Synthesis of Chiral Cyclic α-*p*-Tolylsulphinyl Ketones

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Two new syntheses of optically pure cyclic β-oxo sulphoxides are described. Reactions of (−)-menthyl toluene-*p*-sulphinate with cycloalkanones $(CH_2)_nCO$ (n = 4, 5, and 6) and Pr^i_2NMgBr yield mixtures of diastereoisomeric sulphoxides without epimerization at sulphur. With the cyclopentanone (n = 4) yields are poor owing to competitive autocondensation of the ketone. Reactions of cycloalkanone *N*-phenylimines with the sulphinate in the presence of lithium di-isopropylamide afford, after chromatographic purification, the same mixtures of diastereoisomeric β-oxo sulphoxides with no aldolic condensation product.

The method most frequently used in the synthesis of acyclic enantiometically pure β-oxo sulphoxides involves reaction of α-lithium (*R*)-(−)-*p*-tolyl methyl sulphoxide with esters.[1] The important role of these substrates in asymmetric synthesis,[2] and the inaccessibility of α-arylsulphinylcycloalkanones by this method, prompted us to search for a route to chiral cyclic β-oxo sulphoxides.

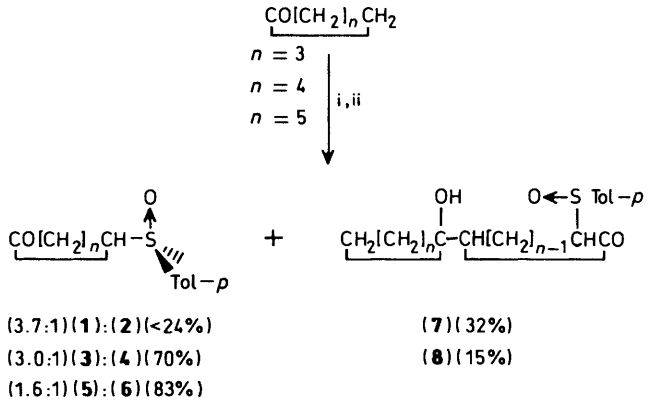
Reactions of lithium or sodium enolates derived from cyclic ketones with (*S*)-(−)-menthyl toluene-*p*-sulphinate were the most obvious methods to these compounds. Nevertheless, Hiroi *et al.*[3] showed that these processes took place with epimerization at sulphur. In a previous communication we described how this problem could be overcome for cyclohexanone using magnesium bases.[4] Here we extend the method to cyclopentanone and cycloheptanone and report an alternative general route to optically pure α-*p*-tolylsulphinylcycloalkanones which in the case of cyclopentanone lead to the corresponding sulphoxide in improved yield.

Results and Discussion

Cycloalkanones react with (*S*)-(−)-menthyl toluene-*p*-sulphinate and Pr^i_2NMgBr to afford, after flash chromatography, mixtures of C-2 epimeric sulphoxides, the relative proportions and total yields of which depend on the size of the ring (Scheme 1).

Cycloheptanone gave a mixture of (**5**) and (**6**) from which (**5**) crystallized diastereoisomerically pure from acetone (m.p. 114—116 °C). Since traces of NaOH quickly epimerize (**5**) into a 1.6:1 mixture of (**5**):(**6**), it is possible to equilibrate these two diastereoisomers and then displace this equilibrium in order to obtain (**5**) pure, by crystallization of this insoluble epimer from acetone containing a few drops of dilute NaOH. Compound (**5**) exhibited [α] = +357° (c = 1, acetone) and its ^1H n.m.r. analysis with Eu(tfc)$_3$ showed an optical purity >95%. Both spectroscopic parameters and optical rotation of (**6**) were obtained from the mixture (**5**) + (**6**).

