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Alternative approach to the synthesis of optically active β-keto sulfoxides by furylhydroperoxides enantioselective oxidations

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Abstract

Enantiomerically enriched β-keto sulfoxides are obtainable by an alternative method to the classical reaction of the enantiomerically pure α-sulfinyl anion with esters or by Andersen's synthesis, through Sharpless modified kinetic resolution of racemic β-keto sulfoxides. High e.e.s are achieved by combining asymmetric oxidation and kinetic resolution using furylhydroperoxides as oxidants.

1. Introduction

Enantiomerically pure sulfoxides represent a convenient class of enantiocontrol elements for realizing useful transformations.[1] In particular, the employment of β-keto sulfoxides in the asymmetric synthesis of several natural compounds[1c] has been frequently reported in a large number of publications. For example, the highly diastereocontrolled reduction[2] of the carbonyl functionality after elimination of the sulfinyl group yields enantiomerically pure carbinols.

Chiral acyclic β-keto sulfoxides are generally available by the condensation of (−)-(*R*)-*p*-tolyl methyl sulfinyl anion and an ester.[3a] Enantiomerically pure sulfinyl cycloalkanones are synthesized by an Andersen-type reaction of an enolate[4] or azaenolate[5] species with a chiral sulfinate ester.

The access to β-keto sulfoxides with a chiral methylsulfinyl group is limited by the fact that O-menthyl methanesulfinates cannot be obtained in an enantiomerically pure form;[6] only recently was their preparation reported, making use of the DAG (diacetone D-glucose) methodology.[7]

In recent years we[8] and others[9] have addressed the reactivity of furylhydroperoxides in Sharpless modified asymmetric epoxidations and sulfoxidations and they have proved successful alternative oxidants to

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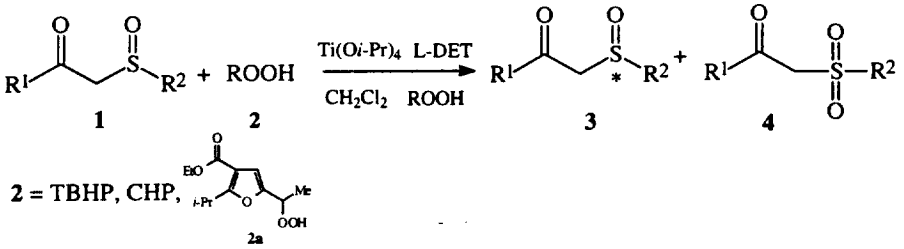
t-butyl hydroperoxide (TBHP) and cumyl hydroperoxide (CHP). Moreover, under the same conditions, they can perform kinetic resolution of racemic aryl methyl sulfoxides.[10] In fact we were able to recover, with good yields and high e.e.s, unreacted starting sulfoxides (e.e.>90%). Intrigued by the possibility of extending the study of kinetic resolution to other types of sulfur compounds we decided to examine if the process was feasible for racemic β-keto sulfoxides (Scheme 1).



Scheme 1.

2. Results and discussion

Racemic β-keto sulfoxides **1** were prepared according to known procedures[3b] and were oxidized with different alkyl hydroperoxides adopting the same conditions as those reported in Table 1.

Two important features appear in Table 1:

(i) With the employment of the commercial hydroperoxides (TBHP and CHP) very low enantiodiscrimination was achieved, consequently only in some examples did an extremely poor kinetic resolution of racemic β-keto sulfoxides occur (entries 1, 2, 6, 9). Next we studied the reactivity of furylhydroperoxide **2a** as oxidant under the same conditions and we found a substantial general improvement in the kinetic resolution of the starting racemic compounds. As can be seen from the data, analogously to aryl methyl sulfoxides, the S-enantiomer was transformed faster to sulfone in the course of the oxidation.

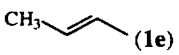
(ii) Both the steric and electronic character of R^1 influenced the efficiency of the process. Increasing bulkiness of R^1 group brought a decrease in enantioselectivity (compare entries 7, 11 and 13), while in the case of R^1=Ph (entry 3) the combination of the steric and electronic character of the phenyl substituent exerted a beneficial effect.

