[Chem. Pharm. Bull. 32(7)2628—2638(1984)]

Studies on Chiral Organo-Sulfur Compounds. II.[1] Stereochemistry of Thermal Chiral Allyl Sulfinate-Sulfone Rearrangements[2]

KUNIO HIROI,* RYUICHI KITAYAMA, and SHUKO SATO

Synthetic Chemistry Division, Tohoku College of Pharmacy
4-4-1, Komatsushima, Sendai, Miyagi 983, Japan

(Received November 8, 1983)

A highly efficient and general synthetic route to optically active sulfinates by the stereospecific boron trifluoride etherate-catalyzed esterification of sulfinamides was developed. Dramatic solvent effects were observed in the thermal transformation of allyl sulfinate derivatives to sulfones. Heating of chiral *trans*- and *cis*-allyl sulfinates, (*S*)-(−)-**3a**, **c**, **e** and (*S*)-(−)-**3b**, **d**, **f**, in *N*,*N*-dimethylformamide at 90—120 °C provided chiral sulfones (*S*)-(+)- and (R)-(−)-**5**, **6**, **7** in good yields, respectively, with exceedingly high stereospecificity.

Keywords——asymmetric transfer; stereospecificity; chiral allyl sulfinate; chiral allyl sulfone; boron trifluoride etherate; thermolysis

A number of new asymmetric synthetic methods[3] have been devised in recent years for the preparation of chiral biologically active compounds, mainly for pharmaceutical use. Quite recently, with the rapid advance of organo-sulfur chemistry[4] much attention has been devoted to the use of chiral organosulfur compounds in asymmetric synthesis.[5] One of the most efficient methodologies for asymmetric induction is intramolecular transfer of asymmetry, by using sigmatropic rearrangements[6] and intramolecular substitution reactions.[7] Thus, to develop asymmetric synthetic methods with chiral organo-sulfur compounds, intramolecular transfer of asymmetry of chiral sulfur atoms to carbon by thermolysis of chiral allyl sulfinates was studied.

Many mechanistic studies on sulfinate-sulfone rearrangements,[8] mostly carried out under solvolytic reaction conditions, have been reported, but there has been no report on the stereochemistry of the rearrangement of chiral allyl sulfinates to sulfones. We describe herein a highly efficient synthesis of chiral allyl sulfinates, and the thermal rearrangement of chiral allyl sulfinates to sulfones.

Synthesis of Chiral Allyl Sulfinates

Several methods have been reported for the preparation of optically active sulfinates, *e.g.*, transesterification of (−)-menthyl *p*-toluenesulfinate,[9] oxidation of sulfenates with (+)-monopercamphoric acid,[10] esterification of sulfinyl chloride using optically active tertiary amines,[11] acid-catalyzed alcoholysis of optically active sulfinamides,[12] partial reaction of racemic sulfinates with optically active Grignard reagents,[13] and optical resolution with cyclodextrin.[14] However most of these methods yield sulfinates of low enantiopurity. In the alcoholysis of optically active sulfinamides catalyzed by strong acids[12] such as benzenesulfonic acid, trifluoromethanesulfonic acid, and trifluoroacetic acid, a rather low degree of stereospecificity was observed in the case of secondary and tertiary alcohols. However our method[2b] of boron trifluoride etherate-catalyzed esterification could overcome the difficulties and provide a facile entry to optically active sulfinates with extremely high enantiopurity.

