclopentadienyl ligand did not effect the enantioselectivity in the oxidation of the titanium enolate **2b** (Entry 7) versus **2a** (Entry 3), the change of the cyclopentadienyl to an isopropoxy ligand as in the enolate **2a** (Entry 3) versus **2c** (Entry 9) lowered the enantioselectivity dramatically to 5% ee. Mechanistically more significant, for all cases (Entry 1−5, 7, 10, 12) the major isomer was (*R*)-2-hydroxy-1-phenyl-1-propanone [(*R*)-**5**], but for complex **2c** the (*S*)-**5** enantiomer was obtained (Entry 9). Replacement of the *gem*-dimethyl group in the dioxolane ring by a *tert*-butyl group as in the titanium complex **1d** (used as 4:1 diastereomeric mixture), also caused a substantial decrease of the enantioselectivity to 13% ee (Entry 10) to afford the (*R*)-**5** isomer. The best result of 63% ee (Entry 12) was obtained on substitution of the phenyl by the steri-

cally more demanding 1-naphthyl groups, as in the enolate **2e**.

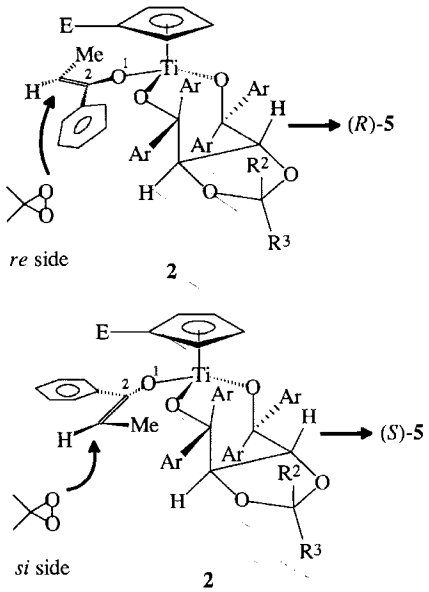
Oxidation of the titanium enolates **2a**, **b**, **d** with 3-phenyl-2-phenylsulfonyloxaziridine (**4**) gave in all cases lower ee values (Entry 6, 8, 11) compared to dimethyldioxirane (Entries 3, 7, 10); in fact, for the enolate complex **2b** (Entry 8) even the opposite enantiomer (*S*)-**5** was produced. The titanium enolate **2e** did not react with the oxaziridine **4**, probably because the enolate moiety is efficiently shielded by the sterically demanding 1-naphthyl groups.

The oxidation of the titanium enolates **2a–e** by dimethyldioxirane resulted in all but one case the (*R*)-**5** stereoisomer as the major product. To rationalize the stereochemical course of this oxyfunctionalization, a graphical representation of the proposed transition states are exhibited in Scheme 1. Since NMR spectra showed a well-defined set of signals, it is assumed that these titanium enolates **2** exist in monomeric form as their chloro percursors **1**[4a–d]. In accordance to literature[11], we suppose that also in these complexes the titanium metal is located in the $C{=}C^2{-}O^1$ plane of the enolate double bond. The two possible conformations of the enolate moiety in the complex **2a**, **b** readily interconvert by 180° rotation around the $C^2{-}O^1$ bond. Thus, the major (*R*)-**5** isomer is derived through attack of the oxidant from the *re* side of the enolate (Scheme 1). In view of the fact that the stereoselectivity is not influenced whether or not the trimethylsilyl group is present in the cyclopentadienyl ligand, this corroborates attack of the dioxirane predominantly from the lower side of the enolate complex **2a**, **b**. As we note in Scheme 1, one aryl group of the diol ligand assumes an axial position, which obliges the trimethylsilyl group to point preferentially towards the enolate moiety. The moderate enantioselectivities for the titanium complexes **2a**, **b** derived presumably from insufficient steric discrimination between the two possible conformations of the enolate ligand. By the use of the bulky 1-naphthyl group in complex **2e** instead of the phenyl groups in complex **2a**, the steric discrimination of the two conformers seems to be more pronounced and, indeed, the highest enantioselectivity (63% ee) was obtained for the oxidation of complex **2e** by dimethyldioxirane.

By replacing the cyclopentadienyl ligand by the more flexible isopropoxy group as in complex **2c**, nearly no steric discrimination is offered towards the attacking dioxirane so that selectivity for the enolate complex **2c** is dramatically reduced to only 5% ee; moreover, the (*S*)-**5** isomer is produced. In addition, complex **2c** should, like its chloro precursor **1c** have a dimeric or even oligomeric structure[10], and, therefore the structural features of the complex **2c** in Scheme 1 no longer apply for the titanium enolate, and mechanistic interpretations become more difficult.