Kinetic resolution of starting compounds also took place when R^1CO was an ester (last entries). Furthermore, the process seems to be slightly influenced by temperature. Very similar stereoselectivity factors were evaluated in reactions conducted at −25°C and 0°C (entries 3, 4, 7 and 8). The lower enantiocontrol that emerged in the kinetic resolution of β-keto sulfoxides compared with the simple aryl methyl sulfoxides[10] is believed to arise from the presence of the co-ordinating carbonyl function (R^1CO). In fact, it could offer a further site of chelation to the titanium chiral complex, forming a structure with a smaller enantiodifferentiation at the oxidation level.

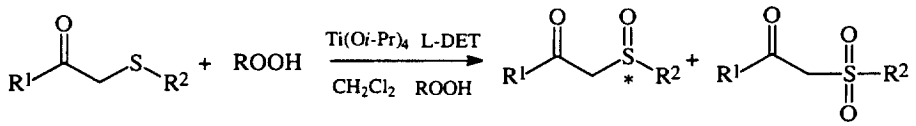
So far the paucity of results reported on the asymmetric oxidation of β-keto sulfides adopting Sharpless modified conditions[12] and the possibility of exploiting kinetic resolution to improve the e.e. of β-keto sulfoxides prompted us to investigate (Scheme 2; Table 2).

We initially chose to investigate the asymmetric oxidation of the model β-keto sulfide **5a** (entries 1, 2 and 3) using Modena's molar ratios[14] (**2**/**5**/Ti(O*i*-Pr)$_4$/L-DET 1/1/1/4). Optimum conditions for yield and enantioselectivity were observed with oxidant **2a** and, as expected, (*R*)-**3a** was recovered preferentially. On the basis of these results and those reported in Table 1 (entries 1, 2, 3) we could have exploited most

Table 1
Kinetic resolution of racemic β-keto sulfoxides **1** with alkyl hydroperoxides

Entry	R^1	R^2	**2**	T(°C)	t(h)	yield **3** (%)[a]	e.e. **3** (%)[b]	E[c]
1	Ph (**1a**)	*p*-Tol	TBHP	-25	65	64	6 (R)	1.3
2	"	"	CHP	-15	66	65	20 (R)	2.6
3	"	"	**2a**	-15	44	45	59 (R)	5.0
4	"	"	"	0	24	57	43 (R)	5.3
5	C_8H_{17} (**1b**)	"	TBHP	-25	43	70	0	1.0
6	"	"	CHP	-15	69	42	20 (R)	1.6
7	"	"	**2a**	-25	44	53	35 (R)	3.1
8	"	"	"	0	46	30	52 (R)	2.5
9	C_5H_{11} (**1c**)	"	TBHP	-25	43	35	6 (R)	1.1
10	"	"	CHP	"	45	80	0	1.0
11	"	"	**2a**	"	44	40	46 (R)	2.8
12	*i*-Pr (**1d**)	"	CHP	"	65	82	0	1.0
13	"	"	**2a**	"	65	58	10 (R)	1.4
14	 (**1e**)	"	"	-15	46	30	59 (R)	2.8
15	CH_3O (**1f**)	Ph	"	-25	51	32	52 (R)	2.6
16	CH_3CH_2O (**1g**)	CH_3	"	-25	48	44	26 (R)[d]	1.9

[a]Isolated yields. Molar ratios used **1** / **2** / Ti(O*i*-Pr)$_4$ / L-DET 2 / 1.6 / 1 / 4. [b]E.e. have been determined by ^{1}H-NMR analysis[11] in the presence of R-(-)-(3,5-dinitrobenzoyl)-α-methylbenzyl amine as shift reagent. Absolute configuration estabilished by comparison of the sign of specific rotation with reported data, see ref. 2,12. [c]Evaluation of stereoselectivity factor $E=k_R/k_S$[13]. [d]Determined by comparison of $[\alpha]_D$ reported value in ref. 12b.



5 **2** **3** **4**

Scheme 2.

successfully both enantioconvergent oxidations only with the use of furyl hydroperoxide **2a** so we ran the experiment increasing the amount of **2a**. The following kinetic resolution of β-keto sulfoxide during the oxidation to sulfone led to the isolation of **3a** in fair yield and with excellent e.e. (entry 4). In order to assess the generality and the scope of the asymmetric oxidation and kinetic resolution one-pot process as an improved Sharpless type procedure, we extended the reactions to several β-keto sulfides.