Treatment of a readily obtainable optically active sulfinamide, (*S*)-(+)-*N*,*N*-diethyl-*p*-toluenesulfinamide (**1**),[12,15] with allyl alcohols **2a**—**g** in toluene in the presence of 1.5 eq of boron trifluoride etherate at 0 °C resulted in the formation of (*S*)-(−)-sulfinates **3a**—**g** in

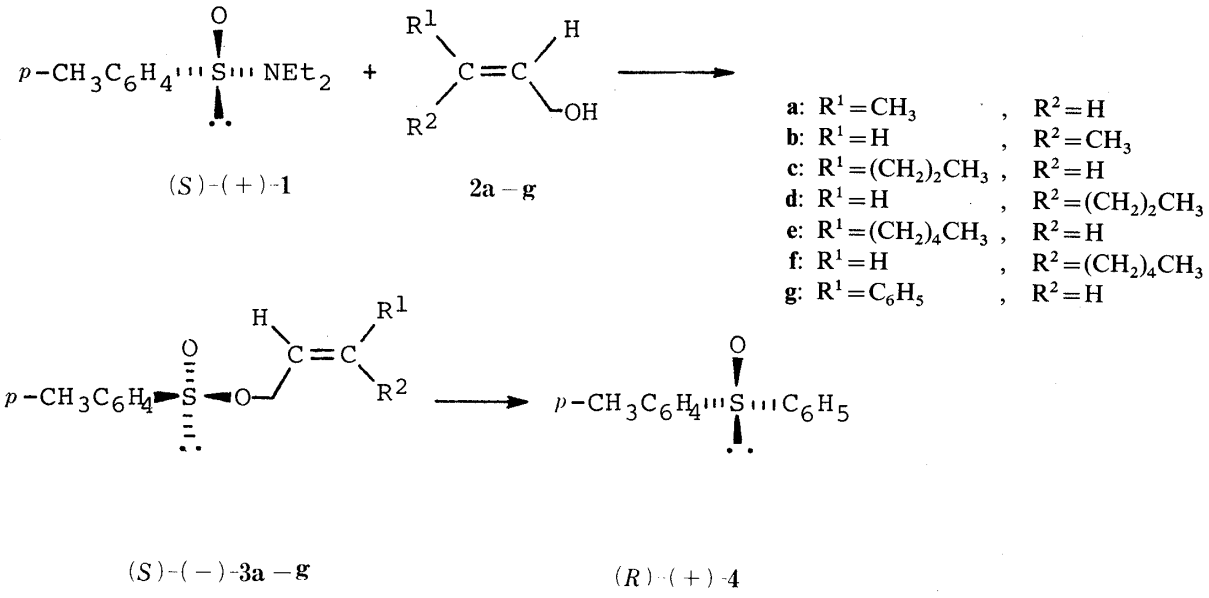


Chart 1

TABLE I. Synthesis of Chiral Sulfinates (*S*)-(−)-**3a**—**g** by the Boron Trifluoride Etherate-Catalyzed Esterification of (*S*)-(+)-*N*, *N*-Diethyl-*p*-toluenesulfinamide (**1**) with Allyl Alcohols **2a**—**g**[a]

2	(*S*)-(+)-**1**[b] e.e. (%)	Reaction time (h)	Products **3a**—**g**		e.e. (%)	Stereospecificity in **1**→**3a**—**g** (%)
			Yield of **3a**—**g** (%)	$[\alpha]_D$ (EtOH)		
2a	60.0	4	99	−124.6° (*c*=0.80, 20 °C)	59.3	98.8
2b	65.0	5	85	−170.4° (*c*=0.36, 18 °C)	60.4	92.9
2c	63.4	4	95	−111.3° (*c*=1.30, 22 °C)	57.5	90.7
2d	72.7	5	94	−137.2° (*c*=0.20, 26 °C)	65.9	90.6
2e	63.4	4	96	−103.1° (*c*=0.50, 20 °C)	56.8	89.6
2f	79.5	5	80	−130.6° (*c*=0.37, 26 °C)	84.3	94.4
2g	63.4	4	94	−40.7° (*c*=2.00, 20 °C)	62.7	98.9

a) (*S*)-(+)-Sulfinamide (**1**) reacted with allyl alcohols **2a**—**g** (3.0 eq) in the presence of boron trifluoride etherate (1.5 eq) in toluene at 0 °C.
b) Enantiomeric excess (%) was calculated from the reported value (compound (*S*)-(+)-**1** with 58.0% enantiomeric excess has been reported to have the optical rotation of $[\alpha]_D$ +71.4° (acetone)).[12]

excellent yields, as listed in Table I. Spectral data for the (*S*)-(−)-sulfinates **3a**—**g** obtained are summarized in Table II.

