Dimethyldioxirane Oxidation of Titanium Enolates: Diastereoselective α-Hydroxylations

Waldemar Adam,* Michael Müller,[1] and Frank Prechtl

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

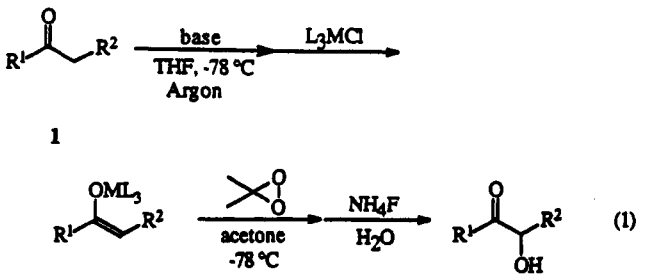
Received February 16, 1994•

The oxidation of titanium enolates, derived from a transmetalation reaction of the corresponding lithium enolates with $(i\text{-PrO})_3TiCl$, $(Et_2N)_3TiCl$, or Cp_2TiCl_2, by dimethyldioxirane has been investigated. Furthermore, the diastereoselective hydroxylation of the chiral metal enolates, e.g., derived from camphor (**1f**), menthone (**1g**), flavanone (**1h**), and 2-benzylcyclopentanone (**1i**), by dimethyldioxirane has been examined. The diastereoselectivity of the oxygen transfer strongly depends on the metal partner coordinated to the enolate. The titanium enolates **4** resulted in much higher diastereoselectivities (up to 96% de) than the corresponding sodium enolates **5** and at least as high if not higher than the silyl enol ethers **6**. Moreover, the aldol reaction of ester-derived sodium enolates with acetone, the unavoidable medium for dimethyldioxirane, could be totally suppressed by the use of the chlorotitanocene enolates **4**. Thus, the oxidation of chiral titanium enolates by dimethyldioxirane represents a general, convenient, effective, and chemo- and diastereoselective synthesis of α-hydroxy carbonyl compounds.

The importance of α-hydroxy carbonyl compounds in organic synthesis has encouraged the development of a variety of methods for their preparation.[2] The most prominent method is the oxidation of enolates by an electrophilic oxygen atom source.[3] In this context, recently it was demonstrated that the oxidation of sodium[4] and lithium[5] enolates by dimethyldioxirane constitutes a convenient synthetic method for acyloins. In the course of our investigations, however, we observed that the oxidation of chiral sodium enolates exhibited poor diastereoselectivity. Moreover, the aldol reaction, especially of ester-derived enolates with acetone, the unavoidable medium for dimethyldioxirane, took place as a side reaction. To circumvent these practical problems, a modification of the dioxirane oxidant seemed unadvisable because dimethyldioxirane is readily prepared[6] and convenient to work with.[7] It appeared more advantageous to modify the metal partner of the enolate, e.g., the use of titanium enolates. On one hand, much valuable data has been accumulated during the last years on the persistence and reactivity of titanium enolates and their use in synthesis, especially in the C–C bond-forming reaction;[8] on the other hand, their deliberate oxidation appears not to have been investigated. Through the variation of the ligands of such titanium enolates, by starting with the proper chlorotitanate and by employing chiral enolates, the opportunity presents itself for diastereoselective oxidations with dimethyldioxirane and suppression of the aldol side reaction. That this is, indeed, the case is demonstrated in the present contribution.

Results

The titanium enolates **2**–**4** were prepared by reacting the lithium enolates with the proper chlorotitanium reagents (eq 1). All attempts to isolate the titanium enolate



2: $ML_3 = Ti(O\text{-}i\text{-}Pr)_3$
3: $ML_3 = Ti(NEt_2)_3$
4: $ML_3 = Ti\,Cp_2Cl$
5: $ML_3 = Na$
6: $ML_3 = SiMe_3$

2a failed, and by ^1H NMR spectroscopy not even traces could be observed. The literature-known titanium enolate

• Abstract published in *Advance ACS Abstracts*, April 15, 1994.

(1) Undergraduate research participant, fall 1990.

(2) (a) Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319–4322. (b) Rubottom, G. M.; Marrero, R. *J. Org. Chem.* **1975**, *40*, 3783–3784. (c) Brown, H. C.; Pai, G. G. *J. Org. Chem.* **1985**, *50*, 1384–1394. (d) Helmchen, G.; Wierzchowski, R. *Angew. Chem.* **1984**, *96*, 59–60; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 60–61. (e) Wong, C. H.; Matos, J. R. *J. Org. Chem.* **1985**, *50*, 1992–1994. (f) D' Accolti, L.; Detomaso, A.; Fusco, C.; Rosa, A.; Curci, R. *J. Org. Chem.* **1993**, *58*, 3600–3601. (g) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949–3954.

(3) (a) Davis, F. A.; Vishwakarma, L. C.; Billmers, J. M. *J. Org. Chem.* **1984**, *49*, 3241–3243. (b) Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703–5742. (c) Davis, F. A.; Sheppard, A. C.; Chen, B.-C.; Haque, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 6679–6690. (d) Davis, F. A.; Chen, B.-C. *Chem. Rev.* **1992**, *92*, 919–934. (e) Gore, M. P.; Vederas, J. C. *J. Org. Chem.* **1986**, *51*, 3700–3704. (f) Camici, L.; Dembech, P.; Ricci, A.; Seconi, G.; Taddei, M. *Tetrahedron* **1988**, *44*, 4197–4206. (g) Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188–196. (h) Vedejs, E.; Larsen, S. *Org. Synth.* **1985**, *64*, 127–137. (i) Gamboni, R.; Tamm, C. *Helv. Chim. Acta* **1986**, *69*, 615–620. (j) Anderson, J. C.; Smith, S. C. *Synlett* **1990**, 107–108.

(4) Adam, W.; Prechtl, F. *Chem. Ber.* **1991**, *124*, 2369–2372.

(5) Guertin, K. R.; Chan, T.-H. *Tetrahedron Lett.* **1991**, *32*, 715–718.

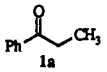
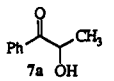
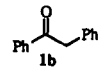
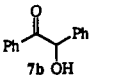
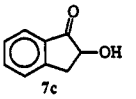
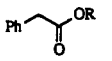
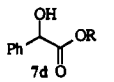
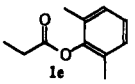
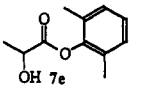
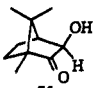
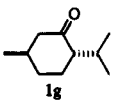
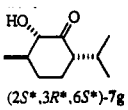
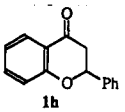
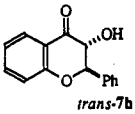
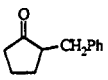
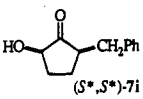
(6) (a) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847–2853. (b) Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377.

