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Diastereoselective oxidation of β-hydroxysulfides with TBHP: a comparative study of titanocenes and Ti(Oi-Pr)$_4$ as catalysts

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Abstract—Titanocene dichlorides and Ti(Oi-Pr)$_4$ have been used as catalysts for the oxidation with *t*-butyl hydroperoxide of racemic β-hydroxysulfides having a stereogenic carbon centre in α- or β- position with respect to the sulfur atom. β-Hydroxysulfides were oxidized in high yields to the corresponding sulfoxides, titanocenes being more chemo- and generally more diastereoselective than Ti(Oi-Pr)$_4$. A divergent stereochemical outcome has been observed when using titanocenes or Ti(Oi-Pr)$_4$ in the oxidation of protected β-hydroxy sulfides. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

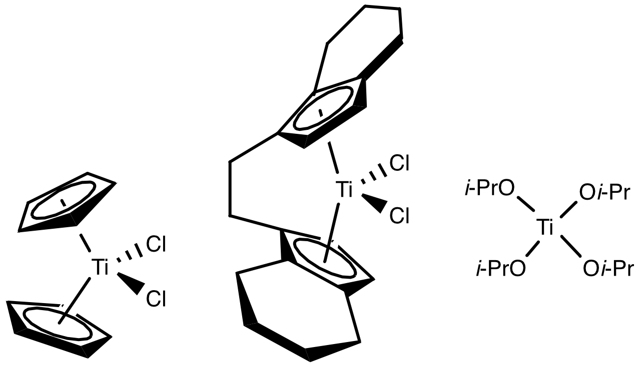
The main employment of metallocenes as catalysts in organic synthesis concerns C–C bond forming reactions.[1] Only some examples of their use, with little success, have been reported in the epoxidation of alkenes.[2] Indeed, recently we have found that metallocenes are useful catalysts in various oxidative processes such as the epoxidation of allylic alcohols,[3] the oxidative cyclization of bishomoallylic alcohols[4] and the sulfoxidation of prochiral sulfides.[5]

β-Hydroxysulfoxides can be prepared via aldol-type reactions with variable diastereoselectivity,[6] via reduction of β-ketosulfoxides with generally high diastereoisomeric ratio.[7] As regards metal-catalyzed oxidative processes only two methods have been reported in the literature: VO(acac)$_2$/*t*-butyl hydroperoxide (TBHP)[8] and Ti(Oi-Pr)$_4$/(+)-DET/TBHP[9] systems. In the vanadium catalyzed transformation the starting compounds were optically pure products, while in the modified Sharpless Ti(IV) system both the diastereo- and the enatioselectivity of the oxidation were studied.

On the grounds of literature findings and on the basis of the encouraging results on the catalytic activity of titanocenes, we decided to examine the employment of titanocene dichlorides and Ti(Oi-Pr)$_4$ as promoters in the oxidation of racemic β-hydroxysulfides using TBHP as oxidant. We thought it would have been interesting to compare the activity of the well-known Ti(Oi-Pr)$_4$ with the titanocene dichlorides, especially on the basis of the different Lewis acidities, coordinating properties as well as steric factors of these Ti(IV) catalysts. Furthermore, there have been no reports on the use of Ti(Oi-Pr)$_4$ as catalyst for this oxidation.

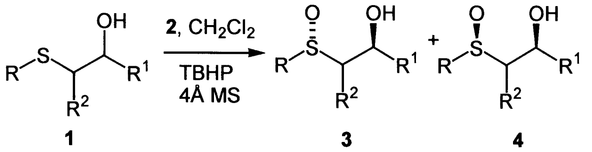
2. Results and discussion

Two titanocene dichlorides: (*bis*-cyclopentadienyl titanium



2a **2b** **2c**

Figure 1.



1a=R=p-Tol, R^1=Me, R^2=H
1b=R=Me, R^1=Ph, R^2=H
1c=R=Me, R^1=H, R^2=Ph

2a=Cp$_2$TiCl$_2$
2b=*rac*-(EBTHI)$_2$TiCl$_2$
2c=Ti(O-*i*-Pr)$_4$

Scheme 1.

Keywords: diastereoselection; oxidation; titanium and compounds; β-hydroxysulfoxides.

