Pergamon

Tetrahedron: Asymmetry Vol. 6, No. 7, pp. 1731-1740, 1995
Elsevier Science Ltd
Printed in Great Britain
0957-4166/95 $9.50+0.00

0957-4166(95)00219-7

Asymmetric Methylene Transfer Reactions II : Asymmetric Synthesis of Oxiranes from Carbonyl Compounds by Methylene Transfer Reaction using Chiral S-Neomenthyl and S-exo-2-Bornyl Sulfoximines +

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Abstract : Three chiral sulfoximines, *viz.*, (1R,Ss)-(-)-S- methyl-S-*exo*-2-bornyl-N-tosyl sulfoximine, **9a**, its epimer at sulfur, (1R,Rs)-(+)-**9b**, and (1R,3S,4S,1'S,Rs)-(+)-S-methyl-S-neomenthyl-N-(camphor-10-sulfonyl) sulfoximine, **19**, were used as methylene transfer reagents in the preparation of nonracemic oxiranes (enantiomeric excess, 19-86%) from prochiral carbonyl compounds. Sulfoximines **9a** and **9b** were found to be less effective (ee, 19-68%) than the corresponding S-neomenthyl sulfoximines **2a** and **2b** (ee, 56- 86%), and, sulfoximine **19**, despite having a chiral auxiliary on nitrogen in place of the tosyl group, was found to be only as effective as the corresponding N-tosyl sulfoximine **2b** in influencing the steric course of these reactions. The absolute configuration at sulfur of all the synthesised sulfoxides and sulfoximines has been established by X-ray studies.

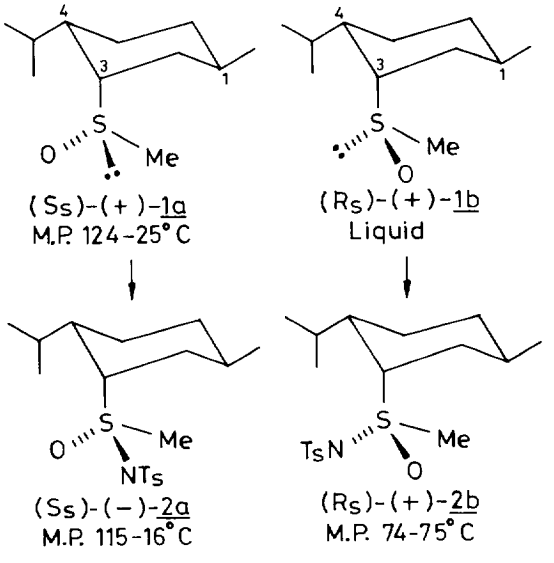
INTRODUCTION

In our previous paper[1] we gave a brief overview of the methods available for the synthesis of chiral oxiranes and presented our results on the asymmetric synthesis of oxiranes from carbonyl compounds using (-)-S-methyl-S-neomenthyl-N-tosyl sulfoximine, **2a**, and its epimer at sulfur, (+)-**2b**, as methylene transfer (MT) reagents. Sodium salts of these sulfoximines on reaction with prochiral aldehydes and ketones gave chiral oxiranes with moderate to high (56-86%) enantiomeric excess (ee). The present paper reports the absolute configuration at sulfur of sulfoximines **2a** and **2b** as determined by X-ray studies and our results on the effect of variation in chiral substituents both at sulfur and at nitrogen of sulfoximines on the extent and kind of asymmetric induction in MT reactions. Meanwhile, other papers have appeared reporting low to moderate (11-43%) ee in similar MT reactions using chiral sulfonium ylides derived from pinene[2] or using chiral S-methyl-S-aryl sulfoximines[3].

+ MRC Communication No.70

RESULTS AND DISCUSSIONS

An epimeric mixture of two sulfoxides[1] (solid and liquid sulfoxides, **1a** and **1b**) resulted when (1R,3R,4S)-(-)-menthol was converted to S-methyl-S-neomenthyl sulfoxide. The absolute configuration at sulfur of (+)-S-methyl-S-neomenthyl sulfoxide (**1a**, m.p. 124-5°C) has now been found to be (S) based on single crystal X-ray structure analysis. Sulfoxides having stereogenic sulfur react with tosyl azide in presence of copper (Kwart-Kahn method[4]) to give sulfoximines with retention of configuration[5] at sulfur. Accordingly, sulfoximine **2a** derived from sulfoxide **1a** should have (S) configuration at sulfur (Scheme 1). The epimeric sulfoxide, **1b** (liquid), and sulfoximine **2b** derived from **1b** then should have (R) configuration at sulfur[6]. This has been confirmed by single crystal X-ray structure analysis of sulfoximine **2b** (ORTEP diagram, Fig 1).