(7) (a) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205–211. (b) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187–1201. (c) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich, CT, 1990; Vol. 2, Chapter I, p 1. (d) Adam, W.; Hadjiarapoglou, L.; Curci, R.; Mello, R. In *Organic Peroxides*; Ando, W., Ed.; Wiley Interscience: Chichester, 1992; pp 195–216. (e) Adam, W.; Hadjiarapoglou, L. *Top Curr. Chem.* (Herrmann, W. A., Ed.) **1993**, *164*, 45–62.

(8) (a) Reetz, M. T.; Peter, R. *Tetrahedron Lett.* **1981**, *22*, 4691–4694. (b) Reetz, M. T. *Pure Appl. Chem.* **1985**, *57*, 1781–1788. (c) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer Verlag: Berlin, 1986. (d) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855–1859. (e) Manriquez, J. M.; Donald, R.; Mc Alister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724. (f) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650–2659. (g) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *104*, 5499–5500.

0022-3263/94/1959-2358$04.50/0

Table 1. Oxidation of Metal Enolates by Dimethyldioxirane (as Acetone Solution)

entry	substrate	base[a]	L_3MCl	convn (%)[b]	yield[c] (%)	de[b] (%)	product[d]
1	 1a	LDA	$(i\text{-PrO})_3TiCl$	51	88(45)		 7a
2		LDA	$(Et_2N)_3TiCl$	32[e]	90(29)		
3		LDA	$(Et_2N)_3TiCl$	98[f]	92(90)		
4		LDA	Cp_2TiCl_2	91	85(77)		
5	 1b	LDA	Cp_2TiCl_2	73	96(70)		 7b
6	 1c	NaHMDS		89	36(32)[g]		 7c
7		LDA	$(i\text{-PrO})_3TiCl$	85	59(50)[h]		
8		LDA	Cp_2TiCl_2	85	82(70)		
9	 1d	NaHMDS		90[i]	67(60)[j]		 7d
10		LDA	$(i\text{-PrO})_3TiCl$	85[k]	14(12)[l]		
11		LDA	Cp_2TiCl_2	71[k]	96(67)		
12	 1e	LDA	Cp_2TiCl_2	87	76(65)		 7e
13	 1f	NaHMDS		75	76(57)	34	 exo-7f
14		LDA		79	89(70)	50	
15		LDA	Me_3SiCl	>98	91(91)	86	
16		LDA	Cp_2TiCl_2	71	94(67)	84	
17	 1g	NaHMDS		76	83(63)	34	 (2S*,3R*,6S*)-7g
18		LDA	Me_3SiCl	>98	97(97)	52	
19		LDA	Cp_2TiCl_2	63	86(54)	92	
20	 1h	NaHMDS		73	51(37)	80	 trans-7h
21		LDA	Me_3SiCl	>98	85(85)	>96	
22		LDA	Cp_2TiCl_2	83	64(53)	>96	
23	 1i	NaHMDS		51	73(37)	6[m]	 (S*,S*)-7i
24		LDA	Me_2SiCl	>98	96(96)	30	
25		LDA	Cp_2TiCl_2	56	89(50)	66	

[a] LDA was used as 0.83–0.40 M stock solution in THF; NaHMDS was used as 0.83–0.40 M stock solution in THF. [b] Determined by ^1H NMR analysis of the crude reaction mixture (error ±3%). [c] Yields corrected for converted starting material; in parentheses are given yields of isolated product. [d] Main diastereomer is shown. [e] 1.5 equiv of dimethyldioxirane was used. [f] 5.0 equiv of dimethyldioxirane was used. [g] By column chromatography also 51% of **8c** was isolated. [h] By column chromatography also 11% of **8c** was isolated. [i] R = Me (see ref 16). [j] By column chromatography also 22% of **8d** (R = Me) was isolated. [k] R = *t*-Bu. [l] By column chromatography also 53% of **8d** (R = *t*-Bu) was isolated. [m] (*S**,*R**)-**7i** was obtained as the main diastereomer.

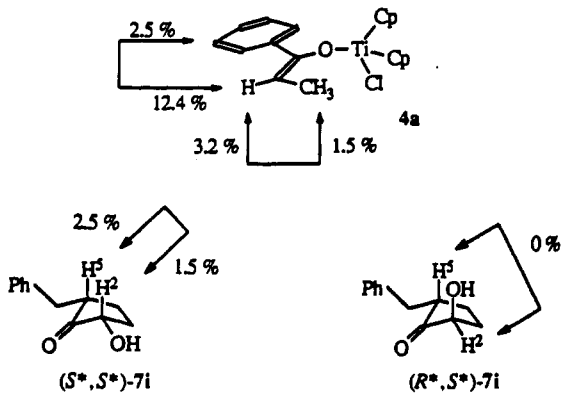
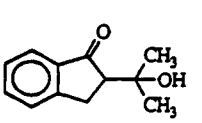


Figure 1. NOE results for the titanium enolate **4a** and the diastereomeric α-hydroxycyclopentanones (*S**,*S**)-**7i** and (*R**,*S**)-**7i**.

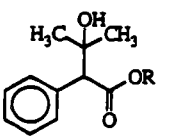
3a,[8a–c] however, could be prepared and isolated without difficulties by following the published procedure. The reaction sequence for **3a** served also for the preparation of the titanium enolate complex **4a** derived from Cp_2TiCl_2 as titanium reagent. The chlorotitanocene enolate **4a** was obtained as a brown powder in 65% yield after recrystallization from ether/pentane (eq 1). The titanium enolate **4a** is not stable at room temperature and decomposes within 1 week. In solution, complex **4a** is inert toward dry molecular oxygen, but it is very sensitive toward moisture.

The *Z* double bond geometry was determined by an NOE experiment (Figure 1). Irradiation of the phenyl ^1H resonances resulted in 12.4% enhancement of the olefinic proton and *vice versa* 2.5%, but no effects on the methyl group. Examination of the crude reaction mixture confirmed that only the *Z* diastereomer was formed during the transmetalation reaction.

The oxidation of the titanium enolates **2–4** with dimethyldioxirane in acetone solution (eq 1) was performed at −78 °C (Table 1) and in all cases gave only the corresponding α-hydroxy carbonyl products **7a–i**, except entries 7 and 10, for which additionally the aldol products **8c,d** were also obtained by reaction of the titanium enolate **2c,d** with acetone.

gi 

8c



8d

The titanium enolates **2a,c,d** which bear three isopropoxy ligands at the central metal, gave on oxidation with

dimethyldioxirane only in low conversions the corresponding hydroxylated products **7a** (51%), **7c** (59%), and **7d** (14%). For enolates **2c,d** (entries 7 and 10), the aldol products **8c,d**, which were the side products in the oxidation of the sodium enolates **5c,d** (entries 6 and 9; for synthesis and oxidation cf. ref 4), could not be suppressed by the use of the Ti(O-*i*-Pr)$_3$ moiety (for **2d** the aldol product **8d** even became the major product).