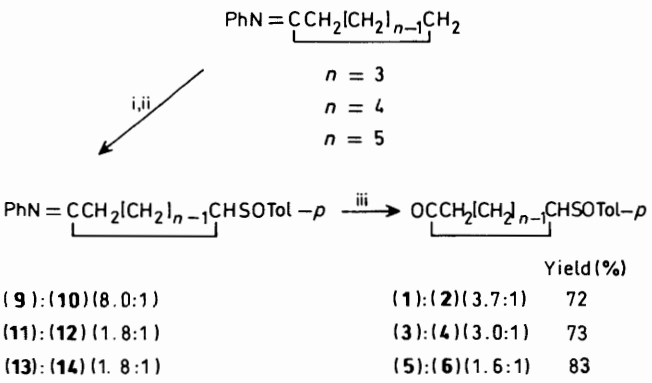
Cyclopentanone, under the conditions of Scheme 1, gave poor yields (24%) of a mixture (**1**):(**2**) (3.7:1). Isolation of pure (±)-(**1**) was possible by crystallization from the racemic mixture (**1**) + (**2**), obtained using (±)-menthyl toluene-*p*-sulphinate as starting product. We were unable to crystallize (**1**) optically pure from the corresponding optically active mixture. Therefore, the optical rotation of (**1**) and (**2**) could not, unfortunately, be determined and the m.p. indicated in the Experimental part corresponds to (±)-(**1**). The major product isolated in this reaction (32%) was identified as (**7**). This



Scheme 1. *Reagents:* i, Pr^i_2NMgBr; ii (*S*)-*p*-TolSO_2Menthyl

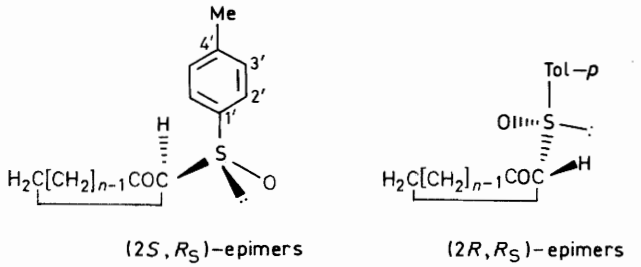
compound is likely to arise from attack of the magnesium enolate resulting from the aldolic reaction product of cyclopentanone on the menthyl toluene-*p*-sulphinate. The alternative route to (**7**), enolization of 2-*p*-tolylsulphinylcyclopentanone and subsequent reaction with cyclopentanone, is not feasible because, in the presence of magnesium base, enolization would occur at C-2 to give a magnesium stable chelate. This was demonstrated by failure to obtain compound (**7**) upon treatment of the (**1**) + (**2**) mixture in sequence with Pr^i_2NMgBr and cyclopentanone. A similar product (**8**) was identified (15%) in the reaction of cyclohexanone[4] whereas the aldolic derivative was not detected among the products formed from cycloheptanone.

In order to improve yields in the case where the aldolic reaction was the favoured process, we designed an alternative synthetic route. Compounds (**3**) + (**4**) had been obtained[5] by reaction of α-lithium cyclohexanone *N*,*N*-dimethylhydrazone with (*S*)-(−)-menthyl toluene-*p*-sulphinate and subsequent hydrolysis. The authors suggested that the hydrolysis step, which involved strong acidic conditions, resulted in epimerization at sulphur and decreased the enantiomeric excess which we estimated as 60%.[4] Having this fact in mind, cycloalkanone imines were thought likely to be better starting materials since they might be hydrolysed under milder conditions. Thus, we prepared the *N*-phenyl imines of the cycloalkanones (n = 3, 4, 5, Scheme 2) which were treated at −78 °C with (*S*)-(−)-menthyl toluene-*p*-sulphinate and lithium di-isopropylamide (LDA) to yield mixtures of diastereoisomeric α-*p*-tolylsulphinyl imines, epimers at C-α, easily identified from the spectroscopic



Scheme 2. *Reagents and conditions:* i, LDA, ii, (*S*)-(−)-menthyl toluene-*p*-sulphinate; iii, 5% H_2SO_4; iv, flash chromatography

Table. Significant parameters in the configurational assignment of compounds (**1**)—(**6**)