Scheme 1

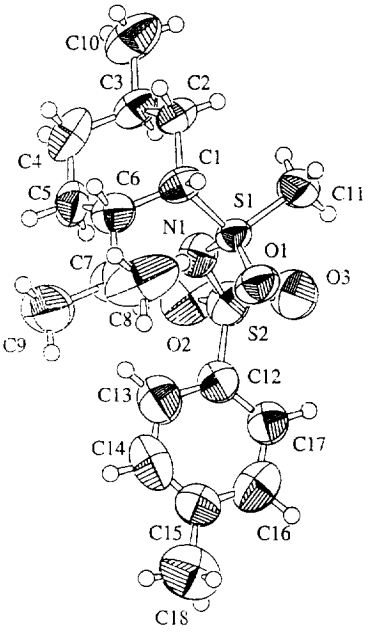


Fig 1 : ORTEP Diagram of **2b**

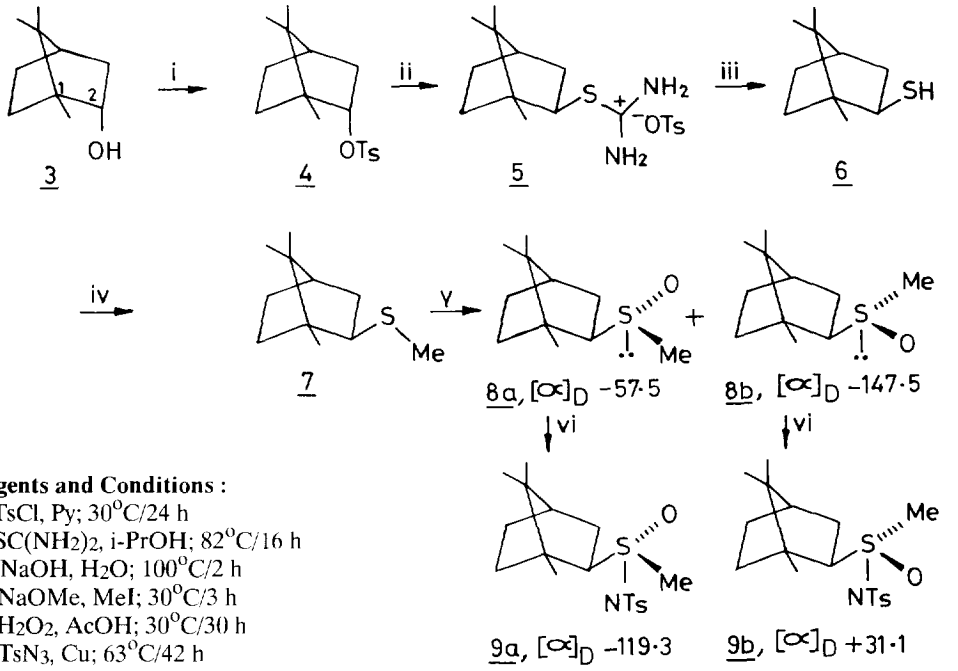
Oxiranes resulting from the reaction of benzaldehydes **10** and **11** with sodium salt of (Ss)-sulfoximine, (Ss)-**2a** had (R) configuration[1]; (Rs)-sulfoximine, (Rs)-**2b** gave (S)- oxiranes. Phenyl ketones **12** and **13** when reacted similarly with (Ss)-**2a** gave oxiranes (-)-**16** and (-)-**17** (absolute configurations not established[7]); when reacted with (Rs)- **2b**, **13** gave (+)-**17**. Thus in all these cases[1], the enantiomer of oxirane obtained with (Rs)-sulfoximine was different from the enantiomer obtained with (Ss)-sulfoximine.

Assuming that replacement of the monocyclic neomenthyl group[1] on sulfur in sulfoximines **2a** and **2b** with the bicyclic *exo*-2-bornyl group should introduce more rigidity in the sulfoximine molecule and more

steric crowding around sulfur atom and that this should result in substantially higher enantioselectivity in MT reactions, we chose the epimeric pair of S-methyl-S-*exo*-2-bornyl-N-tosyl sulfoximines **9a** and **9b** as chiral reagents for this purpose.