The titanium enolates with three diethylamino ligands at the titanium, as represented in complex **3a**, behaved problematically on treatment with dimethyldioxirane in that the enolate moiety as well as the amino ligands were oxidized. Thus, only 32% conversion was obtained by using a 1.5-fold excess (entry 2) of dimethyldioxirane, for complete conversion a 5-fold excess of the oxidant was necessary (entry 3). Because of this unselective behavior of the dimethyldioxirane oxidation, the titanium enolates **3** were not further investigated.

The titanium enolates **4a–i** with two cyclopentadienyl ligands and one chloro ligand at the titanium reacted, compared to enolates **2** and **3**, very selectively and in good conversions with dimethyldioxirane to yield the corresponding α-hydroxy products **7a–i** as the only products. For the enolates **4c,d** (entries 8 and 11) even the formation of the aldol products **8c,d** was totally suppressed. Furthermore, this method is not limited to β-arylated esters since the oxidation of the propionate enolate **4e** also yielded selectively the lactate **7e**, the first example for the synthesis of an aryl lactate. Indeed, despite the steric hindrance, the aryl lactate **7e** is quite sensitive toward moisture and the workup needed to be done quickly, and carefully dried solvents are essential for the column chromatography.

The dimethyldioxirane oxidation of the chiral titanium enolates **4f–i** (entries 16, 19, 22, and 25) resulted in good to excellent diastereomeric excesses (de) of the corresponding hydroxylated products **7f–i**. In comparison, the titanium enolates **4f–i** gave much higher de values than the corresponding sodium enolates **5f–i** and at least as high if not higher than the silyl enol ethers **6f–i**. For example, in the case of camphor (**1f**), the sodium enolate **5** exhibited the lowest de value (de 34%, entry 13), followed by the lithium enolate (de 50%, entry 14), and the highest selectivity was reached for the titanium enolate **4f** (de 84%, entry 16) and the silyl enol ether **6f** (de 86%, entry 15). The same trend was also observed for the enolates derived from menthone (**1g**), flavanone (**1h**) and the cyclopentanone derivative **1i**, for which the sodium enolates **5g** (de 34%, entry 17), **5h** (de 80%, entry 20), and **5i** (de 6%, entry 23) resulted in the lowest diastereoselectivities in the oxidation with dimethyldioxirane. Again, the de values increased for the silyl enol ethers **6g** (de 52%, entry 18), **6h** (de >96%, entry 21), and **6i** (de 30%, entry 24) and reached the maximum for the titanium complexes **4g** (de 92%, entry 19), **4h** (de >96%, entry 22), and **4i** (de 66%, entry 25). Control experiments established that no epimerization took place under these oxidation conditions.

The conversion for the titanium enolates **4g–i** was always lower than for the other examples. The reason for this is that the temperature in the transmetalation reaction could not be raised to 0 °C as for **4a–f**, but had to be kept below −50 °C for several hours to ensure that the lithium enolates were consumed. However, under these reaction conditions, some of the titanium complexes already decomposed to form back the starting material. At higher temperatures the lithium enolates of **1g,i** partially isomerized to the thermodynamically more stable analogs and lower yields of the desired products **7g,i** were obtained. Such isomerization does not occur for titanium enolates.[8g] In the case of the flavanone derivative **4h**, at temperatures higher than −50 °C, decomposition of the enolate to the corresponding *ortho*-hydroxy chalcone occurred.

The stereochemical assignment of the products **7f**[9] and **7h**[10] has been reported. The stereochemistry of the product **7g** was determined by comparison of the coupling $J_{2,3}$ constants of both diastereomers. The main diastereomer (2*S**,3*R**,6*S**)-**7g** possesses a coupling constant of $J_{2,3}$ = 10.1 Hz, which corresponds to *trans* coupling, while for the minor isomer (2*R**,3*R**,6*S**)-**7g**, in agreement with the literature,[11] $J_{2,3}$ = 6.2 Hz corresponds to *cis* coupling.

The assessment of the stereochemistry of the main diastereomer of product **7i** was more difficult. The major isomer of **7i** displays *W* coupling between the 2-H and the 5-H protons, as established by an decoupling experiment (Figure 1), which is consistent with the (*S**,*S**)-**7i** diastereomer. Additionally, an NOE experiment was carried out, which for the major isomer resulted in an enhancement of 2.5% of the 5-H proton on irradiation of the 2-H proton and *vice versa* a 1.5% effect, but no enhancement for the minor isomer. Both experimental facts taken together strongly support the proposed configuration of the main isomer as (*S**,*S**)-**7i**.

Discussion

The hydroxylation of metal enolates by dimethyldioxirane represents a chemoselective way for the synthesis of α-hydroxy carbonyl compounds. In no case of the investigated examples was overoxidation to the corresponding 1,2-dicarbonyl compound observed. For example, in the oxidation of the sodium or titanium enolate of desoxybenzoin (**1b**), the hydroxylated product benzoin (**7b**) was the only product, while for other oxidants like the MoO_5·HMPT·pyridine (MoOPH)[3g] complex or its 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone derivative (MoOPD)[3j] overoxidation to the extent of 39% or 15% was observed.

Our previously reported hydroxylation[4] of carbonyl compounds by dimethyldioxirane, in which sodium enolates were employed, was substantially improved by the use of the titanium enolates, particularly with respect to diastereoselectivity. Thus, since the diastereoselectivity of the oxygen transfer by the dioxirane strongly depends on the metal counterion, the selectivity increases quite generally from the small and only weakly coordinated sodium enolates **5** to the sterically more demanding silyl enols **6** and is highest for the sterically most demanding titanium enolates. Consequently, in view of this trend in the diastereoselectivity, i.e., the steric size of the metal fragment ligated to the enolate, direct coordination of the dioxirane to the metal center appears not to be of significance.

Of note is the preferential *exo* diastereoselectivity in the DMD oxidation of camphor (**1f**), irrespective whether sodium (entry 13), lithium (entry 14), silylated (entry 15), or titanium (entry 16) enolates are employed. This is opposite to the α hydroxylations by the transition metal

(9) Thoren, S. *Acta. Chem. Scand.* **1970**, *24*, 93–98.
(10) Moriarty, R. M.; Prakash, O. *J. Org. Chem.* **1985**, *50*, 151–153.
(11) Friedrich, E.; Lutz, W. *Chem. Ber.* **1980**, *113*, 1245–1263.