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Table 1. Ti(IV)-catalyzed oxidation of **1** by **2**/TBHP systems

Entry	Catalyst (mol%)	**1**	R	R^1	R^2	*T* (°C)	*t* (h)	Yield (%)[a]	dr[b] **3/4**
1	**2a** (1)	**1a**	*p*-Tol	Me	H	0	25	75[c]	58/42
2	**2a** (1)	**1a**	*p*-Tol	Me	H	−20	29	81	57/43
3	**2b** (5)	**1a**	*p*-Tol	Me	H	−20	29	57	62/38
4[d]	**2c** (5)	**1a**	*p*-Tol	Me	H	−20	29	78[e]	60/40
5	**2a** (1)	**1b**	Me	Ph	H	−20	29	97	59/41
6	**2b** (5)	**1b**	Me	Ph	H	−20	29	85	74/26
7[d]	**2c** (5)	**1b**	Me	Ph	H	−20	29	95	65/35
8	**2a** (1)	**1c**	Me	H	Ph	−20	24	88	88/12
9	**2b** (5)	**1c**	Me	H	Ph	−20	24	95	81/19
10[d]	**2c** (5)	**1c**	Me	H	Ph	−20	24	80	81/19

Molar ratio employed: **1a**/TBHP/1/1.2. 4 Å MS were added (3.5 g/mmol of titanocene catalyst).

[a] Isolated yield of both sulfoxide diastereoisomers.

[b] The diastereoisomeric ratios were determined by ^{1}H NMR analysis.

[c] 18% of the corresponding sulfone was detected.

[d] In this reaction activated 4 Å MS were not added.

[e] 6% of the corresponding sulfone was detected.

dichloride) Cp_2TiCl_2 **2a** and [(±)ethylen-*bis*-(4,5,6,7-tetrahydro-1-indenyl)dichlorotitanium(IV)] *rac*-$(EBTHI)_2TiCl_2$ **2b** (Fig. 1) were chosen and studied in catalytic loadings (1–5 mol%) in the presence of activated 4 Å MS[10] in the oxidation of compounds **1a–c** (Scheme 1).

Moreover, a comparative study of their efficiency was carried out using Ti(O*i*-Pr)$_4$ **2c** as promoter in the same process (Scheme 1, Table 1). Di Furia and Modena[9] reported that almost no diastereoselectivity is achievable when the asymmetric carbon atom is located in the β position with respect to the sulfur atom, while a pronounced improvement is observed when the stereogenic carbon centre is placed α to the sulfur atom.

Compound **1a** was initially subjected to the optimized conditions utilized in the oxidation of 2-substituted 1,3-dithianes and 1,3-dithiolanes,[5b] employing Cp_2TiCl_2 in 1 mol% amount at 0°C in the presence of 4 Å MS;[10] the corresponding sulfoxide[11] was isolated in good yield and with poor *anti*/*syn* ratio. The overoxidation to the corresponding sulfone was found to take place in these conditions in 18% yield. In order to improve the chemoselectivity, the reaction was carried out at the lower temperature of −20°C and under these conditions, the sulfoxide was isolated in higher yield (81%) and with comparable diastereoisomeric ratio (entry 2).

When employing catalyst **2b**, the product was obtained in lower yield,[12] but with slightly better diastereoselectivity (entry 3). Ti(O*i*-Pr)$_4$ turned out to be more a reactive catalyst[13] (entry 4); the sulfoxide was produced with lower chemoselectivity (sulfone was detected at the end of the reaction) and with a comparable level of diastereoselectivity.

It has to be noted that the optically pure compound [(*S*)-1-*p*-tolylsulfanyl propan-2-ol **1a**] was converted under the same reaction conditions,[8] using VO(acac)$_2$/TBHP at −20°C in CH_2Cl_2, to the sulfoxide in a modest 51% yield and with a slightly better *anti*/*syn* 66/34 ratio.

When the methyl and aryl groups were inverted in the starting material **1b**, a complete conversion to the final sulfoxide[14] was observed with Cp_2TiCl_2 (entry 5), leading to a similar level of the diastereoselectivity obtained in the oxidation of **1a** (*anti*/*syn* 59/41).