(1R)-(-)-*exo*-2-Bornanethiol, **6**, was prepared from (1R)-(+)-*endo*-2-borneol, **3**, *via* its tosylate, **4**, and isothiouronium p-toluene sulfonate salt, **5**, as per the known procedure[8] (Scheme 2). This thiol was methylated with methyl iodide and the sulfide[9], **7**, was oxidised with hydrogen peroxide to an epimeric (at sulfur) pair of sulfoxides, **8a** and **8b**, (45:55; GC: cyclodex B capillary column).

This mixture could be separated by column chromatography on silica gel into sulfoxide **8a**, minor isomer, $[\alpha]_D$ -57.5, and, **8b**, major isomer, $[\alpha]_D$ -147.5. Reactions of these sulfoximines with p-toluene sulfonyl azide gave the corresponding sulfoximines, **9a** (from **8a**), $[\alpha]_D$ -119.3, and, **9b** (from **8b**), $[\alpha]_D$ +31.1.



Reagents and Conditions :
i. TsCl, Py; 30°C/24 h
ii. $SC(NH_2)_2$, i-PrOH; 82°C/16 h
iii. NaOH, H_2O; 100°C/2 h
iv. NaOMe, MeI; 30°C/3 h
v. H_2O_2, AcOH; 30°C/30 h
vi. TsN_3, Cu; 63°C/42 h

Scheme - 2

High resolution ^1H NMR came in handy to establish clearly the chemical and enantiomeric homogeneity of sulfoxide **8a** and **8b** (besides capillary GC on chiral column) and of sulfoximines **9a** and **9b**. In the case of sulfoxide **8a**, the singlet due to one of the three quarternary methyls of the *exo*-2-bornyl group appears at δ 1.22 whereas in **8b**, all the three singlets appear in the region δ 0.86-0.98. Also, in **8a**, the proton on C-2 (*H*C-S-) appear as a triplet at δ 2.62 away from the S-C*H*$_3$ signal (δ 2.45). Whereas in **8b**, *H*C-S signal appear as a triplet at δ 2.51 at the base of the singlet due to -S-C*H*$_3$ (δ 2.52). Similarly in

sulfoximine **9b** the protons of S-C*H*$_3$ appear as a singlet at δ 3.31 and *H*C-S- signal appear as a triplet downfield centered at δ 3.42. The corresponding signals of **9a** appear at δ 3.46 (3H,s) and at δ 3.29 (1H,t).

S-Methyl-S-*exo*-2-bornyl sulfoxides were low melting solids and could not be utilised for X-ray structure studies. Crystals of sulfoximine **9b** consisted of two independent molecules in one unit cell (ORTEP drawing, Fig. 2). The absolute configuration at sulfur in **9b** was found to be (R). This establishes that sulfoxide **8b** should have (R)-configuration and that sulfoxide **8a** and sulfoximine **9a** should have (S) configuration at sulfur.

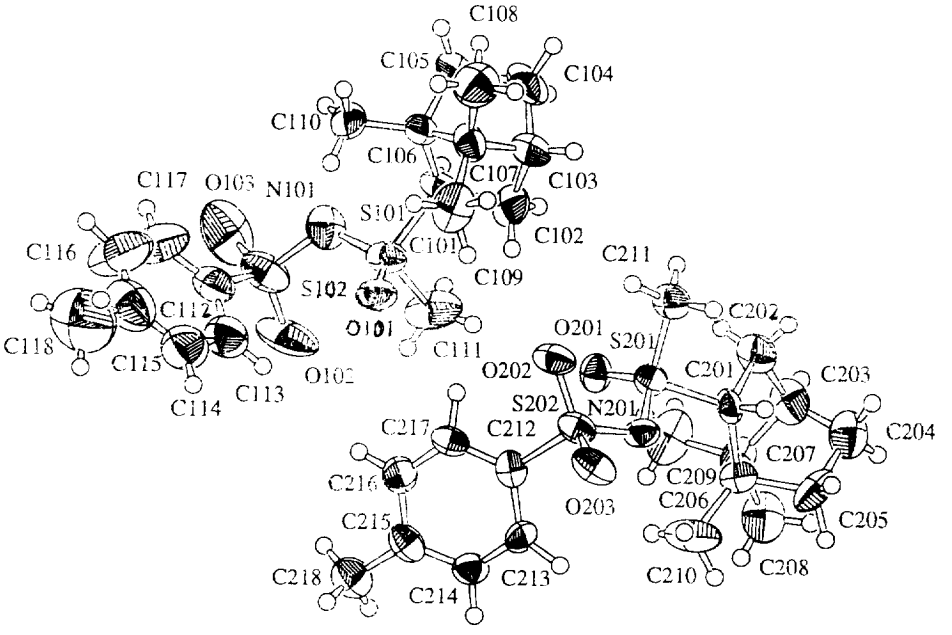
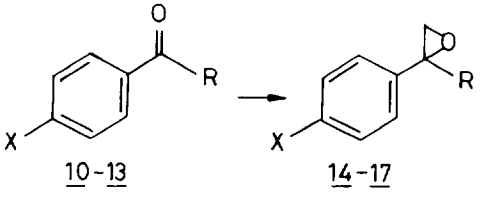