The absolute configurations and the optical rotations of the optically pure sulfinates **3a**—**g** were determined (Table III) by conversion of the resulting sulfinates (−)-**3a**—**g** into (*R*)-(+)-phenyl *p*-tolyl sulfoxide (**4**) of known configuration[16] by treatment with phenylmagnesium bromide, on the basis of inversion of configuration in this transformation.[17]

The stereospecificity was calculated from the optical rotations of the produced sulfinates corrected for the optical purity of the starting sulfinamide **1** used, and the results are summarized in Table I. This boron trifluoride etherate-catalyzed esterification occurred with inversion of configuration, with extremely high stereospecificity.

Solvent Effects on Thermolysis of Allyl Sulfinates

Thermolytic transformation of allyl sulfinates to sulfones was studied by heating in many

TABLE II. Spectral Data for Allyl Sulfinates **3a—g**

3	bp [mp] (°C)	IR ν_{max}^{film} [cm^{-1}]	NMR (CCl_4) δ [ppm]	Exact mass determination Found (Molecular formula, Calcd)
3a	110 (3 mmHg)	1630 (C=C) 1600 (aromatic) 1100 (sulfinate)	1.80 (3H, d, J=5 Hz, CH_3–CH=CH), 2.40 (3H, s, $CH_3C_6H_4$), 3.60—4.53 (2H, m, O–CH_2–CH=C), 5.27—5.77 (2H, m, CH=CH), 7.00—7.73 (4H, m, C_6H_4)	210.0679 ($C_{11}H_{14}O_2S$, 210.0644)
3b	120 (3 mmHg)	1620 (C=C) 1600 (aromatic) 1115 (sulfinate)	1.83 (3H, d, J=6 Hz, CH_3–CH=CH), 2.40 (3H, s, $CH_3C_6H_4$), 3.66—4.66 (2H, m, O–CH_2–CH=C), 5.13—5.73 (2H, m, CH=CH), 7.00—7.73 (4H, m, C_6H_4)	210.0728 ($C_{11}H_{14}O_2S$, 210.0644)
3c	140 (2 mmHg)	1630 (C=C) 1600 (aromatic) 1110 (sulfinate)	0.80 (3H, t, J=6 Hz, CH_3CH_2), 1.00—1.66 (2H, m, CH_2CH_3), 1.66—2.20 (2H, m, CH_2CH=C), 2.40 (3H, s, $CH_3C_6H_4$), 3.66—4.50 (2H, m, OCH_2), 5.06—5.90 (2H, m, CH=CH), 7.00—7.65 (4H, m, C_6H_4)	238.1013 ($C_{13}H_{18}O_2S$, 238.1001)
3d	135 (3 mmHg)	1620 (C=C) 1600 (aromatic) 1110 (sulfinate)	0.85 (3H, t, J=6 Hz, CH_3CH_2), 1.06—1.67 (2H, m, CH_2CH_3), 1.67—2.16 (2H, m, CH_2CH=C), 2.33 (3H, s, $CH_3C_6H_4$), 3.75—4.60 (2H, m, OCH_2), 5.00—5.75 (2H, m, CH=CH), 7.00—7.65 (4H, m, C_6H_4)	238.1003 ($C_{13}H_{18}O_2S$, 238.1001)
3e	164 (2 mmHg)	1630 (C=C) 1600 (aromatic) 1110 (sulfinate)	0.87 (3H, t, J=5 Hz, CH_3CH_2) 1.00—2.20 (8H, m, $(CH_2)_4$), 2.40 (3H, s, $CH_3C_6H_4$), 3.69—4.53 (2H, m, OCH_2), 5.00—5.90 (2H, m, CH=CH), 7.06—7.70 (4H, m, C_6H_4)	266.1315 ($C_{15}H_{22}O_2S$, 266.1290)
3f	170 (3 mmHg)	1630 (C=C) 1600 (aromatic) 1110 (sulfinate)	0.87 (3H, t, J=5 Hz, CH_3CH_2), 1.00—2.20 (8H, m, $(CH_2)_4$), 2.33 (3H, s, $CH_3C_6H_4$), 3.70—4.55 (2H, m, OCH_2), 5.10—5.60 (2H, m, CH=CH), 6.97—7.63 (4H, m, C_6H_4)	266.1343 ($C_{15}H_{22}O_2S$, 266.1290)
3g	[45—47]	1620 (C=C) 1600 (aromatic) 1105 (sulfinate)	2.33 (3H, s, $CH_3C_6H_4$), 3.90—4.80 (2H, m, OCH_2), 5.70—6.70 (2H, m, CH=CH), 7.00—7.90 (9H, m, C_6H_4 and C_6H_5)	272.0863 ($C_{16}H_{16}O_2S$, 272.0857)