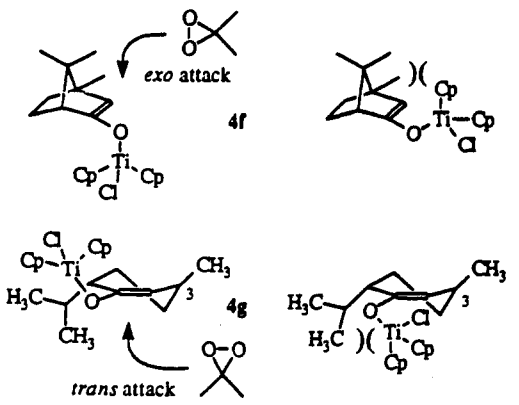


Figure 2. Possible conformations in the oxidation of the chiral titanium enolates **4f** and **4g** by dimethyldioxirane.

oxidants MoOPH[3g] and MoOPD,[3j] for which predominant *endo* diastereoselectivity has been observed in the case of the lithium enolate. This opposite sense in the diastereoselectivity of oxygen transfer between these oxidants appears to be general, since in the α hydroxylation of the menthone enolates, DMD afforded preferentially the (2*S**,3*R**,6*S**)-**7g** diastereomer for the sodium (entry 17), silylated (entry 18), and titanium (entry 19) enolates, while MoOPH[3g] and MoOPD[3j] gave (2*R**,3*R**,6*S**)-**7g** as major product for the lithium enolate.

The limited data on hand do not allow a mechanistic rationalization of these opposite diastereoselectivities between DMD and the transition metal oxidants MoOPH and MoOPD; nevertheless, steric effects appear to operate in the DMD oxidation of the titanium enolates **4f,g**, in which the bulky titanium fragment blocks efficiently one side of the enolate plane. In the case of the camphor titanium enolate **4f**, due to steric interactions with the dimethyl-substituted bridge, the titanium fragment is located predominantly at the *endo* side, which obliges preferential *exo* attack of the dioxirane (Figure 2). In the case of the menthone titanium enolate **4g**, steric interactions with the isopropyl group forces the titanium fragment on the opposite side of the enolate plane and the dioxirane attacks *trans* to the 3-methyl group (Figure 2). Thus, the present novel method offers a convenient and stereoselective synthesis of hitherto difficult to prepare diastereomers.

In the reaction of the sodium enolates of 1-indanone (**1c**) and of the esters **1d** with dimethyldioxirane, hydroxylation by the dioxirane was competed for by aldol reaction of the enolate with acetone (solvent), through which substantial amounts of the aldol products **8c,d** were formed. By the use of the titanium enolates **4c,d**, the aldol reaction was completely suppressed, as confirmed by NMR spectroscopy of the crude reaction mixture since only the hydroxylated products **7c,d** were detected. This chemoselectivity can be rationalized by the fact that in the case of the substantially more covalently bound titanium enolate compared to the more ionic sodium enolate, the nucleophilicity of the enolate is significantly decreased.[8c] The much higher chemoselectivity of the chlorotitanocene enolates **4c,d** compared to the triisopropoxy enolates **2c,d** is presumably based on the lower Lewis acidity of the former.[8c] Thus, lower electrophilic activation of the acetone carbonyl group by the titanium fragment is expected and a preferential reaction with the more electrophilic dioxirane results.

In summary, we have demonstrated that the oxidation of chlorotitanocene enolates by dimethyldioxirane constitutes a convenient and general method for the synthesis of α-hydroxy ketones and esters. The diastereoselectivity of the oxygen transfer strongly depends on the metal partner coordinated to the enolate. The titanium enolates **4** resulted in the highest diastereoselectivities (up to 96% de), i.e., much better than the sodium enolates **5** and at least as good if not better than the silyl enol ethers **6**. Moreover, the aldol reaction of ester-derived sodium enolates with acetone, the unavoidable medium for dimethyldioxirane, can be totally suppressed by the use of the chlorotitanocene enolates **4**. Thus, the α hydroxylation of titanium enolates by dimethyldioxirane offers an effective chemo- and diastereoselective preparation of α-hydroxy carbonyl compounds.

Experimental Section

Melting points: Büchi 535. IR: Perkin-Elmer 1420. ^{1}H and ^{13}C NMR: Bruker AC 200 (200 MHz) or WM 250 (250 MHz); chemical shifts refer to TMS. All solvents were purified by standard literature methods; THF and diethyl ether were distilled under an argon gas atmosphere from potassium/benzophenone. The silyl enol ethers **6f**,[12] **6g**,[11] and **6h**[13] were synthesized as described for **6i**; the titanium complexes **3a**,[8a,c] (i-PrO)$_3$TiCl,[14] (Et_2N)$_3$TiCl,[15] and Cp_2TiCl_2[16] were prepared according to literature. LDA was prepared and titrated according to the literature procedure[3h] and used as a stock solution in THF. Dimethyldioxirane (as acetone solution) was prepared following the published procedure[6] and dried for 2 days over molecular sieves (4 Å) at −20 °C before use. All glassware employed in the preparation of organometallic compounds was dried under vacuum (heat gun/0.1 Torr), and all their reactions were run under an argon gas atmosphere.

2-Hydroxy-1-phenyl-1-propanone (7a) by Oxidation of Titanium Complex 2a with Dimethyldioxirane. A 3.20-mL (2.40 mmol) portion of 0.75 M LDA solution in THF was cooled under an argon gas atmosphere to −78 °C and a solution of 268 mg (2.00 mmol) of **1a** in 2 mL of dry THF was added dropwise with stirring. After 30 min, 2.25 mL of a 1.05 M (2.36 mmol) (i-PrO)$_3$TiCl solution in pentane was added, and the reaction mixture was allowed to reach −30 °C within 1 h. After the mixture was cooled to −78 °C, 34 mL of a 0.0700 M solution (2.38 mmol) of dimethyldioxirane cooled at −78 °C was rapidly added under vigorous stirring. After 1 min, the reaction mixture was hydrolyzed by the addition of 2 mL of an aqueous, saturated NH_4F solution, and stirring was continued for 1 h at room temperature. The reaction mixture was filtered over Celite, and the filtrate was concentrated under vacuum (20 °C/20 Torr) to about 1 mL. The residue was taken up in about 40 mL of *tert*-butyl methyl ether and dried over $MgSO_4$. The solvent was evaporated under vacuum (20 °C/20 Torr), and the residue was purified by column chromatography (silica gel, 3:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether) to yield 134 mg (45%) of **7a** as a colorless oil (for spectral data see above).