Fig 2 : ORTEP Drawing of **9b**

Four carbonyl compounds, **10-13**, were used as substrates for synthesis of chiral oxiranes using sulfoximines **9a** and **9b** as MT reagents (Scheme 3). The asymmetric induction achieved with each reagent is given in Table 1.



	X	R
10, 14	H	H
11, 15	Cl	H
12, 16	H	Me
13, 17	Cl	i-Pr

Scheme - 3

It is observed that reactions of S-*exo*-2-bornyl sulfoximines with prochiral carbonyl compounds giving nonracemic oxiranes are comparatively slower than those of S-neomenthyl sulfoximines under the same conditions. The yields of oxiranes also were generally lower.

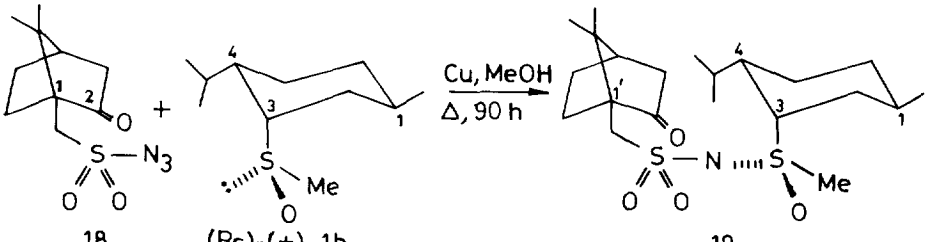
Table 1 : Asymmetric Induction in Oxirane Synthesis using Sulfoximines 9a & 9b

No.	Carbonyl Substrate	Product Oxirane With sulfoximine **9a**		With sulfoximine **9b**	
		Identity	ee(%)GC*	Identity	ee(%)GC*
1.	Benzaldehyde **10**	(S)-(-)-**14**	28.6 (b)	(S)-(-)-**14**	28.5 (b)
2.	4-Chlorobenzaldehyde **11**	(S)-(-)-**15**	21.7 (b)	(S)-(-)-**15**	18.6 (b)
3.	Acetophenone **12**	(-)-**16**	a > b+	(+)-**16**	56.9 (b)
4.	1-(4-Chlorophenyl) -2-methyl Propan-1-one **13**	(-)-**17**	58.1 (b)	(+)-**17**	68.2 (a)

* Cyclodex B capillary column, 25m x 0.25 mm;
'a' denotes the fast eluting enantiomer in excess ; 'b' denotes the slow eluting enantiomer in excess.
\+ Reaction sluggish ; unconverted acetophenone interferes in GC.

It came as a surprise to us that changing the neomenthyl moiety on sulfur to a more rigid bicyclic chiral auxiliary such as *exo*-2-bornyl group resulted actually in lower ee in oxiranes synthesised. Not only that, both (Ss)- and (Rs)- sulfoximines, **9a** and **9b**, gave the same (S)-oxiranes when the substrates were benzaldehydes, though, when phenyl ketones were used as substrate, each sulfoximine gave different enantiomer of oxirane (as in the case of S-neomenthyl sulfoximines).

As one chiral auxiliary attached to sulfur of sulfoximine molecule led to an ee of upto 86% in oxirane synthesis[1], we wanted to investigate whether a chiral auxiliary on nitrogen, in addition to that on sulfur would enhance the asymmetric induction in MT reactions. Such a reagent could be prepared by using (+)-camphor-10-sulfonyl azide[10], **18**, in place of p-toluene sulfonyl azide used in the preparation of sulfoximines **2a** and **2b**. Reaction (Scheme 4) of (1R,3S,4S,Rs)-(+)-**1b** with (1S)-(+)-camphor-10-sulfonyl azide was slow, but ultimately (90 h) gave (1R,3S,4S,1'S,Rs)-(+)-S-methyl-S-neomenthyl-N-(camphor-10-sulfonyl) sulfoximine, **19**, in 76% yield as a crystalline solid, mp 137-38° C, $[\alpha]_D$ +82.7.