kinds of solvent, and dramatic solvent effects were observed in the thermolysis.

Heating of (±)-*trans*-crotyl and (±)-*trans*-2-hexenyl *p*-toluenesulfinate (**3a**) and (**3c**) in *N,N*-dimethylformamide (DMF) at 90—110 °C gave the corresponding γ-rearranged sulfones, (±)-1-buten-3-yl and (±)-1-hexen-3-yl *p*-tolyl sulfone (**5**) and (**6**), in excellent yields (84—100%). The use of DMF as a solvent in this thermolysis resulted in much higher yields of the sulfones than were obtained under the thermal conditions using other solvent systems (Table IV).

The structures of the products (±)-**5** and **6** were confirmed by comparison of the spectral data with those of authentic sulfones prepared by alkylation of allyl *p*-tolyl sulfone with methyl and propyl iodides.

Thermolysis of cinnamyl (±)-*p*-toluenesulfinate (**3g**) in refluxing dioxane and toluene gave an α-rearranged sulfone, cinnamyl *p*-tolyl sulfone (**9**), in 64 and 63% yields. The structure

TABLE III. Determination of the Absolute Configuration and the Optical Rotations of Optically Pure (−)-**3a**—**g** by Conversion of Allyl *p*-Toluenesulfinates (−)-**3a**—**g** into (*R*)-(+)-Phenyl *p*-Tolyl Sulfoxide (**4**)[a]

Starting sulfinates (−)-**3a**—**g**		Product (*R*)-(+)-**4**		e.e. (%)[c]	(−)-**3a**—**g**	
3a—**g**	$[\alpha]_D$ (EtOH)[b]	Yields (%)	$[\alpha]_D$ (acetone)[b]		Abs. config. of (−)-**3a**—**g**[d]	$[\alpha]_D$ (EtOH) of optically pure (−)-**3a**—**g**
3a	−136.9° (c=1.20)	89[e]	+14.4° (c=0.46)	65.2	*S*	−210.0°
3b	−170.4° (c=1.81)	86[e]	+13.3° (c=1.45)	60.4	*S*	−282.1°
3c	−109.4° (c=1.34)	80[e]	+12.4° (c=0.66)	56.5	*S*	−193.6°
3d	−137.2° (c=1.10)	83[e]	+14.5° (c=1.45)	65.9	*S*	−208.2°
3e	−103.1° (c=0.52)	67[f]	+12.5° (c=0.37)	56.8	*S*	−181.5°
3f	−130.6° (c=1.86)	53[f]	+18.5° (c=1.24)	84.3	*S*	−154.9°
3g	−40.4° (c=1.19)	62[f]	+13.7° (c=0.28)	62.1	*S*	−65.1°

a) Sulfinates (−)-**3a**—**g** reacted with phenylmagnesium bromide at −78 °C for 2 h in THF.
b) Measured at 18—22 °C.
c) Enantiomeric excess (%) of the product **4** was calculated from the reported optical rotation of optically pure (*R*)-(+)-**4** ($[\alpha]_D$ +22° (acetone)).[16]
d) Absolute configurations of (−)-**3a**—**g** were determined from the streochemistry of the product **4** obtained on the basis of inversion of configuration in these conversions.
e) Purified by preparative TLC using ether–hexane (2:1).
f) Purified twice by preparative TLC using ether–hexane (2:1) and benzene–ethanol (6:1).