2-Hydroxy-1-indanone (7c) and 2-(1-Hydroxy-1-methylethyl)-1-indanone (8c) through Oxidation of Titanium Enolate 2c with Dimethyldioxirane. By following the procedure for the oxidation of **2a**, 92.0 mg (50%) of **7c** and 21.0 mg (9%) of **8c** were obtained as oils, after column chromatography (silica gel, 6:1 CH_2Cl_2/*tert*-butyl methyl ether), by starting from 165 mg (1.25 mmol) of **1c**, 1.50 mL of a 1.05 M (1.58 mmol) (i-PrO)$_3$TiCl solution in pentane, and 20 mL of a 0.0740 M (1.48

(12) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437–6445.
(13) (a) Morita, H. *J. Chromatogr.* **1974**, *101*, 189–192. (b) Li, L.; Rui, Y. *Beijung Daxue Xuebao, Ziran Kexueban* **1990**, *26*, 421–428; *Chem. Abstr.* **1991**, *114*, 185079w. (c) Li, L.; Rui, Y. *Gaodeng Xuexiao Huaxue Xuebao* **1991**, *12*, 777–779; *Chem. Abstr.* **1992**, *116*, 128581w.
(14) Reetz, M. T.; Steinbach, R.; Kesseler, K. *Angew. Chem. Suppl.* **1982**, 1899–1905.
(15) Reetz, M. T.; Urz, R.; Schuster, T. *Synthesis* **1983**, 540.
(16) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281–4284.

mmol) dimethyldioxirane solution. The spectral data for **7c**[17] and **8c**[18] match those reported.

***tert*-Butyl 2-Hydroxy-2-phenylacetate (7d) and *tert*-Butyl 2-(1-Hydroxy-1-methylethyl)-2-phenylacetate (8d) through Oxidation of Titanium Enolate 2d with Dimethyldioxirane.** By following the procedure for the oxidation of **2a**, 50.0 mg (12%) of **7d** as a colorless amorphous solid, mp 65–66 °C (lit.[2c] mp 66–67 °C), and 223 mg (45%) of **8d** as colorless needles, mp 54–55 °C, were obtained after column chromatography (silica gel, 4:1 CH_2Cl_2/*tert*-butyl methyl ether), by starting from 165 mg (1.25 mmol) of **1c**, 1.50 mL of a 1.05 M (1.58 mmol) $(i\text{-PrO})_3TiCl$ solution in pentane, and 20 mL of a 0.0740 M (1.48 mmol) dimethyldioxirane solution. The spectral data for **7d**[2c] match those reported. Spectral data for **8d**: IR (CCl_4) 3480 cm^{-1} (OH), 3065, 3040, 3005, 2950, 2907, 1688 (C=O), 1583 (C=C); ^1H NMR (200 MHz, $CDCl_3$) δ 1.02 (s, 3 H), 1.37 (s, 9 H), 1.41 (s, 3 H), 3.46 (s, 1 H), 3.91 (s, 1 H, O*H*), 7.26–7.41 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.8 (q), 27.9 (q), 29.6 (q), 61.0 (d), 71.7 (s), 81.7 (s), 127.3 (d), 128.1 (d), 129.5 (d), 135.7 (s), 173.8 (s). Anal. Calcd for $C_{15}H_{22}O_3$ (250.3): C, 71.97; H, 8.86. Found: C, 71.66; H, 9.04.

2-Hydroxy-1-phenyl-1-propanone (7a) by Oxidation of Titanium Enolate 3a with Dimethyldioxirane with 1.5 Equiv of DMD. To a −78 °C cooled solution of 368 mg (0.930 mmol) of **3a** in pentane was rapidly added 20 mL of a 0.0740 M (1.48 mmol) dimethyldioxirane solution. After 1 min, the reaction mixture was hydrolyzed by the addition of 1 mL of an aqueous, saturated NH_4Cl solution and stirred for 1 h at room temperature. The reaction mixture was filtered over Celite, and the filtrate was concentrated under vacuum (20 °C/20 Torr) to about 1 mL. The residue was taken up in 20 mL of *tert*-butyl methyl ether, washed with 2 N HCl (2 × 5 mL) and a saturated, aqueous NaCl solution (5 mL), and dried over $MgSO_4$. After removal of the drying agent, the solvent was evaporated under vacuum (20 °C/20 Torr), and the residue was purified by column chromatography [silica gel, 3:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] to yield 40.0 mg (29%) of **7a** as a colorless oil. Its spectral data match those reported.[3c]

With 5.0 Equiv of DMD. By following the procedure for the oxidation of **3a**, 130 mg (90%) of **7a** was obtained after column chromatography (silica gel, 6:1 CH_2Cl_2/*tert*-butyl methyl ether) as a colorless oil by starting from 382 mg (0.960 mmol) of **3a** and 68 mL of a 0.0740 M (5.03 mmol) dimethyldioxirane solution (for spectral data see above).

Preparation of Chlorotitanocene Enolate 4a. A 1.60-mL (1.10 mmol) portion of 0.70 M LDA solution in THF was cooled under an argon gas atmosphere to −78 °C, and a solution of 134 mg (1.00 mmol) of **1a** in 2 mL of dry THF was added dropwise with stirring. After 30 min, a solution of 250 mg (1.00 mmol) of Cp_2TiCl_2 in 20 mL of dry THF was added within 15 min. The resulting red solution was allowed to reach 0 °C within 3 h. The solvent was removed by distillation under vacuum (0 °C/0.1 Torr), the residue was dissolved in 20 mL of dry ether, and the precipitated LiCl was removed by suction filtration under an argon gas atmosphere. The filtrate was concentrated under vacuum (0 °C/0.1 Torr) to 5 mL, and 30 mL of pentane was slowly added to the stirred solution. After 1 h of stirring at 0 °C, the brown precipitate was collected by suction filtration under an argon gas atmosphere, washed with small portions of pentane (2 × 2.5 mL), and dried under vacuum (20 °C/0.1 Torr) to yield 226 mg (65%) of a brown powder: mp 140 °C dec; ^1H NMR (200 MHz, $CDCl_3$) δ 1.72 (d, J = 6.97 Hz, 3 H), 4.98 (q, J = 6.96 Hz, 1 H), 6.33 (s, 10 H), 7.20–7.52 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.9 (q), 96.9 (d), 117.6 (d), 125.4 (d), 127.1 (d), 128.0 (d), 139.5 (s), 166.7 (s). Anal. Calcd for $C_{19}H_{19}ClOTi$ (346.7): C, 65.82; H, 5.52. Found: C, 65.40; H, 5.83.

General Procedure for the Oxidation of the Chlorotitanocene Enolates 4a–c and 4f–i by Dimethyldioxirane. One equiv of ketone **1** was added dropwise under an argon gas atmosphere to 1.1 equiv of a −78 °C cooled LDA solution in THF. After being stirred for about 30 min, to the reaction mixture was slowly added at −78 °C a solution of 1.1 equiv of titanocene dichloride in THF (about 0.06 M), the reaction mixture was allowed to reach 0 °C within 3 h, and the solvent was removed by distillation (0 °C/0.1 Torr). In the case of ketones **1f–h** the reaction mixture was kept at −50 °C for 12 h and the solvent was removed by distillation (−30 to −25 °C/0.1 Torr). The residue was cooled to −78 °C and taken up in 10 mL of CH_2Cl_2. To the reddish brown solution was rapidly added 1.2 equiv of a −78 °C cold 0.07–0.10 M solution of dimethyldioxirane in acetone under vigorous stirring. After 1 min, the reaction mixture was hydrolyzed by addition of 1 mL of a saturated, aqueous NH_4F solution, stirred for about 12 h at room temperature, filtered over Celite, and evaporated under vacuum (20 °C/20 Torr). The residue was taken up in about 20 mL of *tert*-butyl methyl ether and dried over Na_2SO_4. The solvent was evaporated under vacuum (20 °C/20 Torr) and the residue purified by column chromatography.