			Chemical shifts (δ/p.p.m.)[b]					
Compd.	|α|	E.e.	H(2)	C-1	C-2	C-3	C-1′	C-2′
(**1**)		>95%	3.27	211.3	70.2	19.7	138.1	123.2
(**2**)		>95%	3.77	210.6	68.2	22.2	136.6	124.1
(**3**)	+292	>95%	3.38	205.2	74.3	24.6	138.8	124.5
(**4**)	≈ +96[a]	>95%	3.53	204.8	73.1	27.7	137.6	125.1
(**5**)	+357	>95%	3.49	208.6	76.6	21.8	138.6	124.2
(**6**)	≈ −70[a]	>95%	3.79	207.6	74.8	23.8	136.6	124.8

[a] Estimated from the values obtained for the corresponding mixtures. [b] Assignment is based on DEPT and ^1H-^{13}C 2-D experiments.

parameters of the crude reaction mixture. In no case were products of similar structure to that of (**7**) and (**8**) detected. Flash chromatography of these mixtures, previously washed with 5% H_2SO_4, gave rise to the corresponding cyclic α-sulphinyl ketones (Scheme 2). Optical rotations of the various epimers obtained by this method were identical with those of the samples resulting from magnesium enolates. This indicates that no epimerization at sulphur takes place.

The ^1H and ^{13}C n.m.r. spectra of the isomers (**1**), (**3**), and (**5**) differed from those of their epimers (**2**), (**4**), and (**6**), in a highly systematic way within the series of oxo sulphoxides (**1**)—(**6**) (see Table 1). Such differences suggested that the configuration must be identical for each group of epimers. Configurational assignments for (**3**) and (**4**) have unequivocally been established on the basis of the stereochemistry of the alcohols obtained from their reduction with DIBAL.[4] Thus, we assigned the same configuration to compounds (**1**) and (**5**) as that established for (2*S*,R_S)-(**3**) and to (**2**) and (**6**) that established for (2*R*,R_S)-(**4**). Such assignments are supported by the fact that (**3**) and (**5**) exhibited a higher positive optical rotation than their corresponding epimers (**4**) and (**6**), and they were the only ones which could be crystallized from their mixtures. Further, reduction studies on the oxo sulphoxides (**1**), (**2**), (**5**), and (**6**), also similar to those carried out on (**3**) and (**4**), support the assignments made.

Experimental

General.—The solvents and reagents were purified and dried by standard techniques. Silica gel used in chromatography was Merck F-254 (TLC) or 60 (230—400 mesh) (column). M.p.s were measured on a Büchi 594392 type S apparatus in open capillary tubes and are uncorrected. Mass spectra (m.s.) were determined in a HP-5985 spectrometer in the electron impact (e.i.) ionization mode at 70 eV. Mass data are reported in mass unit (*m*/*z*) and the values in brackets refer to the relative intensity from the base peak (as 100%). The i.r. spectra were obtained on a Philips PU 9716. All the n.m.r. spectra were recorded in $CDCl_3$ on a Bruker WP-200-SY spectrometer. Shifts were reported in p.p.m. downfield from internal TMS. Diastereoisomer ratios were established by integration of the signals corresponding to the proton at C-2 in the crude mixtures. Optical purity was determined by ^1H n.m.r. analysis using the chiral shift reagent Eu(tfc)$_3$. The racemic compounds required for this determination were obtained from (±)-menthyl-toluene-*p*-sulphinate following the same procedure.

Cyclic α-p-Tolylsulphinyl Ketones from Cycloalkanones: General Procedure.—A solution of Pr^i_2NMgBr was prepared from ethylmagnesium bromide (0.9M solution in ether; 60 ml and Pr^i_2NH (5.15 g, 51 mmol). After ether evaporation by passage of a stream of dry N_2, benzene (50 ml) was added. To the resulting suspension, cooled at 0 °C, a solution of cycloalkanone (35 mmol) and (*S*)-(−)-menthyl toluene-*p*-sulphinate (4.00 g, 13 mmol) in benzene (50 ml) was added. The mixture was stirred at 0 °C for 3 h and at room temperature for 13 h, after which it was quenched by the addition of 10% NH_4Cl (150 ml). The organic layer was separated, washed with water, dried ($MgSO_4$), filtered, and concentrated under reduced pressure.