TABLE IV. Studies on Thermal Rearrangement of the Sulfinates **3a** and **3b** to the Sulfones **5** and **6**

3	Solvent[a]	Reaction conditions		Product	Product yield (%)	Recovery **3** (%)
		Reaction temp. (°C)	Reaction time (h)			
3a	EtOH	80	10	**5**	10	30 (30)[b]
3a	EtOH–H_2O (3:2)	90	6	**5**	31	— (20)[b]
3a	THF	66	24	—	—	90
3a	DME	82	8	—	—	80
3a	Dioxane	101	19	—	—	80
3a	Dioxane–H_2O (3:1)	90	42	**5**	20	20
3a	Toluene	110	6	**5**	21	31
3a	Xylene	144	2	**5**	31	20
3a	DMF	90—100	12	**5**	86—100	—
3b	DMF	95	18	**6**	24	50
3b	DMF	110	18	**6**	84	—
3b	DMF	120	20	**6**	70	—

a) THF = tetrahydrofuran; DME = 1,2-dimethoxyethane.
b) Yields of ethyl *p*-toluenesulfinate are given in parentheses.

of **9** was confirmed by spectral comparison with an authentic sample[18] prepared from cinnamyl chloride and sodium *p*-toluenesulfinate. However, heating of **3g** in DMF at 90 °C provided a γ-rearranged sulfone, 3-phenyl-1-propen-3-yl *p*-tolyl sulfone (**8a**), in 36% yield together with the carbon–carbon double bond isomerized sulfone, 1-phenyl-1-propen-1-yl *p*-tolyl sulfone (**8b**) (12% yield). Thermolysis of (±)-**3g** under the normally used solvolytic reaction conditions (ethanol–H_2O 2:1, at 90 °C) gave an ester-exchanged product, ethyl *p*-

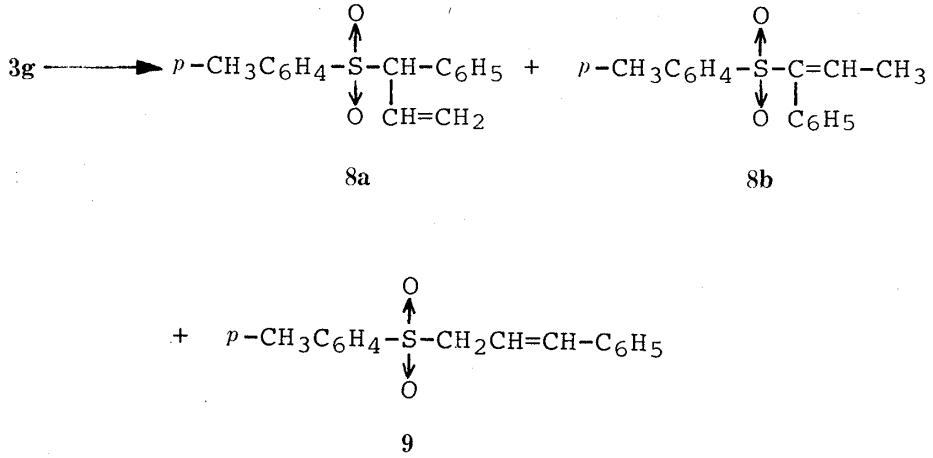


Chart 2

TABLE V. Studies on Thermal Rearrangement of Cinnamyl *p*-Toluenesulfinate (**3g**) to Sulfones