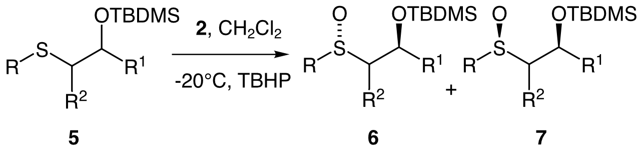
Titanocene **2b** improved the *anti*/*syn* ratio of the product (entry 6), which was isolated in very good yield, again proving to be the more diastereoselective (*anti*/*syn* 74/26) catalyst among the three and when using Ti(O*i*-Pr)$_4$ the sulfoxide was isolated in high yield but with lower stereoselecivity (entry 7). Surprisingly, with the Ti(O*i*-Pr)$_4$/(+)-DET/TBHP[9] system, **1b** was oxidized, under the same reaction conditions (CH_2Cl_2 at −20°C), but with stoichiometric metal loadings, in very poor yield (20% yield) and with a comparable diastereisomeric ratio (*anti*/*syn* 68/32). The presence of the optically pure ligand [(+)-DET] lowered the reaction rate and did not produce any positive influence on the diastereo- and the enantioselectivity of the process; in fact the two diastereoisomers proved to be almost racemic products.

When the stereogenic carbon centre was placed α to the sulfur atom, as in compound **1c**, the diastereoselectivity markedly increased, confirming that the stereochemical recognition is amplified.[9] Cp_2TiCl_2 was the best catalyst in terms of the diastereoselective ratio observed (*anti*/*syn* 88/12) (entry 8) and the product[15] was recovered in high yield. **2b** and **2c** proved to be very efficient (especially the titanocene **2b**, entry 9) but less diastereoselective than **2a** (entries 9 and 10).

Then, we thought it would be interesting to study the sulfoxidation of the hydroxy protected sulfides **5**, in order to investigate if the presence of the hydroxy group could influence the diastereoselectivity of the oxidation (Scheme 2, Table 2). Compounds **1**, protected as *t*-butyldimethylsilyl ethers **5**, were less reactive than **1** and so 5 mol% of Cp_2TiCl_2 catalyst was employed.[16]

5a was oxidized by titanocene **2a** in very good yield (Table 2, entry 1), with a low *anti*/*syn* ratio, but the opposite preference for the *syn* diastereoisomer **6a**[17] was observed with respect to the reaction carried out on the unprotected β-hydroxysulfoxide **1a** (Table 1, entry 1).

The more sterically demanding catalyst **2b** reacted very slowly, even at 0°C, with almost no diastereoselectivity



5a=R=*p*-Tol, R^1=Me, R^2=H
5b=R=Me, R^1=Ph, R^2=H
5c=R=Me, R^1=H, R^2=Ph

Scheme 2.

Table 2. Ti(IV)-catalyzed oxidation of **5** by **2**/TBHP systems at −20°C

Entry	Catalyst (mol%)	5	R	R^1	R^2	*t* (h)	Yield (%)[a]	dr[b] **6/7**
1	**2a** (5)	**5a**	*p*-Tol	Me	H	30	80	44/56
2	**2b** (5)	**5a**	*p*-Tol	Me	H	48	34	53/47
3	**2b** (5)	**5a**	*p*-Tol	Me	H	24	45[c]	54/46
4	**2c** (5)	**5a**	*p*-Tol	Me	H	24	70[d,e]	72/28
5	**2a** (5)	**5b**	Me	Ph	H	24	89	46/54
6	**2b** (5)	**5b**	Me	Ph	H	48	64	49/51
7	**2c** (5)	**5b**	Me	Ph	H	5	85[d,f]	58/42
8	**2a** (5)	**5c**	Me	H	Ph	24	83	77/23
9	**2b** (5)	**5c**	Me	H	Ph	24	48	79/21
10	**2c** (5)	**5c**	Me	H	Ph	5	72[d,e]	85/15

Molar ratio employed: **5**/TBHP/1/1.2. 4 Å MS were added (3.5 g/mmol of titanocene catalyst).

[a] Isolated yield of both sulfoxide diastereoisomers.

[b] The diastereoisomeric ratios were determined by ^{1}H NMR analysis; the *syn* and *anti* diastereoisomers were identified after desilylation by comparison with the spectroscopic data of **3/4**.

[c] This reaction was carried out at 0°C.

[d] In this reaction activated 4 Å MS were not added.

[e] 8% of sulfone was detected.

[f] 10% of sulfone was detected.

(entries 2 and 3). Ti(O*i*-Pr)$_4$ **2c** showed to be less chemoselective, but a good diastereoisomeric ratio (*anti*/*syn* 72/28) was achieved, better than the one determined on the unprotected sulfoxides **3/4a** (Table 1, entry 4).

In the case of compound **5b** titanocenes **2a** and **2b** (entries 5 and 6) gave a slight preference for the *syn* diastereoisomer, while **2c** was found to be a more reactive catalyst furnishing a not negligible amount of sulfone and maintaining the *anti* preference for the oxidation.