Acting together, the two oxidations employing furylhydroperoxide **2a** accounted for the high e.e. detected for compounds **3** susceptible to further enhancement, increasing the extent of conversion to sulfone. A control experiment was carried out with CHP on compound **5h** (entry 7) and as expected the

Table 2
Asymmetric oxidation and kinetic resolution as combined routes to chiral β-keto sulfoxides

Entry	R^1	R^2	2	T(°C)	t(h)	yield 3 (%)[a]	e.e. 3 (%)[c]
1	Ph (**5a**)	*p*-Tol	CHP	-25	21	56[b]	50 (R)
2	"	"	TBHP	"	17	70[b]	52 (R)
3	"	"	**2a**	"	17	89[b]	62 (R)
4	"	"	"	"	71	61 (36)	97 (R)
5	C_8H_{17} (**5b**)	"	"	"	48	52 (38)	87 (R)
6	CH_3 (**5h**)	*p*-Tol	"	"	44	60 (34)	87 (R)
7	CH_3 (**5h**)	*p*-Tol	CHP	"	45	66 (30)	63 (R)
8	CH_3CH_2O (**5g**)	CH_3	**2a**	"	18	47 (50)	86 (R)[d]
9	*i*-Pr (**5d**)	*p*-Tol	"	"	46	64 (34)	51 (R)
10	*t*-BuO (**5i**)	"	"	"	89	72 (0)	42 (R)

[a]Isolated yields. Yields in parenthesis refer to sulfone. Molar ratios used **5** / **2** / Ti(O*i*-Pr)$_4$ / L-DET 1 / 2 / 1 / 4. [b]Molar ratios used **5** / **2** / Ti(O*i*-Pr)$_4$ / L-DET 1 / 1 / 1 / 4. [c]See note 2 in Table 1. [d] See last note in Table 1.

corresponding β-keto sulfoxide was recovered with a modest e.e. compared to that obtained with oxidant **2a** (entry 6). Although moderate e.e.s were checked with the furyl hydroperoxide, when R^1 is a sterically demanding group (entries 9 and 10), the previous optical purity data concerning asymmetric oxidation of compound **5i** under Sharpless modified conditions with TBHP was very low (9% e.e.).[12b]

To the best of our knowledge those are the highest e.e.s ever reported in asymmetric oxidation of β-keto sulfides using the Ti(O*i*-Pr)$_4$/tartrate system.

3. Conclusions

Kinetic resolution under Sharpless modified conditions of racemic sulfoxides using furylhydroperoxides as oxidants has proved to have a wider application, to include functionalized β-keto sulfoxides. Moreover, the combined enantioconvergent oxidations open up an additional approach to the synthesis of optically active β-keto sulfoxides.

4. Experimental

4.1. General

^{1}H-NMR and ^{13}C-NMR spectra were recorded with Bruker DRX 400 MHz and Bruker AM 250 MHz spectrometers. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), hept (heptuplet), m (multiplet), dd (double doublet), ss (sharp singlet). Chemical shifts are reported in (δ) ppm relative to internal $CDCl_3$ δ (7.26) for ^{1}H-NMR and $CDCl_3$ δ (77.0) for ^{13}C-NMR. Optical rotations were measured with a JASCO Dip-1000 digital polarimeter at λ=589 nm. Silica gel (230–400 mesh Merck) was used for flash chromatography. Analytical thin layer chromatography was carried out on Merck Kieselgel F_{254} plates. Enantiomeric excesses of compounds **3** were measured by ^{1}H-NMR analysis on the AB system of CH_2SO^* in $CDCl_3$:CCl_4 (3:1) solutions with the presence of a stoichiometric amount

of R-(−)-(3,5-dinitrobenzoyl)-α-methylbenzyl amine. Dichloromethane was stored over activated 4 Å molecular sieves.

Compounds **5a**, **5b**, **5d** and **5i** were synthesized according to procedures reported in the literature.[15] Other chemicals (Aldrich, Fluka or Lancaster) were used as supplied.