Solvent	Reaction conditions		Products (%)			Recovery **3g**
	Reaction temp. (°C)	Reaction time (h)	**8a**	**8b**	**9**	
THF	66	9	—	—	—	96
DME	82	15	—	—	—	90
Dioxane	101	18	—	—	64	—
CH_3CN	82	10	—	—	—	60
Benzene	80	20	—	—	—	94
Toluene	110	18	—	—	63	—
DMF	90	13	36	14	—	40
DMF	100	12	10	—	—	38
DMF	110	12	3	5	1	—
EtOH–H_2O[a] (2:1)	90	2	—	—	—	—

a) Ethyl *p*-toluenesulfinate was obtained in 63% yield.

toluenesulfinate, instead of sulfones.

Thermolysis of Chiral Allyl Sulfinates

The chiral *trans*-allyl sulfinates (*S*)-(−)-**3a**, **c**, **e**, **g** obtained above were heated in DMF under the reaction conditions given in Table VI, affording the corresponding sulfones (*S*)-(+)-**5**, **6**, **7** and (−)-**8a** in good yields with extremely high stereospecificity. In the thermolysis of *cis*-allyl sulfinates (*S*)-(−)-**3b**, **d**, **f**, a slightly higher temperature was required to complete the conversion of the sulfinates into sulfones. Thermolysis of (*S*)-(−)-**3b**, **d**, **f** in DMF at 120 °C provided the corresponding sulfones (*R*)-(−)-**5**, **6**, and **7** with high stereospecificity. No α-rearranged sulfone was detected in any case. The stereospecificities were determined by nuclear magnetic resonance (NMR) analyses with a shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)[Eu(hfc)$_3$]. The reaction conditions used and the results are summarized in Table VI.

The absolute configurations of the products **5**, **6**, and **7** were determined by chemical correlation of the corresponding saturated sulfones **14a**—**c** with the authentic sulfones.

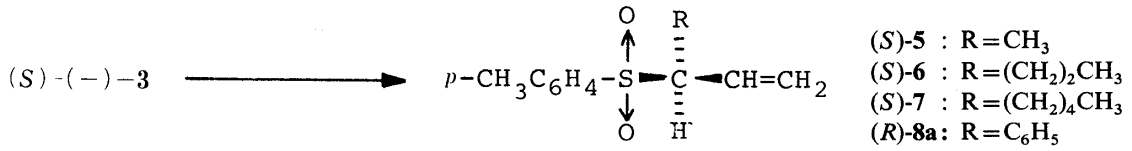
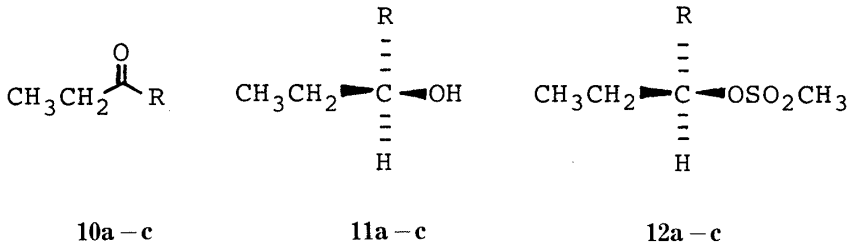


Chart 3

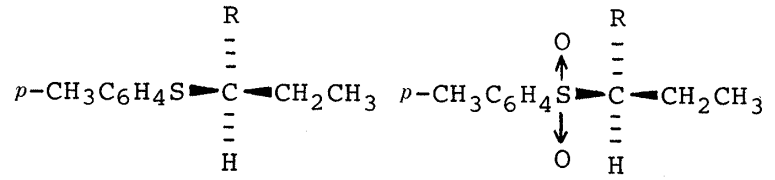
TABLE VI. Stereospecificity in Thermal Rearrangement of Chiral *trans*- and *cis*-Allyl Sulfinates **3a**—**g** to Sulfones **5**—**8**