In the last example, catalysts **2a** and **2b**, furnished the protected sulfoxides **6/7c** with reduced *anti*/*syn* ratio (entries 8 and 9) compared to the results obtained in entries 8 and 9 in Table 1. On the contrary, with catalyst **2c**, the product was synthesized with a diastereoselective ratio (*anti*/*syn* 85/15) higher than the one measured for the **3/4** mixture (Table 1, entry 10).

From these findings, a different stereochemical outcome emerged in the Ti(IV) catalyzed oxidation of protected sulfides **5** with respect to unprotected sulfides **1**.

In the oxidation of sulfides **5** with titanocenes **2a** and **2b**, a general preference for the *syn* diastereoisomer or a decreased *anti*/*syn* ratio was observed in the product. Ti(O*i*-Pr)$_4$ maintained the *anti* selectivity in both oxidations and furnished in some cases a better *anti*/*syn* ratio for the final protected sulfoxides with respect to **3/4** products. This stereochemical outcome for the Ti(O*i*-Pr)$_4$ catalyzed oxidation was rather different from Ti(O*i*-Pr)$_4$/(+)-DET/TBHP system;[9] in fact, in the oxidation of protected β-hydroxysulfides with the chiral Ti(IV) catalyst, irrespective to the protecting group employed, a lower *anti*/*syn* ratio with respect to the oxidation of the unprotected β-hydroxysulfides was always found.

In conclusion, we have discovered a synthetically useful catalytic activity of titanocenes and set up a methodology of diastereoselective oxidation of β-hydroxysulfides, which compares favorably with the other available metal-catalyzed procedures.[8,9] Catalytic loadings of titanocene dichlorides are needed (1–5 mol%) to chemoselectively produce the final β-hydroxysulfoxides in high yields. The diastereoselectivity reached is comparable and in some cases better than the previous metal-catalyzed oxidations and showed to be dependent on the structure of the starting sulfide and position of the stereogenic carbon centre. A reversed stereochemical preference for the *syn* products has been observed in the oxidation of hydroxy protected sulfides. From this study it emerged that Ti(O*i*-Pr)$_4$, without the presence of any chiral ligand, is a suitable catalyst for the diastereoselective oxidation of β-hydroxysulfides, being more reactive but less chemoselective than titanocenes. The stereochemical preference for the *anti* sulfoxides is maintained in the oxidation of unprotected and protected β-hydroxysulfides.

3. Experimental

3.1. General

All reactions were carried out under a dry nitrogen atmosphere. Glassware was flame-dried (0.05 Torr) before use. Catalysts **2a** and **2c** were purchased from Aldrich and used without further purification. Titanocene **2b** was purchased from Boulder Scientific. Dichloromethane was used freshly distilled. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel plates (0.25 mm) and visualized by UV light or by 10% H_2SO_4/ethanol spray test. Flash chromatography was performed on Merck silica gel (60, particle size: 0.040–0.063 mm). NMR spectra were recorded in $CDCl_3$ solutions on a Bruker DRX 400 spectrometer (400 MHz) at room temperature. Chemical shifts are reported relative to the residual solvent peak ($CHCl_3$: δ_H=7.26). EIMS spectra were performed on Polaris Trace 2000 spectrometer. IR spectra were recorded with a Bruker Vector 22 spectrophotometer.

Yields of products **3/4** and **6/7** refer to isolated pure compounds. Compound **1a** was synthesized according to Ref. 8; compounds **1b** and **1c** were synthesized according to Ref. 9b.

anti/*syn* ratios of β-hydroxysulfoxides **3/4** were determined by integrating the characteristic peaks of the two diastereomers in the ^{1}H NMR spectra of the crude reaction mixtures.

3.2. General procedure for the silylation of 1

To dry CH_2Cl_2 (9 mL) under argon atmosphere at 0°C was added **1** (6.4 mmol), *tert*-butyldimethylsilyl chloride (1.26 g, 8.4 mmol) and imidazole (572 mg, 8.4 mmol), with stirring. The mixture was stirred until completion of the reaction by TLC monitoring. Then, water (9 mL) was added to the reaction mixture and stirring was maintained for a few minutes. The reaction mixture was extracted with CH_2Cl_2 (3×20 mL) and the organic phase was dried with $MgSO_4$ and after filtration the solvent was removed in vacuo.