2-Hydroxy-1-phenyl-1-propanone (7a). By following the above procedure, 116 mg (77%) of **7a** was obtained as a colorless oil after column chromatography [silica gel, 3:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 134 mg (1.00 mmol) of **1a**, 275 mg (1.10 mmol) of Cp_2TiCl_2, and 13 mL of a 0.0920 M (1.20 mmol) dimethyldioxirane solution (for spectral data see above).

1-Hydroxy-β-phenylacetophenone (7b). By following the above procedure, 146 mg (70%) of **7b** was obtained as a colorless powder, mp 132–134 °C (lit.[19] mp 132–135 °C), after column chromatography [silica gel, 3:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether], by starting from 196 mg (1.00 mmol) of **1b**, 275 mg (1.10 mmol) of Cp_2TiCl_2, and 13 mL of a 0.0900 M (1.17 mmol) dimethyldioxirane solution. Its spectral data match those of the commercially available material.

2-Hydroxy-1-indanone (7c). By following the above procedure, 110 mg (70%) of **7c** was obtained as a pale yellow oil after column chromatography [silica gel, 6:1 CH_2Cl_2/*tert*-butyl methyl ether] by starting from 134 mg (1.00 mmol) of **1c**, 274 mg (1.10 mmol) of Cp_2TiCl_2, and 19 mL of a 0.0630 M (1.20 mmol) dimethyldioxirane solution (for spectral data see above).

3-Hydroxy-1,7,7-trimethyl[2.2.1]bicycloheptan-2-one (7f). By following the above procedure, 113 mg (67%) of **7c** was obtained as a colorless powder, mp 209–212 °C (lit.[9] *exo* isomer mp 210–211 °C), after column chromatography [silica gel, 2:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 152 mg (1.00 mmol) of **1f**, 274 mg (1.10 mmol) of Cp_2TiCl_2, and 13 mL of a 0.0920 M (1.20 mmol) dimethyldioxirane solution. The *exo*:*endo* ratio was 93:7, as determined by ^1H NMR analysis of the α-hydroxy protons *exo* 3-H [δ = 3.72 (s)] and *endo* 3-H [δ = 4.18 (d)] directly on the crude reaction mixture. Its spectral data match those reported.[9]

(2*S,3*R**,6*S**)-2-Hydroxy-3-methyl-6-(1-methylethyl)cyclohexanone (7g).** By following the above procedure, 91.0 mg (54%) of **7g** was obtained as a colorless liquid after column chromatography [silica gel, 20:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 154 mg (1.00 mmol) of **1g**, 275 mg (1.10 mmol) of Cp_2TiCl_2, and 14 mL of a 0.0870 M (1.22 mmol) dimethyldioxirane solution. The 2*S**:2*R** ratio was 76:24, as determined by ^1H NMR analysis of the α-hydroxy protons (2*S**)-H [δ = 3.63 (dd)] and (2*R**)-H [δ = 4.35 (dd)] directly on the crude reaction mixture: IR (NaCl) 3500–2400 (OH), 2935, 2900, 2850, 1690 (C=O); ^1H NMR (250 MHz, $CDCl_3$) δ 0.88 (d, J = 6.56 Hz, 3 H), 0.93 (d, J = 6.46 Hz, 3 H), 1.16 (d, J = 6.05 Hz, 3 H), 1.25–1.62 (m, 3 H), 1.80–1.87 (m, 1 H), 2.02–2.21 (m, 3 H), 3.63 (dd, J = 10.14, 4.02 Hz, 1H), 3.68 (d, J = 4.17 Hz, 1 H, O*H*); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.8 (q), 19.2 (q), 21.2 (q), 26.1 (d), 28.6 (t), 31.3 (t), 44.0 (d), 54.4 (d), 80.8 (d), 212.0 (s). Anal. Calcd for $C_{10}H_{18}O_2$ (170.2): C, 70.55; H, 10.66. Found: C, 70.65; H, 10.99.

***trans*-3-Hydroxyflavanone (7h).** The reaction was carried out by following the above procedure, with the exception that after the addition of Cp_2TiCl_2, the reaction mixture was kept at −78 °C for 10 h and was oxidized at −78 °C without changing the solvent. By following the described workup, 60.0 mg (53%) of *trans*-**7h** was obtained as a colorless powder, mp 184–185 °C

(17) Shellhamer, D. F.; Carter, D. L.; Chiaco, M. C.; Harris, T. E.; Henderson, R. D.; Low, W. S. C.; Metcalf, B. T.; Willis, M. C.; Heasley, V. L.; Chapman, R. D. *J. Chem. Soc., Perkin Trans. 2* **1991**, 401–403.

(18) Mitra, R. B.; Muljiani, Z.; Reddy, G. B. *Synth. Commun.* **1986**, *16*, 1099–1108.

(19) Kreiser, W. *Liebigs Ann. Chem.* **1971**, *745*, 164–168.

(lit.[10] mp 184–186 °C) after column chromatography [silica gel, 1:1 CH_2Cl_2/petroleum ether (50–60 °C)] by starting from 106 mg (0.470 mmol) of **1h**, 135 mg (0.540 mmol) of Cp_2TiCl_2, and 7 mL of a 0.0860 M (0.600 mmol) dimethyldioxirane solution. In the ^1H NMR spectrum of the crude reaction mixture only the signals for *trans*-**7h** were observed; its spectral data match those reported.[10]