3	3 e.e. (%)	Reaction conditions[a]		Product 5—8			Stereospecificity in 3→5—8 (%)
		Reaction temp. (°C)	Reaction time (h)	Product	Yield (%)	$[\alpha]_D$ (EtOH)	
(*S*)-**3a**	57.4	90	12	(*S*)-**5**	86	+4.4° (*c*=2.0, 18 °C)	86.8
(*S*)-**3b**	45.9	120	20	(*R*)-**5**	76	−4.1° (*c*=2.3, 20 °C)	88.9
(*S*)-**3c**	57.5	110	18	(*S*)-**6**	84	+18.0° (*c*=0.6, 21 °C)	83.6
(*S*)-**3d**	51.7	120	20	(*R*)-**6**	67	−14.7° (*c*=2.1, 26 °C)	82.2
(*S*)-**3e**	56.8	110	20	(*S*)-**7**	70	+16.6° (*c*=0.8, 26 °C)	80.8
(*S*)-**3f**	84.3	120	20	(*R*)-**7**	67	−28.4° (*c*=2.1, 27 °C)	86.1
(*S*)-**3g**	62.1	90	18	**8a**	36[b]	−13.7° (*c*=1.0, 20 °C)	—

a) Chiral sulfinates **3a**—**g** were heated in DMF.
b) A double bond-isomerized product (**8b**) derived from **8a** was obtained in 14% yield, and 40% of the starting material, (*S*)-**3g**, was recovered.



10a—**c** **11a**—**c** **12a**—**c**

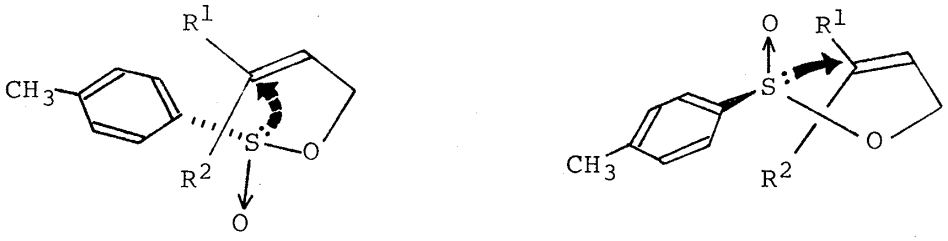


13a—**c** **14a**—**c**

a: R=CH_3
b: R=$(CH_2)_2CH_3$
c: R=$(CH_2)_4CH_3$

Chart 4

Asymmetric reduction of ketones **10a**—**c** with $LiAlH_4$ modified with (−)-menthol,[19] or (1*R*,2*S*)-(−)-*N*-methylephedrine[20] gave optically active alcohols (*R*)-**11a**,[21] (*S*)-**11b**,[22] and (*R*)-**11c**.[23] Substitution of the mesylates **12a**—**c**, prepared from the alcohols **11a**—**c**, with sodium *p*-tolylthiolate occurred with inversion of configuration,[24] giving (*S*)-**13a**, (*R*)-**13b**, and (*S*)-**13c**, respectively. Subsequent oxidation of the sulfides **13a**—**c** with $NaIO_4$[25] provided the authentic optically active saturated sulfones (*S*)-(−)-**14a**, (*R*)-(+)-**14b**, and (*S*)-(−)-**14c**. The allyl sulfones (+)-**5**, **6**, and **7** obtained by the above thermolysis were reduced with



15a 15b

Chart 5

diimide[26] to give (−)-**14a**, (+)-**14b**, and (+)-**14c**, respectively. Therefore the absolute configurations of the allyl sulfones **5**, **6**, and **7** were determined as (*S*)-(+)-**5**, **-6**, and **-7**.

Thus, the thermolysis of *trans*- and *cis*-allyl sulfinates (*S*)-**3a**, **c**, **e** and (*S*)-**3b**, **d**, **f** provided (*S*)- and (*R*)-allyl sulfones **5**, **6**, and **7**, respectively.