18 (Rs)-(+)-1b 19

Scheme-4

Four carbonyl compounds, **10-13**, were each reacted with sodium salt of sulfoximine (Rs)-(+)-**19** at room temperature to give the corresponding oxiranes, **14-17**. The asymmetric induction achieved is given in Table 2.

Table 2 : Asymmetric Induction in Oxirane Synthesis with Sulfoximine, 19

No.	Carbonyl Substrate	Product oxiranes with sulfoximine (Rs)-(+)-**19**	
		Identity	ee(%)GC*
1.	Benzaldehyde, **10**	(S)-(-)-**14**	61.0 (b)
2.	4-Chlorobenzaldehyde, **11**	(S)-(-)-**15**	49.9 (b)
3.	Acetophenone, **12**	(+)-**16**	86.1 (b)
4.	1-(4-chlorophenyl)-2-methyl Propan-1-one, **13**	(+)-**17**	81.2 (a)

* as in Table 1.

It is apparent from data in Table 2, that replacement of the achiral tosyl group with a chiral auxiliary on nitrogen in S-methyl-S-neomenthyl sulfoximine has no significant additive effect on the extent of asymmetric induction in MT reactions.

Attempts to extend the applicability of these reactions to aliphatic carbonyl compounds such as n-heptanal, 2-octanone, phenoxy acetaldehyde, etc have not met with success (very poor yield, < 10%, under the same conditions as for **10-13**; other side products). Work with other carbonyl compounds is under way.

In conclusion, we state that in asymmetric methylene transfer reactions using chiral sulfoximines, chirality on sulfur alone does not lead to significant ee in oxirane synthesis. A chiral substituent on nitrogen does not contribute to any extent in inducing asymmetry in oxiranes. Whereas, a chiral substituent on sulfur of sulfoximines leads to fairly high ee in oxiranes produced. Out of the two chiral substituents on sulfur we investigated, neomenthyl group is clearly superior to *exo*-2-bornyl group in both chemical yields as well as ee of oxiranes in MT reactions.

EXPERIMENTAL

General : All melting points are uncorrected. Optical rotations were measured at 25°C in chloroform (unless otherwise stated) on a JASCO model DIP-370 digital polarimeter. Chiral GC analyses were done on a Cyclodex B capillary column, 30M x 0.25mm (J & W Scientific) using a Hewlett-Packard model 5890 Gas Chromatograph. Spectra were obtained using following instruments : IR spectra: Perkin Elmer Model 781; ^{1}H-NMR spectra: Perkin Elmer R-32 (90 MHz); High resolution ^{1}H-NMR and ^{13}C-NMR Spectra:

GE NMR QE 300, Bruker AM 360, GEM-200; Mass spectra: TRIO-1 GCMS, and Finnigan Mat-1020; HRMS : VG-ZAB-E.

(1R)-(-)-exo-2-Bornanethiol, **6**

Following a published [8] procedure, (1R)-(+)-*endo*-2-borneol, **3**, $[\alpha]_D$ +37.18 (c, 5.05; MeOH) was converted through reaction of its tosylate, **4**, with thiourea to (1R)-(-)-*exo*-2-bornyl isothiouronium salt, **5**, $[\alpha]_D$ -54.19 (c, 2.56; MeOH) which on treatment with alkali gave (1R)-(-)-*exo*-2-bornanethiol, **6**, $[\alpha]_D$ -52.27 (c, 12.11; MeOH) as a white waxy solid. Reported[8] $[\alpha]_D$ for (+)-isomer, +48.3 (c, 11.8; MeOH).

S-Methyl-S-exo-2-bornyl sulfoxides, **8a** *and* **8b**

(1R)-(-)-*exo*-2-Bornanethiol, **6**, (21.0 g; 123 mmol) was added to a solution of sodium methoxide (7.32 g; 136 mmol) in methanol (110 mL), the mixture stirred at 25°C for 1 h and to this was added methyl iodide (19.3 g, 136 mmol). The alkylation was complete in 3 h. (GC:10% SE 30, 1.8 m, 170°C). Methanol was distilled off from the reaction mixture. The residue was taken up in ether (125 ml), washed with water (3 x 25 mL), dried(Na_2SO_4), freed from solvent and distilled (95°C/6 mm) to give S-methyl-S-*exo*-2-bornyl sulfide,[9] **7**, 20.38 g (yield, 89.7%) $[\alpha]_D$ -78.0 (c, 3.14); **IR** (film): 1390, 1375, 1312, 1280, 1130, 1085, 1030, 932, 800 cm^{-1}. ^{1}**H-NMR** (CCl_4) : δ 0.83, 1.00, 1.02 (3H each, s, -C-C*H*$_3$), 2.12 (3H, s, - S-C*H*$_3$), 2.60 (1H, t, J = 8 Hz; -*H*C-S-Me).