4.2. *Typical experimental procedure of kinetic resolution*

To a solution of CH_2Cl_2 (10 ml), at room temperature and under an argon atmosphere were added Ti(O*i*-Pr)$_4$ (1 mmol), L-DET (4 mmol) and **1** (2 mmol). The resulting pale yellow solution was stirred at −20°C for 20 min. Then **2** (1.6 mmol) dissolved in 10 ml of CH_2Cl_2 was added to the mixture and the reaction was monitored by TLC. Water was added (4 ml) to the solution at −20°C and vigorous stirring was maintained for 1 h at room temperature. The white gel was filtered through Celite and thoroughly washed with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and then removed *in vacuo*. Flash chromatography of the crude mixture (petroleum ether/AcOEt) furnished the desired β-keto sulfoxides.

4.3. *5-(1-Hydroperoxyethyl)-3-ethoxycarbonyl-2-isopropylfuran* **2a**

The procedure for the synthesis and the spectroscopic data of compound **2a** are reported in the literature.[16]

4.4. *Typical experimental procedure of combined asymmetric oxidation and kinetic resolution*

To a solution of CH_2Cl_2 (7 ml), at room temperature and under an argon atmosphere were added Ti(O*i*-Pr)$_4$ (1 mmol), L-DET (4 mmol) and **5** (1 mmol). The stirred mixture was cooled to −20°C for 20 min. Then **2** (2 mmol) dissolved in 7 ml of CH_2Cl_2, was added and the reaction was monitored by TLC. The procedure is then the same as that reported above. Spectroscopic data of compounds **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g** and **3i** are consistent with the published data.[1a,2a,b,c,3a,12b]

4.5. *(R)-(*p*-Tolylsulfinyl)methyl phenyl ketone* **3a**

$[\alpha]_D^{24}$ +174.1 (*c* 1.1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): 2.37 (s, 3H), 4.39 (AB system, 2H, *J*=14.1 Hz), 7.24–7.30 (m, 2H), 7.38–7.61 (m, 5H), 7.82–7.88 (m, 2H); ^{13}C-NMR ($CDCl_3$): 21.1, 65.9, 124.2, 128.8. 130.0, 134.1, 136.0, 140.1, 142.2, 191.6. Anal. calcd for $C_{15}H_{14}SO_2$: C, 69.74; H, 5.46%. Found: C 69.61; H, 5.38%.

4.6. *(R)-(*p*-Tolylsulfinyl)methyl* n*-octyl ketone* **3b**

$[\alpha]_D^{24}$ +118.7 (*c* 1.3, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): 0.86 (t, 3H *J*=6.8 Hz), 1.10–1.42 (m, 8H), 1.43–1.60 (m, 2H), 2.30–2.60 (m, 5H), 3.80 (AB system, 2H, *J*=13.4 Hz), 7.30–7.36 (m, 2H), 7.49–7.58 (m, 2H); ^{13}C-NMR ($CDCl_3$): 14.0, 21.4, 22.5, 23.0, 29.0, 29.2, 29.6, 31.7, 45.0, 68.0, 124.0, 130.0, 139.7, 142.1, 201.8. Anal. calcd for $C_{17}H_{26}SO_2$: C, 69.34; H, 8.90%. Found: C, 69.50; H, 8.84%.

4.7. *(R)-(*p*-Tolylsulfinyl)methyl* n*-pentyl ketone* **3c**

$[\alpha]_D^{24}$ +85.8 (*c* 1.1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): 0.86 (t, 3H, 7.0 Hz), 1.14–1.38 (m, 4H), 1.42–1.58 (m, 2H), 2.35–2.62 (m, 5H), 3.80 (AB system, 2H, *J*=13.4 Hz), 7.23–7.36 (m, 2H), 7.49–7.58 (m, 2H);

^{13}C-NMR ($CDCl_3$): 13.7, 21.4, 22.3, 22.7, 44.9, 68.2, 124.1, 130.1, 140.5, 142.1, 201.7. Anal. calcd for $C_{14}H_{20}SO_2$: C, 66.63; H, 7.99%. Found: C, 66.81; H, 8.11%.