3.2.1. *tert*-Butyl-dimethyl-(1-methyl-2-*p*-tolylsulfanyl-ethoxy)-silane 5a. Purification by column chromatography on silica gel (petrol/diethyl ether 98/2) gave **5a** in 72% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 3H), 0.04 (s, 3H), 0.87 (s, 9H), 1.24 (d, 3H, J=6.1 Hz), 2.31 (s, 3H), 2.84 (dd, 1H, J=12.9, 6.8 Hz), 3.02 (dd, 1H, J=12.9, 5.4 Hz), 3.92 (m, 1H), 7.08 (d, 2H, J=8.2 Hz), 7.25 (d, 2H, J=8.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.8, −4.7, 18.0, 20.9, 23.0, 25.8, 43.3, 67.9, 129.5, 129.6, 133.3, 135.6. IR ν_{max} (KBr): 2930, 1478, 1235, 1060, 830 cm^{-1}. Anal. Calcd for $C_{16}H_{28}OSSi$: C, 64.80; H, 9.52, S, 10.81. Found: C, 64.61; H, 9.43, S, 10.74.

3.2.2. *tert*-Butyl-dimethyl-(2-methylsulfanyl-1-phenyl-ethoxy)-silane 5b. Purification by column chromatography on silica gel (petrol/diethyl ether 96/4) gave **5b** in 71% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.11 (s, 3H), 0.07 (s, 3H), 0.88 (s, 9H), 2.03 (s, 3H), 2.68 (dd, 1H, J=13.4, 5.3 Hz), 2.83 (dd, 1H, J=13.4, 7.3 Hz), 4.78 (dd, 1H, J=7.3, 5.3 Hz), 7.22–7.36 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.9, −4.7, 16.6, 18.2, 25.8, 44.8, 75.1, 126.0, 127.4, 128.1, 144.0. IR ν_{max} (KBr): 2929, 1476, 1237, 1065, 730 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSSi$: C, 63.77; H, 9.28, S, 11.35. Found: C, 63.59; H, 9.18, S, 11.43.

3.2.3. *tert*-Butyl-dimethyl-(2-methylsulfanyl-2-phenyl-ethoxy)-silane 5c. Purification by column chromatography on silica gel (petrol/diethyl ether 98/2) gave **5c** in 88% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.07 (s, 3H), −0.02 (s, 3H), 0.83 (s, 9H), 1.98 (s, 3H), 3.29–3.82 (m, 3H), 7.21–7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.5, 14.6, 18.2, 25.8, 53.9, 67.2, 127.1, 128.2, 140.1. IR ν_{max} (KBr): 2929, 1468, 1252, 1072, 770 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSSi$: C, 63.77; H, 9.28, S, 11.35. Found: C, 63.64; H, 9.20, S, 11.40.

3.3. General procedure for the oxidation of 1 and 5 catalyzed by 2

To dry CH_2Cl_2 (4 mL) under argon atmosphere at rt was added: activated 4 Å MS (3.5 g/mmol of titanocene catalyst), **2a**, **2b** or **2c** (1 or 5 mol%) and TBHP (220 μL, 1.2 mmol, 5.5 M solution in decane), with stirring. Stirring was maintained for 30 min, then the temperature was lowered to the reported value in Tables 1 and 2, sulfide **1** and **5** (1 mmol) was added and stirring was maintained for the time reported in Tables 1 and 2. At the end of the reaction, the mixture was filtered to remove molecular sieves and extracted with a saturated solution of Na_2SO_3. The organic phase was then treated with $MgSO_4$ and the solvent removed in vacuo. When using **2c** no molecular sieves were added. The crude reaction mixtures were purified by silica gel column chromatography eluting starting with $CHCl_3$ to $CHCl_3/CH_3OH$ 96/4 mixtures, giving compounds **6/7a–c** in yields reported in Table 2.

3.3.1. (*syn/anti*) *tert*-Butyl-(2-methanesulfinyl-1-phenyl-ethoxy)-dimethyl-silane 6b/7b. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.15 (s, 3H, *syn*), −0.14 (s, 3H, *anti*), 0.07 (s, 3H, *syn*), 0.11 (s, 3H, *anti*), 0.88 (s, 9H, *syn*), 0.89 (s, 9H, *anti*), 2.58 (s, 3H, *anti*), 2.60 (s, 3H, *syn*), 2.87 (dd, 1H, J=12.8, 2.4 Hz, *anti*), 2.97 (dd, 1H, J=12.8, 6.8 Hz, *syn*), 2.97 (dd, 1H, J=12.8, 10.6 Hz, *anti*), 3.27 (dd, 1H, J=12.8, 6.1 Hz, *syn*), 5.12 (dd, 1H, J=6.8, 6.1 Hz, *syn*), 5.21 (dd, 1H, J=10.6, 2.4 Hz, *anti*), 7.27–7.40 (m, 5H). IR ν_{max} (KBr): 2928, 1471, 1250, 1105, 1028, 735 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2SSi$: C, 60.35; H, 8.78, S, 10.74. Found: C, 60.21; H, 8.67, S, 10.66.