The results for the oxidation of titanium enolates **2a**, **b**, **d** with oxaziridine as oxidant were rather unexpected in that lower enantioselectivities were obtained than for dioxirane. In fact, the sterically most demanding enolate complex **2e** resisted oxidation by the oxaziridine. For the enantioselective oxidation of lithium enolates by chiral oxaziridines calculations suggested that the coordination of the oxidant to the lithium cation plays a prominent role to account for the observed selectivities[12]. Thus, it was expected that the use of oxaziridine should through its coordination to the chiral metal center result in better stereoselectivity than that of the dioxirane oxidant. Presumably the titanium(IV) atom in the enolate complex **2** is sterically overloaded to allow such coordination, and consequently the enantioselectivity is low.

Scheme 1. Oxidation of the titanium enolates **2** by dimethyldioxirane (**3**)



	R^2	R^3	Ar	E
a	Me	Me	Ph	H
b	Me	Me	Ph	$SiMe_3$
d	H	*t*Bu	Ph	H
e	Me	Me	1-Naphthyl	H

In summary, the present results demonstrate that dimethyldioxirane oxidation of optically active titanium enolates proceed enantioselectively with up to 63% ee. Further variations of the metal center, the chiral ligand sphere, and the oxidant should prove worthwhile in optimizing the enantioselectivity of such oxyfunctionalizations.

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Experimental

Melting points: Büchi 535. – IR: Perkin-Elmer 1420. – ^1H and ^{13}C NMR: Bruker AC 200 (200 MHz) or WM 250 (250 MHz); chemical shifts refer to TMS. – HPLC: Pump: Waters twin 510; detector: Waters 486 (λ = 254 nm); column: Chiralcel OD, Daicel Chemical Industries, Ltd. – All solvents were purified by standard literature methods; THF and diethyl ether were distilled under Ar from potassium/benzophenone. – Complexes **1a**[4a], **1b**[4b] and **1c**[10] and 3-phenyl-2-phenylsulfonyloxaziridine[9] (**4**) were prepared according to literature procedures. LDA was synthesized and standardized according to the literature procedure[13] and used as a

stock solution in THF. Dimethyldioxirane (**3**) was prepared as acetone solution by following the published procedure[5] and dried over molecular sieves (4 Å) at −20°C before use. All glassware employed in the preparation of the organometallic compounds was vacuum-dried (heat gun/0.1 Torr), and all reactions with the enolate complexes were run under Ar.

Chloro(η⁵-cyclopentadienyl)[(4R,5R)-2-(1,1-dimethylethyl)-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanolato(2−)-O^α,O^α']titanium (**1d**): 5.19 g (10.5 mmol) of (4*R*,5*R*)-2-(1,1-dimethylethyl)-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanol[10,14] was suspended in 100 ml of cyclohexane, and ca. 90 ml thereof was again removed by distillation under Ar. After cooling to room temperature, 80 ml of dry Et_2O and 2.30 g (10.5 mmol) of $CpTiCl_3$[15] were added. To this reaction mixture was added within 1 h a solution of 2.34 g (23.1 mmol) of triethylamine in 25 ml of Et_2O, and stirring was continued for 64 h at this temperature. The solid material was collected by filtration under Ar and the residue extracted with boiling toluene (2 × 50 ml). The combined toluene filtrates were concentrated under vacuum (40°C/0.1 Torr) to ca. 15 ml until the first crystals precipitated and was then left standing for 48 h at 5°C for complete crystallization. The complex **1d** was collected by filtration under Ar to yield 2.14 g (33%) of a colorless solid. The mother liquor was concentrated to ca. 1 ml, 10 ml of pentane was added, and on standing an additional 0.91 g (12%) of a colorless powder was obtained. The total yield was 3.05 g (45%). The diastereomeric ratio was determined by ^{1}H-NMR integration of the *tert*-butyl (δ = 0.59 and 0.85) and the C_5H_5 signals (δ = 6.21 and 6.51) and was found to be 81:19 for both fractions. – IR (CH_2Cl_2): $\tilde{\nu}$ = 3025 cm^{-1}, 2955, 2900, 2870, 1595, 1487, 1460, 1415, 1194, 1095, 1060, 1037, 1013, 969, 922, 820, 640. – ^{1}H NMR (200 MHz, $CDCl_3$) for main diastereoisomer: δ = 0.85 (s, 9H, *t*Bu), 3.38 (s, 1H, 2-H), 4.77 (d, *J* = 6.57 Hz, 1H, 4- or 5-H), 4.87 (d, *J* = 6.59 Hz, 1H, 5- or 4-H), 6.21 (s, 5H, C_5H_5), 7.18−7.72 (m, 20H, arom. H). – ^{13}C NMR (50 MHz, $CDCl_3$) for main diastereoisomer: δ = 24.6 (q), 33.2 (s), 80.3 (d), 83.4 (d), 96.9 (s), 97.5 (s), 108.9 (d), 141.5 (s), 142.5 (s), 146.4 (s), 146.6 (s); arom. C atoms (d) for main and minor diastereoisomers: δ = 126.8 (d), 126.9 (d), 127.0 (d), 127.3 (d), 127.4 (d), 127.5 (d), 127.6 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.5 (d), 128.9 (d). – ^{1}H NMR (200 MHz, $CDCl_3$) for minor diastereomer: δ = 0.59 (s, 9H, *t*Bu), 3.40 (s, 1H, 2-H), 4.76 (d, *J* = 6.33 Hz, 1H, 4- or 5-H), 5.08 (d, *J* = 6.32 Hz, 1H, 5- or 4-H), 6.51 (s, 5H, C_5H_5), 7.18 (m, 20H, arom. H). – ^{13}C NMR (50 MHz, $CDCl_3$) for minor diastereomer: δ = 24.2 (q, C-7), 33.1 (s, C-6), 79.4 (d, C-4 or -5), 80.2 (d, C-5 or -4), 97.0 (s, C-8 or -9), 97.1 (s, C-9 or -8), 109.4 (d, C-2), 141.4 (s), 142.2 (s), 145.7 (s), 146.1 (s). – $C_{38}H_{37}ClO_4Ti$ (641.0): calcd. C 71.20, H 5.82; found C 70.91, H 5.80.