2-p-*Tolylsulphinylcyclopentanone* (**1**) *and* (**2**). Chromatography of the crude reaction mixture using chloroform–acetone (9:1) as eluant allowed us to separate the aldolic reaction product (**7**) (32% yield) and the crude oxo sulphoxides (**1**) and (**2**) with a small amount of menthol. Pure oxo sulphoxides were obtained by subsequent chromatography (ethyl acetate–hexane, 9:1) as a colourless oil, (**1**)/(**2**) (3.7:1), $[\alpha]_D^{20}$ = +440° (*c* 1, acetone), 24% yield. Racemic (**1**) was separated from the racemic mixture by crystallization from acetone–hexane.

(2*S*,R_S)-(**1**) M.p. 87—89 °C, $\nu_{max.}$(KBr): 2 955, 1 740, 1 400, 1 250, 1 160, 1 140 and 810 cm^{-1}; *m*/*z* 224 [(*M* + 2)$^+$, 2], 222 (*M*$^+$, 29), 139 (100), 123 (3), 91 (24), 77 (14), 65 (21), and 55 (44); δ_H 7.50 and 7.33 (AA′BB′ system 4 H, Tol), 3.27 (t, *J* 8.6 Hz, 1 H, 2-H), 2.42 (s, 3 H, CH_3) and 2.63—1.65 (m, 6 H); δ_C 211.3 (CO), 140.7 (C-4′), 138.1 (C-1′), 129.3 (C-3′), 123.2 (C-2′), 70.2 (C-2), 38.5 (C-5), 20.7 (CH_3), 19.7 (C-3), and 18.3 (C-4).

(2*R*,R_S)-(**1**) δ_H 7.50 and 7.33 (AA′BB′ system, 4 H, Tol), 3.77 (dd, *J* 5.5 and 9.1 Hz, 1 H, 2-H), 2.42 (s, 3 H, CH_3), and 2.63—1.50 (m, 6 H); δ_C 210.6 (CO), 141.4 (C-4′), 136.6 (C-1′), 129.2 (C-3′), 124.1 (C-2′), 68.2 (C-2), 38.5 (C-5), 22.2 (C-3), 20.7 (CH_3), and 18.3 (C-4). These data were obtained from a 3.7:1 mixture of (**1**) and (**2**).

5-(1-*Hydroxycyclopentyl*)-2-p-*tolylsulphinylcyclopentanone* (**7**). M.p. 136—137 °C (crystallized from acetone), $[\alpha]_D^{20}$ = +475. (*c* 1, acetone); $\nu_{max.}$(KBr) 3 480, 2 960, 1 740, 1 370, 1 140, 1 090, 1 050, and 810 cm^{-1}; *m*/*z* 306 (*M*$^+$, 9), 222 (3), 167 (15), 150 (35), 139 (84), 91 (41), 83 (57) and 55 (100); δ_H 7.47 and 7.32 (AA′BB′ system, 4 H, Tol), 3.31 (dd, *J* 8.6 and 10.6 Hz, 1 H, 2-H), 2.42 (s, 3 H, CH_3), and 2.54—1.45 (m, 14 H). δ_C 212.7 (CO), 141.3 (C-4′), 138.2 (C-1′), 129.7 (C-3′), 123.6 (C-2′), 81.5 (C-2),

71.8 (C-1″), 58.8 (C-5), 38.4 and 37.4 (C-2″ and C-5″), 23.5, 23.0, 22.9, 21.2 (CH_3), and 15.5.