2-Hydroxy-5-(phenylmethyl)cyclopentanone (7i). By following the above procedure, 95.0 mg (50%) of **7i** was obtained as a colorless oil after column chromatography [silica gel, 1:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 174 mg (1.00 mmol) of **1i**, 274 mg (1.10 mmol) of Cp_2TiCl_2, and 16 mL of a 0.0770 M (1.23 mmol) of dimethyldioxirane solution. The *R**,*R**:*R**,*S** ratio was 83:17, as determined by ^1H NMR analysis of the α-hydroxy protons (*S**,*S**)-H [δ = 4.20 (ddd)] and (*R**,*S**)-H [δ = 3.90 (dd)] directly on the crude reaction mixture: IR (NaCl) 3650–3130 (OH), 3105, 3080, 3055, 2995, 2965, 2900, 1765 (C=O), 1613 (C=C), 1590 (C=C). (2*S**,5*S**)-**7i**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.44–2.00 (m, 3 H), 2.08 (m, 1H), 2.48–2.68 (m, 1 H), 2.53 (dd, *J* = 13.0, 10.1 Hz, 1 H), 2.98 (s, 1 H, O*H*), 3.13 (dd, *J* = 13.0, 3.56 Hz, 1 H), 4.20 (ddd, *J* = 8.45, 8.30, 1.74 Hz, 1 H), 7.08–7.35 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.0 (t), 28.4 (t), 36.0 (t), 45.3 (d), 75.2 (d), 126.4 (d), 128.4 (d), 128.9 (d), 139.0 (s), 218.7 (s). (2*R**,5*S**)-**7i**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.34–1.58 (m, 2H), 1.87–2.05 (m, 1 H), 2.17–2.48 (m, 2 H), 2.73 (dd, *J* = 13.7, 8.77 Hz, 1 H), 2.98 (s, 1 H, O*H*), 3.10 (dd, *J* = 13.6, 4.39 Hz, 1 H), 3.90 (dd, *J* = 11.52, 8.09 Hz, 1 H), 7.08–7.35 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.5 (t), 29.0 (t), 36.2 (t), 47.7 (d), 76.1 (d), 126.4 (d), 128.4 (d), 128.8 (d), 138.7 (s), 219.0 (s). Anal. Calcd for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42. Found: C, 75.86; H, 7.51.

***tert*-Butyl 2-Hydroxy-2-phenylacetate (7d).** A 1.33-mL (1.10 mmol) portion of 0.83 M LDA solution in THF was cooled under an argon gas atmosphere to −78 °C, and a solution of 178 mg (1.00 mmol) of **1d** in 2 mL of dry THF was added dropwise while stirring. After 30 min, a solution of 274 mg (1.10 mmol) of Cp_2TiCl_2 in 16 mL of dry THF was added within 15 min. The resulting dark red solution was allowed to reach −30 °C within 3 h, and after the mixture was cooled to −78 °C, 16 mL of a 0.0720 M solution of dimethyldioxirane cooled at −78 °C was rapidly added with vigorously stirring. After 1 min, the reaction mixture was hydrolyzed by addition of 1 mL of an aqueous, saturated NH_4F solution, and the stirring was continued for 3 h at room temperature. The reaction mixture was filtered over Celite, and the filtrate was concentrated under vacuum (20 °C/20 Torr) to about 1 mL. The residue was taken up in about 20 mL of *tert*-butyl methyl ether and dried over $MgSO_4$. The solvent was evaporated under vacuum (20 °C/20 Torr) and the residue purified by column chromatography [silica gel, 4:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] to yield 142 mg (68%) of a colorless amorphous solid, mp 65.5–66 °C (lit.[2c] mp 66–67 °C); for spectral data see above.

2′,6′-(Dimethyl)phenyl 2-Hydroxypropanoate (7e). The reaction was carried out as described for **7d**, with the exception that after hydrolysis the reaction mixture was stirred only for 1 h at room temperature. After the described workup, 127 mg (65%) of **7e** was obtained as colorless cubes, mp 32–34 °C, after column chromatography [silica gel, 4:1 petroleum ether (50–60 °C)/methyl *tert*-butyl ether as eluent] and distillation [150 °C (air bath)/1 Torr] by starting from 178 mg (1.00 mmol) of **1e**, 274 mg (1.10 mmol) of Cp_2TiCl_2, and 16 mL of a 0.0740 M (1.19 mmol) dimethyldioxirane solution: IR (CCl_4) 3520 (OH), 3045, 3014, 3005, 1734 (C=O), 1595; ^1H NMR (250 MHz, $CDCl_3$) δ 1.66 (d, *J* = 6.91 Hz, 3 H), 2.15 (s, 6 H), 3.03 Hz (d, *J* = 5.57 Hz, 1 H, O*H*), 4.62 (dq, *J* = 6.88 Hz, *J* = 5.59 Hz, 1 H), 7.08 (s, 3 H); ^{13}C-NMR (63 MHz, $CDCl_3$) δ 16.2 (q), 20.6 (q), 66.7 (d), 126.2 (d), 128.8 (d), 129.8 (s), 147.7 (s), 173.6 (s). Anal. Calcd for $C_{11}H_{14}O_3$ (194.23): C, 68.02; H, 7.27. Found: C, 67.80; H, 7.35.

General Procedure for the Oxidation of the Sodium Enolates 5c,g–i by Dimethyldioxirane. A solution of 1.0 equiv of the carbonyl substrates **1c,g–i** in 2 mL of dry THF was slowly added to a cooled (−78 °C) solution of sodium hexamethyldisilazane (1.2 equiv, 0.5 M) under an argon gas atmosphere. In the case of **1c**, the sodium enolate was generated at −10 °C. After being stirred for 1 h, the cold solution was rapidly added to a solution of dimethyldioxirane cooled at −78 °C (1.2 equiv, 0.07–0.10 M in acetone). To the reaction mixture was added after 1 min 0.5 mL of an aqueous, saturated NH_4Cl solution and the resulting mixture allowed to reach room temperature. The solvent was evaporated under vacuum (20 °C/20 Torr), and the residue was taken up in 20 mL of *tert*-butyl methyl ether and dried over Na_2SO_4. After removal of the drying agent, the solvent was evaporated (20 °C/20 Torr) and the residue purified by column chromatography.

2-Hydroxy-1-indanone (7c) and 2-(1-Hydroxy-1-methylethyl)-1-indanone (8c). By following the above procedure, 47.0 mg (32%) of **7c** and 86.0 mg (45%) of **8c** were obtained as oils after column chromatography (silica gel, 6:1 CH_2Cl_2/*tert*-butyl methyl ether) by starting from 134 mg (1.00 mmol) of **1c** and 16 mL of a 0.0730 M (1.20 mmol) dimethyldioxirane solution (for spectral data see above).

(3*R,6*S**)-2-Hydroxy-3-methyl-6-(1-methylethyl)cyclohexanone (7g).** By following the above procedure, 132 mg (42%) of (2*S**,3*R**,6*S**)-**7g** and 66.0 mg (21%) of (2*R**,3*R**,6*S**)-**7g** were obtained (total yield 63%) as colorless liquids after column chromatography [silica gel; 20:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 284 mg (1.84 mmol) of **1g** and 29 mL of a 0.0830 M (2.40 mmol) dimethyldioxirane solution. The 2*S**:2*R** ratio was 67:33, as determined by ^1H NMR analysis of the α-hydroxy protons (2*S**)-H [δ = 3.63 (dd)] and (2*R**)-H [δ = 4.35 (d)] directly on the crude reaction mixture (for spectral data of (2*S**,3*R**,6*S**)-**7g** see above). The spectral data for (2*R**,3*R**,6*S**)-**7g** match those reported.[11]

***trans*-3-Hydroxyflavanone (7h).** By following the above procedure, 57.0 mg (37%) of *trans*-**7h** was obtained as a colorless powder, mp 184–185 °C (lit.[10] mp 185–186 °C) after column chromatography [silica gel, 1:1 CH_2Cl_2/petroleum ether (50–60 °C)] by starting from 212 mg (0.950 mmol) of **1h** and 14 mL of a 0.0860 M (1.20 mmol) dimethyldioxirane solution. The *trans*:*cis* ratio was 90:10, as determined by ^1H NMR analysis of the α-hydroxy protons *trans* 3-H [δ = 4.64 (d)] and *cis* 3-H [δ = 4.92 (d)] directly on the crude reaction mixture (for spectral data see above).