Chloro(η⁵-cyclopentadienyl)[(4R,5R)-2,2-dimethyl-α,α,α',α'-tetrakis(1-naphthyl)-1,3-dioxolane-4,5-dimethanolato(2−)-O^α,O^α']titanium (**1e**) (as diethyl ether solution): 1.59 g (2.22 mmol) of (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-α,α,α',α'-tetrakis(1-naphthyl)-4,5-dimethanol[14] · 0.5 C_6H_{12} was suspended in 20 ml of cyclohexane, and ca. 18 ml thereof was removed by destillation under Ar. After cooling to room temperature, 20 ml of dry Et_2O and 489 mg (2.22 mmol) of $CpTiCl_3$[15] were added. To this reaction mixture was administered within 30 min a solution of 494 mg (4.88 mmol) of triethylamine in 5 ml of Et_2O, and stirring was continued for 24 h at this temperature. The precipitated $Et_3N \cdot HCl$ was collected by filtration under Ar and washed with 5 ml of Et_2O. The concentration of the stock solution of complex **1e** in Et_2O was estimated to be 0.065 M on the basis of isolated $Et_3N \cdot HCl$ (587 mg, 96%).

General Procedure for the Oxidation of the Titanium Enolates **2** *by Dimethyldioxirane* (**3**): 1.0 equiv. of propiophenone (0.5−0.4 mmol) was added dropwise under Ar to 1.1 equiv. of a cold LDA solution in THF at −78°C. After stirring for ca. 30 min, to the reaction mixture was slowly added at −78°C a solution of 1.0 equiv. of complex **1** in ca. 10 ml THF (in the case of **1e**, an equimolar amount of the stock solution of **1e** in Et_2O was used), and stirring was continued for 3 h at the respective temperature (see Table 1). The resulting yellow solution was cooled to the desired temperature (see Table 1), and 1.2 equiv. of an equally cold 0.08−0.1 M solution of dimethyldioxirane (**3**) in acetone was rapidly added while vigorously stirring. After 1 min, the reaction mixture was hydrolyzed by addition of 1 ml of a satd. aqueous NH_4F solution per 0.5 mmol of complex **1**, the mixture was stirred for ca. 12 h at room temperature, filtered through Celite, and concentrated under vacuum (20°C/20 Torr). The residue was taken up in ca. 15 ml of *tert*-butyl methyl ether and dried with Na_2SO_4. The solvent was evaporated under vacuum (20°C/20 Torr), and the residue was purified by column chromatography [silica gel; petroleum ether (boiling range 50−60°C)/*tert*-butyl methyl ether (3:1)]. The enantiomeric excess (% ee) was determined on a chiral HPLC column [Chiracel OD; *n*-hexane/2-propanol (9:1) as eluent; flow rate 0.6 ml/min]. The retention times for the two enantiomers were 14.9 min for (*S*)-**5** and 16.7 min for (*R*)-**5**. The optical purity and absolute configuration were determined by optical measurements and comparison with the reported values[3c]. The spectral data matched those reported.

General Procedure for the Oxidation of Titanium Enolates **2** *by 3-Phenyl-2-phenylsulfonyloxaziridine* (**4**): 1.0 equiv. of the lithium enolate of propiophenone (0.5−0.4 mmol) was slowly treated at −78°C with 1.0 equiv. of **1a−e**. After complete addition, the dry ice/acetone cooling bath (−78°C) was replaced by an ice bath (0−5°C), and stirring was continued for 3 h. The reaction mixture was cooled again to −78°C, and 1.2 equiv. of the oxaziridine **4**, dissolved in 2 ml of THF, was added dropwise to the enolate solution. After 30 min, the reaction mixture was hydrolyzed by addition of 1 ml of a satd. aqueous NH_4F solution per 0.5 mmol of complex **1**, the mixture was stirred for ca. 12 h at room temperature, filtered through Celite, and dried with Na_2SO_4. The solvent was evaporated under vacuum (20°C/20 Torr) and the residue purified by column chromatography [silica gel; petroleum ether (boiling range 50−60°C)/*tert*-butyl methyl ether (3:1)]. The enantiomeric excess was determined as described above.

☆ Dedicated to Professor *Helmut Werner* on the occasion of his 60th birthday.

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