*4.8. (R)-(*p*-Tolylsulfinyl)methyl isopropyl ketone* ***3d***

$[\alpha]_D^{24}$ +95.9 (*c* 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): 1.00 (d, 3H, *J*=6.8 Hz), 1.08 (d, 3H, *J*=6.8 Hz), 2.41 (s, 3H), 2.58 (hept, 1H, *J*=6.8 Hz), 3.92 (AB system, 2H, *J*=14.0 Hz), 7.26–7.38 (m, 2H), 7.51–7.60 (m, 2H); ^{13}C-NMR ($CDCl_3$): 17.2, 17.3, 21.4, 42.2, 66.8, 124.1, 130.0, 140.0, 142.1, 205.5. Anal. calcd for $C_{12}H_{16}SO_2$: C, 64.25; H, 7.19%. Found: C, 64.42; H, 7.07%.

*4.9. (R)-(*p*-Tolylsulfinyl)methyl trans-β-methylvinyl ketone* ***3e***

$[\alpha]_D^{24}$ +142.8 (*c* 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): 1.83 (dd, 3H, J_1=6.9 Hz, J_2=1.3 Hz), 2.37 (s, 3H), 3.93 (AB system, 2H, *J*=13.5 Hz), 6.09 (dd, 1H, J_1=15.8 Hz, J_2=1.3 Hz), 6.63 (dq, 1H, J_1=15.8 Hz, J_2=6.9 Hz), 7.26–7.32 (m, 2H), 7.47–7.54 (m, 2H); ^{13}C-NMR ($CDCl_3$): 18.4, 21.3, 66.2, 124.0, 129.8, 131.7, 139.7, 141.9, 146.9, 190.5. Anal. calcd for $C_{12}H_{14}SO_2$: C, 64.84; H, 6.35%. Found: C, 64.75; H, 6.27%.

4.10. (R)-Methyl phenylsulfinyl acetate ***3f***

$[\alpha]_D^{24}$ +78.8 (*c* 1.3, acetone); ^{1}H-NMR ($CDCl_3$): 3.68 (s, 3H), 3.74 (AB system, 2H, *J*=13.6 Hz), 7.51 (m, 3H), 7.65 (m, 2H); ^{13}C-NMR ($CDCl_3$): 52.6, 61.4, 123.9, 129.3, 131.7, 142.9, 165.1. Anal. calcd for $C_9H_{10}SO_3$: C, 54.53; H, 5.08%. Found: C, 54.67; H, 5.00%.

4.11. (R)-Ethyl methylsulfinyl acetate ***3g***

$[\alpha]_D^{18}$ −43.0 (*c* 0.9, acetone); ^{1}H-NMR ($CDCl_3$): 1.30 (t, 3H, *J*=7.0 Hz), 2.70 (s, 3H), 3.69 (AB system, 2H, *J*=13.6 Hz), 4.24 (q, 2H, *J*=7.0 Hz); ^{13}C-NMR ($CDCl_3$): 14.1, 39.4, 57.9, 62.1, 164.9. Anal. calcd for $C_5H_{10}SO_3$: C, 39.99; H, 6.71%. Found: C, 40.10; H, 6.62%.

*4.12. (R)-(*p*-Tolylsulfinyl)methyl acetone* ***3h***

$[\alpha]_D^{24}$ +165.0 (*c* 0.9, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): 2.24 (s, 3H), 2.43 (s, 3H), 3.78 (AB system, 2H, *J*=13.4 Hz), 7.31–7.36 (m, 2H), 7.51–7.55 (m, 2H); ^{13}C-NMR ($CDCl_3$): 21.3, 31.9, 68.5, 123.9, 130.0, 139.4, 142.1, 199.4. Anal. calcd for $C_{10}H_{12}SO_2$: C, 61.20; H, 6.16%. Found: C, 61.09; H, 6.22%.

*4.13. (R)-*t*-Butyl (*p*-tolylsulfinyl) acetate* ***3i***

$[\alpha]_D^{20}$ +61.4 (*c* 1.5, ethanol); ^{1}H-NMR ($CDCl_3$): 1.35 (s, 9H), 2,37 (s, 3H), 3.64 (AB system, 2H, *J*=13.6 Hz), 7.27–7.31 (m, 2H), 7.52–7.57 (m, 2H); ^{13}C-NMR ($CDCl_3$): 21.2, 27.7, 62.6, 83.1, 124.5, 130.0, 140.1, 142.4, 164.0. Anal. calcd for $C_{13}H_{18}SO_3$: C, 61.39; H, 7.13%. Found: C, 61.51; H, 7.05%.

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