2-Hydroxy-5-(phenylmethyl)cyclopentanone (7i). By following the above procedure, 140 mg (37%) of **7i** was obtained as a colorless oil after column chromatography [silica gel; 1:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 348 mg (2.00 mmol) of **1i** and 28 mL of a 0.0830 M (2.32 mmol) dimethyldioxirane solution. The *R**,*R**:*R**,*S** ratio was 47:53, as determined by ^1H NMR analysis of the α-hydroxy protons (*R**,*R**) 2-H [δ = 4.20 (ddd)] and (*R**,*S**) 2-H [δ = 3.90 (dd)] directly on the crude reaction mixture (for spectral data see above).

Trimethyl[[2-(methylphenyl)cyclopent-5-en-1-yl]oxy]silane (6i). A 1.00-g (5.74 mmol) portion of **1i**, dissolved in 5 mL of THF, was added dropwise at −78 °C to 16 mL (6.88 mmol) of a 0.43 M LDA solution in THF. After 30 min of stirring at this temperature, 748 mg (6.89 mmol) of trimethylchlorosilane was added and the reaction mixture was allowed to reach 0 °C within 2 h. All volatile materials were removed by distillation under vacuum (20 °C/20 Torr), and the residue was taken up in about 20 mL of pentane. The reaction mixture was filtered over Celite and washed with 5 mL of pentane. The combined filtrates were concentrated under vacuum (20 °C/20 Torr) and the residue purified by distillation to yield 928 mg (66%) of a colorless liquid, bp 120 °C/0.5 Torr: IR (NaCl) 3100, 3060, 2990, 2880, 1660, 1510 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.25 (s, 9 H), 1.50–1.64 (m, 1 H), 1.84–1.99 (m, 1 H), 2.10–2.20 (m, 2 H), 2.41 (dd, *J* = 13.5, 9.72 Hz, 1 H), 2.77 (m, 1 H), 3.05 (dd, *J* = 13.5, 4.09 Hz, 1 H), 4.64 (dd, *J* = 4.05, 2.20 Hz, 1 H), 7.15–7.35 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.03 (q), 26.7 (t), 27.4 (t), 39.1 (t), 46.5 (d), 101.6 (d), 125.6 (d), 128.1 (d), 129.7 (d), 141.2 (s), 157.1 (s). Anal. Calcd for $C_{15}H_{22}OSi$ (246.42): C, 73.11; H, 9.00. Found: C, 73.44; H, 9.46.

General Procedure for the Oxidation of Silyl Enol Ethers 6f–i by Dimethyldioxirane. One equiv of the silyl enol ether was dissolved in about 2 mL of CH_2Cl_2, cooled under an argon gas atmosphere to −78 °C, and treated with 1.2 equiv of a −78 °C cold dimethyldioxirane solution in acetone (0.070–0.100 M). The reaction mixture was stirred for 30 min at this temperature, a suspension of 1.2 equiv of NH_4F in about 10 mL MeOH was added, and the reaction mixture was allowed to reach room

temperature. After 3 h, the solvent was removed by distillation under vacuum (20 °C/20 Torr) and the residue was purified by column chromatography.

3-Hydroxy-1,7,7-trimethyl[2.2.1]bicycloheptan-2-one (7f). By following the above procedure, 182 mg (91%) of **7f** was obtained as a colorless solid, mp 209–213 °C (lit.[9] mp 212 °C for the *exo* isomer **7f**), after column chromatography [silica gel; 1:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 266 mg (1.19 mmol) of **6f**, 20 mL of a 0.0690 M (1.38 mmol) dimethyldioxirane solution, and 51.0 mg (1.38 mmol) of NH_4F. The *exo*:*endo* ratio was 93:7, as determined by ^1H NMR analysis of the α-hydroxy protons *exo*-3-H [δ = 3.72 (s)] and *endo*-3-H [δ = 4.18 (d)] directly on the crude reaction mixture (for spectral data see above).

(3*R,6*S**)-2-Hydroxy-3-methyl-6-(1-methylethyl)cyclohexanone (7g).** By following the above procedure, 132 mg (78%) of (2*S**,3*R**,6*S**)-**7g** and 22.0 mg (19%) of (2*R**,3*R**,6*S**)-**7g** were obtained as colorless liquids after column chromatography [silica gel; 20:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 227 mg (1.00 mmol) of **6g**, 14 mL of a 0.0860 M (1.20 mmol) dimethyldioxirane solution, and 44.0 mg (1.19 mmol) of NH_4F. The 2*S**:2*R** ratio was 76:24, as determined by ^1H NMR analysis of the α-hydroxy protons (2*S**)-H [δ = 3.63 (dd)] and (2*R**)-H [δ = 4.35 (d)] directly on the crude reaction mixture (for spectral data see above).

***trans*-3-Hydroxyflavanone (7h).** By following the above procedure, 172 mg (85%) of *trans*-**7h** was obtained as a colorless powder, mp 184–185 °C (lit.[10] mp 185–186 °C), after column chromatography [silica gel, 1:1 CH_2Cl_2/petroleum ether (50–60 °C)] by starting from 249 mg (0.840 mmol) of **6h**, 15 mL of a 0.0630 M (0.950 mmol) dimethyldioxirane solution, and 35.0 mg (0.950 mmol) of NH_4F. In the ^1H NMR spectrum of the crude reaction mixture only *trans*-**7h** was observed (for spectra data see above).

2-Hydroxy-5-(phenylmethyl)cyclopentanone (7i). By following the above procedure, 132 mg (96%) of **7i** was obtained as a colorless oil after column chromatography [silica gel; 1:1 petroleum ether (50–60 °C)/*tert*-butyl methyl ether] by starting from 154 mg (0.620 mmol) of **6i**, 8 mL of a 0.0930 M (0.750 mmol) dimethyldioxirane solution, and 27.8 mg (0.750 mmol) of NH_4F. The *R**,*R**:*R**,*S** ratio was 65:35, as determined by ^1H NMR analysis of the α-hydroxy protons (*R**,*R**) 2-H [δ = 4.20 (ddd)] and (*R**,*S**) 2-H [δ = 3.90 (dd)] directly on the crude reaction mixture (for spectral data see above).

Acknowledgment. For their generous financial support we thank the Deutsche Forschungsgemeinschaft (SFB 347 "Selektive Reaktionen Metall-aktivierter Moleküle") and the Fonds der Chemischen Industrie.