2-p-*Tolylsulphinylcyclohexanone* (**3**) *and* (**4**). These compounds were obtained by flash chromatography on silica gel (ethyl acetate–CCl_4, 9:1) from the crude reaction mixture as a colourless oil which crystallized with time [(3):(4) 3.0:1], 70% yield. The aldolic condensation product (**8**) was isolated in 15% yield. The pure diastereoisomer (**3**) was isolated by crystallization from acetone–hexane (60% yield).

(2*S*,R_S)-(**3**) M.p. 114—115°, $[\alpha]_D^{20}$ = +292, (*c* 1, acetone); $\nu_{max.}$(Nujol) 2 900, 1 705, 1 460, 1 380, 1 080, 1 040, and 810 cm^{-1}; *m*/*z* 236 (M^+, 20), 167 (15), 149 (47), 139 (61), 97 (53), 69 (100), 57 (90), and 43 (75); δ_H 7.52 and 7.31 (AA′BB′ system, 4 H, Tol), 3.38 (ddd, *J* 1.2, 5.6 and 9.6 Hz, 1 H, 2-H), 2.53 (m, 1 H, 6e-H), 2.41 (s, 3 H, CH_3), and 2.44—1.55 (m, 7 H); δ_C 205.2 (CO), 141.5 (C-4′), 140.0 (C-1′), 129.7 (C-3′), 124.5 (C-2′), 74.3 (C-2), 42.3 (C-6), 26.3, 24.6 (C-3), 23.0, and 21.3 (CH_3).

(2*R*,R_S)-(**4**). δ_H 7.52 and 7.31 (AA′BB′ system, 4 H, Tol), 3.53 (t, *J* 6.8 Hz, 1 H, 2-H), 2.41 (s, 3 H, CH_3) and 2.53—1.55 (m, 8 H); δ_C 204.8 (CO), 141.9 (C-4′), 137.6 (C-1′), 129.7 (C-3′) 125.1 (C-2′), 73.1 (C-2), 42.8 (C-6), 27.7 (C-3), 24.8, 22.6 and 21.3 (CH_3). These data were obtained from a 3:1 mixture of (**3**) and (**4**).

6-(1-*Hydroxycyclohexyl*)-2-p-*tolylsulphinylcyclohexanone* (**8**). M.p. 154—155 °C (crystallized from acetone), $[\alpha]_D^{20}$ = +79. (*c* 0.7, acetone); $\nu_{max.}$(Nujol) 3 380, 2 900, 1 707, 1 460, 1 380, 1 020, and 965 cm^{-1}; *m*/*z* 334 (M^+, 0.1), 306 (3), 222 (3), 167 (17), 149 (100), 91 (65), 83 (34), 67 (36), and 55 (51); δ_H 7.58 and 7.32 (AA′BB′ system, 4 H, Tol), 3.67 (dd, *J* 5.8 and 12.5 Hz, 1 H, 2-H), 3.02 (br s, 1 H, OH), 2.41 (s, 3 H, CH_3) and 2.55—1.07 (m, 17 H); δ_C 210.1 (CO), 141.9 (C-4′), 137.2 (C-1′), 129.5 (C-3′), 125.9 (C-2′), 76.1 (C-2), 71.7 (C-1″), 59.7 (C-6), 35.8 and 33.7 (C-2″ and C-6″), 28.7, 28.6, 25.6, 24.3, 21.5, and 21.2 (CH_3).

2-p-*Tolylsulphinylcycloheptanone* (**5**) *and* (**6**). Crystallization of the crude reaction from hexane at −20 °C afforded a 2.8:1 mixture of (**5**) and (**6**) in 68% yield. The residue obtained from evaporation of mother liquors was chromatographed to give a 1.6:1 mixture of (**5**):(**6**) (15% yield). Pure (**5**) crystallized from the mixture in a solution of acetone containing a few drops of 1% NaOH solution (82% yield).