3.3.2. (*anti/syn*) *tert*-Butyl-(2-methanesulfinyl-2-phenyl-ethoxy)-dimethyl-silane 6c/7c. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.04 (s, 3H, *anti*), −0.02 (s, 3H, *anti*), 0.03 (s, 3H, *syn*), 0.07 (s, 3H, *syn*), 0.82 (s, 9H, *anti*), 0.86 (s, 3H, *syn*), 2.15 (s, 3H, *syn*), 2.28 (s, 3H, *anti*), 3.55 (dd, 1H, J=9.4, 5.0 Hz, *syn*), 3.67 (dd, 1H, J=5.2, 3.8 Hz, *anti*), 4.02 (dd, 1H, J=10.8, 5.0 Hz, *syn*), 4.12 (dd, 1H, J=10.6, 3.1 Hz, *anti*), 4.30 (m, 1H, overlapped, *syn*), 4.34 (dd, 1H, J=10.5, 5.1 Hz, *anti*), 7.26–7.42 (m, 10H). ^{13}C NMR (400 MHz, $CDCl_3$) δ −5.8, −5.8, 18.1, 25.7, 35.4, 36.7, 61.1, 61.6, 68.6, 72.1, 128.4, 128.5, 128.7, 129.0, 129.4, 133.9. IR ν_{max} (KBr): 2928, 1471, 1256, 1109, 1034, 837, 778 cm^{-1}. EIMS *m/z*: 299 (M+1, 12), 235 (24), 179 (52), 177 (33), 161 (29), 121 (21), 105 (27), 75 (44), 73 (100). Anal. Calcd for $C_{15}H_{26}O_2SSi$: C, 60.35; H, 8.78, S, 10.74. Found: C, 60.20; H, 8.68, S, 10.65.

3.4. Deprotection of silylated 6/7

To dry THF (3 mL) under argon atmosphere at rt were added: the **6/7** mixture (0.420 mmol), then TBAF (0.840 mL, 0.840 mmol, 1 M in THF solution), with stirring. The mixture was stirred until TLC monitoring showed the reaction to be complete. Then, the reaction was quenched with water and the mixture was extracted with CH_2Cl_2 (3×40 mL). The organic phase was dried with $MgSO_4$ and the solvent removed in vacuo. The ^{1}H NMR of the crude mixtures matched with the reported spectral data of *anti/syn* **3/4** isomers.

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10. We have found that the activity of titanocenes is markedly improved when activated molecular sieves are added. See Refs. 4,5.
11. Spectral data of compounds **3/4a** matched with the literature. See Ref. 8.
12. Catalyst **2b** is generally less reactive than **2a**. See Refs. 3,4,5b.
13. Ti(O*i*-Pr)$_4$ is known to be very prone to ligand exchange. Then, the coordination of the oxidant and presumably the hydroxysulfide to the metal centre is faster, hence increasing the activity of this catalyst in the oxidation.
14. Spectral data of compounds **3/4b** matched with the literature. See Ref. 9b.
15. Spectral data of compounds **3/4c** matched with the literature: Alcudia, F.; Brunet, E.; Sanchez, F. *An. Quim.* **1979**, *75*, 162.
16. It has been reported that β-hydroxysulfides are more reactive compared to simple sulfides in the VO(acac)$_2$/TBHP catalyzed sulfoxidation. The hydroxy group of the sulfide might be involved in the transition state thus facilitating the 1,2-vanadium shift process accompanying the peroxide oxygen transfer to the sulfur atom. See Bortolini, O.; Di Furia, F.; Modena, G. *J. Mol. Catal.* **1983**, *19*, 319.
17. Spectral data of compounds **6/7a** matched with the literature: Kita, Y.; Shibata, N.; Yoshida, N.; Fujita, S. *J. Chem. Soc., Perkins Trans. 1* **1994**, *22*, 3335.