To this sulfide, **7**, (9.22 g; 50 mmol) in acetic acid (3 mL) was added hydrogen peroxide (30% w/w; 5.7 g, 50 mmol) and the mixture stirred at 25-30°C for 30 h (monitoring by TLC). The reaction mixture was taken up in ether (60 mL), washed with water, potassium carbonate (5% soln; 20 mL) and water, dried (Na_2SO_4) and freed from solvent. The crude sulfoxides (8.24 g; yield, 82.5%; diastereomer ratio, **8b** : **8a**, 55:45; GC: chiral column, Relative Retention Time, 1.00:1.15) were separated into pure components by column chromatography over silica gel (eluent : n-hexane-acetone, 60:40) and were distilled, b.p. 120°C (bath)/0.5mm.

Major isomer, **8b** : Elutes first from the column; m.p. 38-39°C; $[\alpha]_D$ -147.52 (c, 2.30); **IR** (film): 1395, 1375, 1310, 1050, 1025, 945, 690 cm^{-1}; ^{1}**H-NMR** ($CDCl_3$): δ 0.86, 0.96, 0.98 (3H each, s, -C-C*H*$_3$), 2.52 (3H,s, -S-C*H*$_3$), 2.51 (1H, t, J = 7 Hz, -*H*C-S-); ^{13}**C-NMR**($CDCl_3$) : δ 13.42, 19.87, 20.07 (all C- *C*H$_3$), 27.34, 28.56, 39.12, 40.27, 45.00 (-S-*C*H$_3$), 47.43, 49.54, 71.58 (H*C*-S). Anal : Calc. for $C_{11}H_{20}SO$; C, 65.95, H, 10.06; Found: C, 65.70; H, 10.33.

Minor isomer, **8a** : m.p. 51-52°C; $[\alpha]_D$ - 57.50 (c, 2.25) ; **IR** (film) : 1390, 1375, 1300, 1130, 1050, 960, 942, 680 cm^{-1}. ^{1}**H-NMR** ($CDCl_3$) : δ 0.89, 0.95, 1.22 (3H each, s, -C-C*H*$_3$) 2.45 (3H,s, S-C*H*$_3$), 2.45 (3H, s, S-C*H*$_3$), 2.62 (1H, t, J = 8Hz, - *H*C-S-). ^{13}**C-NMR** ($CDCl_3$) : δ 13.61, 19.55, 20.05 (-*C*H$_3$), 26.98, 31.77, 37.53, 39.02, 44.82 (-S-*C*H$_3$), 47.52, 49.64, 73.13 (- H*C*-S-). Anal. Calc for $C_{11}H_{20}SO$: C, 65.95; H, 10.06; Found; C, 65.83, H, 10.23.

(1R,Rs)-(+)-S-Methyl-S-exo-2-bornyl-N-tosyl Sulfoximine, **9b**

A mixture of (1R,Rs)-(-)-S-methyl-S-*exo*-2-bornyl sulfoxide, **8b**, (5.16 g, 26 mmol), tosyl azide (10.77 g; 55 mmol), copper powder (1.10 g) and methanol (30 mL) was refluxed for 42 h. After distilling off methanol, the residue was stirred with a saturated solution of Na_2EDTA (80 mL) for 30 minutes. The reaction mixture was extracted with chloroform (120 mL). The chloroform solution was treated with charcoal (3 g) filtered, washed with NaOH solution (10%; 50 mL x 2) and water, dried(Na_2SO_4) and freed from solvent. The residue (11.25 g) was purified by column chromatography over SiO_2 (eluent: hexane-acetone, 80:20) to give pure sulfoximine, **9b** (7.8 g; yield, 82%) which after recrystallisation (twice from hexane-acetone, 80:20 and once from EtOH) showed mp. 141-42°C, $[\alpha]_D$ + 31.07 (c, 2.73). **IR** (nujol): 1600, 1380, 1320, 1285, 1220, 1148, 1055, 1030, 820, 780, 710, 660 cm^{-1}; **^{1}H-NMR** ($CDCl_3$): δ 0.81, 0.91,1.07 (3H each, s, C-C*H*$_3$) 2.38 (3H, s, Ar-C*H*$_3$), 3.31 (3H, s, S-C*H*$_3$), 3.42 (lH, t, J = 9Hz; -*H*C-S-), 7.23, 7.80 (2H each, d, J = 8.4 Hz, Ar-C*H*); **^{13}C-NMR**($CDCl_3$): δ 12.76, 20.08, 20.37, 21.34, 44.57 (all *C*H$_3$), 26.30, 32.00, 39.80 (all -*C*H$_2$-), 41.49, 72.04 (both -*C*H-), 126.38, 128.95 (four Ar -*C*H), 47.76, 53.54 (quarternary *C*), 141.00, 142.23 (Ar-*C*-); **EIMS**, m/z (%) : 369 (M^+, 1) 234 (7), 155 (34), 137 (78), 121 (28), 107 (15), 93 (53), 91 (100), 81 (85), 67 (17); Anal. Calcd for $C_{18}H_{27}NO_3S_2$: C, 58.50; H, 7.36; N, 3.77; Found: C, 58.21; H, 7.32; N, 3.52.