(2*S*,R_S)-(**5**). M.p. 114—116,$[\alpha]_D^{20}$ = +357. (*c* 1, acetone); $\nu_{max.}$(KBr) 2 940, 1 700, 1 460, 1 315, 1 090, 1 040, and 820 cm^{-1}; *m*/*z* 250 (M^+, 15), 139 (59), 111 (47), 83 (24), and 55 (100); δ_H 7.52 and 7.32 (AA′BB′ system, 4 H, Tol), 3.49 (dd, *J* 4.5 and 10.8 Hz, 1 H, 2-H), 2.53—2.32 (m, 2 H, 6e-H and 6a-H), 2.41 (s, 3 H, CH_3) 2.12—1.79 (m, 5 H), and 1.59—1.23 (m, 3 H); δ_C 208.6 (CO), 141.1 (C-4′), 138.6 (C-1′), 129.3 (C-3′), 124.2 (C-2′), 76.6 (C-2), 43.2 (C-7), 28.8, 27.1, 24.0, 21.8 (C-3), and 20.8 (CH_3).

(2*R*,R_S)-(**6**) δ_H 7.52 and 7.32 (AA′BB′ system, 2.48 H, Tol), 7.48 and 7.32 (AA′BB′ system, 1.52 H, Tol), 3.79 (dd, *J* 4.4 and 11.5 Hz, 1 H, 2-H), 2.41 (s, 3 H, CH_3), 2.53—1.79 (m, 7 H) and 1.64—1.20 (m, 3 H); δ_C 207.6 (CO), 141.5 (C-4′), 136.6 (C-1′), 129.4 (C-3′), 124.8 (C-2′), 74.8 (C-2), 43.6 (C-7), 29.4, 23.8 (C-3), 24.2, 21.6, and 21.0 (CH_3). These data were obtained from a 1.6:1 mixture of (**5**) and (**6**).

Cyclic α-p-*Tolylsulphinyl Ketones from* N-*Phenylimines of Cycloalkanones: General Procedure.*—To a solution of LDA (31.3 mmol) in THF (100 ml) was added *via* a transfer needle a solution of the imine (36.7 mmol)[6] in THF (50 ml) at −78 °C. The mixture was then placed in an ice-bath and stirred for 30 min, and finally stirred for 1 h without cooling. After this time, the mixture was recooled to −78 °C, and a solution of (*S*)-(−)-menthyl toluene-*p*-sulphinate (13.6 mmol) in THF (50 ml) added *via* a transfer needle. The reaction mixture was stirred for 10 min at −78 °C and then quenched with NH_4Cl. Work-up produced the corresponding α-sulphinyl imines (relative ratios are indicated in Scheme 2) and menthol.

(**9**) + (**10**) (8.0:1 mixture). δ_H 7.55 and 7.73 (AA′BB′ system, 4 H, Tol), 7.28 (m, 2 H, C_6H_4N), 7.10 (m, 1 H, C_6H_4N), 6.88 (m, 2 H, 2 2-H C_6H_4N), 4.25 [dd, *J* 5.8 and 8.6 Hz, 0.11 H, 2-H (**10**)], 3.66 [t, *J* 7.8 Hz, 0.89 H, 2-H (**9**)], 2.38 (s, 3 H, CH_3), and 2.40—1.62 (m, 6 H); δ_C 176.2 [CN (**9**)], 175.2 [CN (**10**)], 150.8—114.7 (16 C), 69.7 [C-2 (**9**)], 68.3 [C-2 (**10**)], 31.6 [C-3 (**9**)], 31.3 ([C-3 (**10**)] and 22.6—19.6 (6 C), *m*/*z* 297 (M^+, 2), 249 (21), 158 (100), 139 (19), 130 (25), 104 (11), 91 (31), 77 (82), 65 (47), and 41 (26).