(1R,Ss)-(-)-S-Methyl-S-exo-2-bornyl-N-tosyl Sulfoximine, **9a**

Treatment of (1R,Ss)-(-)-S-methyl-S-*exo*-2-bornyl sulfoxide **8a** (1.64 g) with tosyl azide as above gave, after chromatography (1.23 g; yield, 41%) and crystallisation, sulfoximine **9a**, m.p. 126-27°C, $[\alpha]_D$ -119.27 (c, 2.49): **IR** (nujol) : 1600, 1380, 1305, 1225, 1150, 1075, 780, 700cm^{-1}; **^{1}H-NMR** ($CDCl_3$): δ 0.85, 0.96, 1.20 (3H each, s, -C-C*H*$_3$), 2.39 (3H, s, Ar-C*H*$_3$), 3.29 (1H, t, J = 9Hz, -*H*C-S-), 3.46 (3H, s, -S-C*H*$_3$) 7.25, 7.82 (2H each, d, J = 8.2 Hz, Ar-C*H*-); **^{13}C-NMR** ($CDCl_3$): δ 12.79, 20.19, 20.52, 21.33, 43.90 (all -*C*H$_3$) 26.32, 32.78, 40.08 (all -*C*H$_2$), 44.21, 73.87 (both -*C*H-), 125.89, 128.77 (four Ar-*C*H-), 47.99, 51.91 (quarternary -*C*-) 140.88, 141.97 (Ar-*C*-); **EIMS**, m/z (%): 370 (M^+ + H, 11), 368 (M^+-H, 12), 354 (3), 296 (4), 234 (100), 216 (31), 202 (5) 187 (4), 172 (4), 149 (3), 131 (4); Exact mass, M^+ + 1 : 370.1506, $C_{18}N_{28}NO_3S_2$ requires 370.1511.

Preparation of oxiranes with **9a** *and* **9b**

General procedure is given in Ref. 1. Reactions of carbonyl compounds with S-*exo*-2-bornyl sulfoximines were generally slower compared to S-neomenthyl sulfoximines. The isolated yields of oxiranes were lower in the range of 25-53% (*vs* 42-80% with S-neomenthyl sulfoximines).

(1R,3S,4S,1'S,Rs)-(+)-S-Methyl-S-neomenthyl-N-(Camphor-10-sulfonyl) Sulfoximine, **19**

(1R,3S,4S,Rs)-(+)-S-Methyl-S-neomenthyl sulfoxide[1], **1b**, (6.0 g, 30 mmol), (1S)-(+)-camphor -10-sulfonyl azide **18**, (24.1 g; 97 mmole) $[\alpha]_D$ +47.68 (c, 4.74) [prepared[10] from (1S)-(+)-camphor-10-sulfonic acid] freshly precipitated copper powder (3.1 g) and dry methanol (40 mL) were refluxed for 90 h (TLC: sulfoxide spot - too faint). Methanol was distilled out and the crude product stirred with saturated aqueous solution of Na_2EDTA (120 mL). The reaction mixture was extracted with chloroform

(150 mL). The organics were stirred with activated charcoal (4 g) for 2 h, filtered, washed with 10% aqueous NaOH (50 mL x 2) and water (70 mL x 2), dried (Na_2SO_4) and freed from solvent to give crude product (17.38 g). Successive trituration of this crude product with n-hexane (20 mL x 3) and with n-hexane-chloroform (90:10) (25 mL x 4) followed by solvent removal from each extract gve unchanged sulfoxide, **1b** (1.50 g) and sulfoximine **19** (8.90 g) respectively (remaining solids, 5.70 g; possibly camphor-10-sulfonamide and its anhydroamide[10] resulting from the competing reaction of azide with methanol). The hexane-chloroform extract was purified by column chromatography (SiO_2, 300 g; eluent, hexane-ethyl acetate, 2:1). Crystallisation of the eluate from ethyl acetate gave pure sulfoximine, **19**, (7.31 g, yield based on consumed sulfoxide, 76%), m.p. 137-38°C; $[\alpha]_D$ + 82.7 (c, 1.92). **IR** (nujol): 1740, 1310, 1300, 1285, 1235, 1210, 1140, 1095, 1055, 805, 780 cm^{-1}. **^{1}H-NMR** ($CDCl_3$) : δ 0.90,1.16 (3 Heach, s, -C-C*H*$_3$), 0.92, 1.00, 1.10 (3H each, d, J = 6Hz, -HC-C*H*$_3$), 3.50 (3H, s, -S-C*H*$_3$), 3.16, 3.72 (1H each, d, J = 14 Hz, -O_2S-C*H*$_2$), 3.66 (1H, q, J = 2.7 Hz, -S-C*H*); **^{13}C-NMR** ($CDCl_3$) : δ 19.76, 20.10, 21.56, 22.17, 22.26 (all -C-C*H*$_3$) 44.96 (-S-C*H*$_3$); 23.84, 24.79, 25.97, 26.89, 29.00, 34.75, 36.44, 42.60, 42.66, 47.80, 49.28, 53.78, 58.95, 64.67, 215.52 (-C=O); **EIMS**, m/z (%) : 431 (M^+, 1), 294 (55), 278 (24), 230 (18), 215 (86), 151 (56), 139 (64), 138 (71), 123 (62), 109 (60), 95 (83), 83 (100); Anal. calcd for $C_{21}H_{37}NO_4S_2$: C, 58.43; H, 8.64; N, 3.24; Found : C, 58.25; H, 8.94; N, 3.12.

Preparation of oxiranes with **19**

General procedure as given in ref. 1.

Single-crystal X-ray Diffraction Analysis[11] :

All X-ray data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using Cu-Kα radiation with a graphite monochromator. Data were corrected for Lorentz and Polarization effects and secondary extinction but not for absorption. Structures were solved using direct methods (SIR- 92) and refined by full matrix least square methods in the teXsan program suite.

Crystal data for (1R,3S,4S,Ss)-(+)-S-Methyl-S-neomenthyl sulfoxide, **1a** : Colourless needle crystal, $C_{11}H_{22}OS$, orthorhombic, space group $P2_12_12_1$, a = 5.3742 (3) Å, b = 11.154 (3) Å, c = 20.785 (3) Å, V = 1246.0 (3) Å^3, Z = 4, ρ(calc) = 1.08 g/cm^3, μ(Cu-Kα) = 27.7 cm^{-1}, R = 0.038, Rw = 0.041.

Crystal data for (1R, 3S, 4S, Rs)-(+)-S-Methyl-S-neomenthyl-N-tosyl sulfoximine, **2b**: Colourless random crystal, $C_{18}H_{29}NO_3S_2$, tetragonal, space group $P4_12_12$, a = 10.630 (1) Å, c = 36.027 (3) Å, V = 4071.2(5) Å^3, Z = 8, ρ(calc) = 1.21 g/cm^3, μ(Cu-Kα) = 24.9 cm^{-1}. R = 0.034, Rw = 0.036.

Crystal data for (1R,Rs)-(+)-S-Methyl-S-*exo*-2-bornyl-N-tosyl sulfoximine, **9b** : Colourless needle crystal, $C_{18}H_{27}NO_3S_2$, monoclinic, space group $P2_1$, a = 15.2781 (9) Å, b = 7.635(1) Å, c = 17.764 (1) Å, β = 110.958(4)°, V = 1935.1(3) Å^3, Z = 4 (two molecules per asymmetric unit), ρ(calc) = 1.27 g/cm^3, μ(Cu-Kα) = 29.4 cm^{-1}, R = 0.050, Rw = 0.053.

ACKNOWLEDGEMENT

We are grateful to Dr. Sasikumar Pillai of University of Alabama, USA, Dr. Satendra Singh of University of Oklahoma, USA and Dr. A.V. Bedekar of Kyoto University, Japan for ^{13}C-NMR and high resolution ^{1}H-NMR and Mass spectra and to Dr. M. Ravindranathan of IPCL R&D Centre, Baroda for Mass spectra and microanalysis.

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11. Experimental details, atomic coordinates, e.s.ds, bond lengths, bond angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

(*Received in UK* 16 *May* 1995; *accepted* 21 *June* 1995)