(**11**) + (**12**) (1.8:1 mixture). δ_H 7.65 and 7.35 (AA′BB′ system, 4 H, Tol), 7.23 (m, 2 H, C_6H_4N), 7.10 (m, 1 H, C_6H_4N), 6.53 (m, 2 H, 2 2-H, C_6H_4N), 3.57 [m, 0.64 H, 2-H (**11**)], 3.57 [m, 0.36 H, 2-H, (**12**)], 2.42 (s, 3 H, CH_3), and 2.40—1.50 (m, 8 H); δ_C 168.8 [CN, (**11**)], 169.0 [CN, (**12**)], 149.0—114.1 (16 C), 73.3 [C-2 (**11**)], 70.6 [C-2 (**12**)], 31.0 [C-3 (**11**)], 31.1 [C-3 (**12**)], and 28.1—21.3 (8 C); *m*/*z* 311 (M^+, 5), 263 (66), 172 (71), 143 (31), 139 (31), 104 (30), 91 (35), 77 (100), 65 (30), 51 (35), and 41 (54).

(**13**) + (**14**) (1.8:1 mixture). δ_H 7.65 and 7.33 (AA′BB′ system, 4 H, Tol), 7.20 (m, 2 H, C_6H_4N), 7.12 (m, 1 H, C_6H_4N), 6.61 (m, 2 H, 2 2-H, C_6H_4N), 3.96 [dd, *J* 5.3 and 11.5 Hz, 0.36 H, 2-H (**14**)], 3.65 [dd, *J* 5.3 and 11.1 Hz, 0.64 H, 2-H (**13**)], 2.43 [s, 1.92 H, CH_3 (**13**)], 2.41 [s, 1.08 H, CH_3 (**14**)], and 2.41—1.22 (m, 10 H); δ_C 172.9 [CN (**13**)], 171.0 [CN (**14**)], 150.0—115.2 (16 C), 73.8 [C-2 (**13**)], 71.8 [C-2 (**14**)], 31.9 [C-3 (**13**)], 31.6 [C-3 (**14**)], and 28.0—18.9 (10 C); *m*/*z* 325 (M^+, 7), 277 (63), 186 (44), 139 (18), 130 (39), 104 (50), 91 (37), 77 (100), 69 (67), 55 (87), and 41 (96).

To obtain the oxo sulphoxides, the isolation procedure was modified as follows: after quenching the reaction mixture with NH_4Cl, a solution of 5% H_2SO_4 (100 ml) and ether (100 ml) were added and the resulting aqueous layer was extracted twice with ether. The ethereal phase was washed twice with 5% H_2SO_4 and saturated aqueous $NaCO_3H$. Work-up produced a crude reaction mixture containing menthol, starting cycloalkanone, and the β-oxo sulphoxide. Flash chromatography on silica gel (eluant ethyl acetate–hexane [1:1 for (**1**), (**2**), (**5**), and (**6**), and ethyl acetate–hexane: 2:1 for (**3**) and (**4**)] afforded mixtures of the oxosulphoxides (**1**) and (**2**) (3.7:1) in 72% yield, (**3**) and (**4**) (3.0:1) in 73% yield, and (**5**) and (**6**) in 83% yield.

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References

1 N. Kunieda, J. Nokami, and M. Kinosita, *Chem. Lett.*, 1974, 369.
2 G. Solladié, *Chem. Scr.*, 1985, **25**, 149; G. H. Posner, *Chem. Scr.*, 1985, **25**, 157; G. H. Posner, *Acc. Chem. Res.*, 1987, **20**, 72; G. Solladié and J. Hutt, *Tetrahedron Lett.*, 1987, **28**, 797.
3 K. Hiroi and N. Matsuyama, *Chem. Lett.*, 1986, 65. In the case of cyclohexanone a 17% enantiomeric excess was determined when NaH was used as the base (see ref. 4).
4 M. C. Carreño, J. L. Garcia Ruano and A. Rubio *Tetrahedron Lett.*, 1987, **28**, 4861.
5 L. Banfi, L. Colombo, C. Gennari, R. Annunziata, and F. Cozzi, *Synthesis*, 1982, 829.
6 K. Taguchi and F. H. Westheimer, *J. Org. Chem.*, 1971, **36**, 1570.

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