On the basis of the high stereospecificity in this transformation, the complete retention of chirality in the recovered starting sulfinates if the reaction was halted at any stage, and the exclusive formation of γ-sulfones without any α-ones, it can be concluded that these reactions occur by a concerted cyclic intramolecular mechanism, *e.g.* a [2,3] sigmatropic rearrangement. Thus, the mechanistic pathway for this transfer of asymmetry from sulfur to carbon can be rationalized as follows. The steric interference between the tolyl group and the substituents R^1 and R^2 would be much more severe in the cyclic intramolecular transition state **15a** than in **15b**, and so (*S*)-(−)-**3a**, **c**, **e** and (*S*)-(−)-**3b**, **d**, **f** rearrange preferentially *via* the transition state **15b** to provide (*S*)-(+)- and (*R*)-(−)-**5**, **6**, and **7**, respectively, with high stereospecificity. Thermolysis of **3g** led to the formation of a more ionic intermediate, consequently providing the α-rearranged product **9** under some reaction conditions (Table V).

Thus, a highly stereospecific transfer of chirality from sulfur to carbon may be accomplished in good yields by this thermolysis of chiral *trans*- and *cis*-allyl sulfinates.

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. Thin-layer or preparative thick layer plates were made of E. Merck Silica gel 60PF-254 activated by drying at 140 °C for 3.5 h.

Infrared (IR) spectra were obtained in the indicated state with a Hitachi 215 spectrometer. NMR spectra were determined in the indicated solvent with a Hitachi R-24B high resolution NMR spectrometer; chemical shifts are given in ppm from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra (MS) were taken on a Hitachi RMU-6MG or RMU-7M spectrometer. Optical rotations were measured on a Union-Giken PM-101 polarimeter.

Preparation of Optically Active Sulfinates (*S*)-(−)-3a—g

General Procedure——A dry 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar was flushed with nitrogen and maintained under a positive pressure of nitrogen. A solution of (*S*)-(+)-*N,N*-diethyl-*p*-toluenesulfinamide (**1**) (200 mg, 0.95 mmol),[12] having the enantiomeric purity given in Table I, in 1 ml of anhydrous toluene was added to the flask, followed by addition of a solution of an allyl alcohol **2a**—**g** (2.85 mmol) in 0.5 ml of anhydrous toluene. A solution of boron trifluoride etherate (203 mg, 1.43 mmol) in 0.5 ml of anhydrous toluene was added to the above mixture at 0 °C and the reaction mixture was stirred at 0 °C for the time given in Table I. The reaction mixture was diluted with ether, then washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was subjected to preparative thin-layer chromatography (TLC) (ether–hexane 1 : 1) to give the corresponding optically active allyl sulfinate (*S*)-(−)-**3a**—**g**. The chemical yield, the enantiomeric excess of the sulfinates, and the stereospecificity of the reactions are summarized in Table I. Spectral data for the (*S*)-(−)-sulfinates **3a**—**g** obtained are listed in Table II.

Reaction of (*S*)-(−)-*trans*-Crotyl *p*-Toluenesulfinate (3a) with Phenylmagnesium Bromide——A dry 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar was flushed with nitrogen and maintained under a positive pressure of nitrogen. A solution of 111 mg (0.53 mmol) of (*S*)-(−)-**3a** ($[\alpha]_D^{22}$ −136.9° (*c*=0.46, EtOH)) in 1.5 ml of anhydrous tetrahydrofuran (THF) was added to the flask, followed by the dropwise addition of a 2 M THF solution of phenylmagnesium bromide (0.34 ml, 0.69 mmol) at −78 °C. The reaction mixture was stirred at −78 °C

for 2 h, then warmed to 0 °C, quenched with 10% aqueous HCl, and extracted with ether. The ethereal layers were combined, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane 2 : 1) to give 101 mg (89% yield) of (*R*)-(+)-phenyl *p*-tolyl sulfoxide (**4**)[16] with 65.2% enantiomeric excess ($[\alpha]_D^{22}$ +14.4° (*c* = 0.46, acetone)).

Reactions of other optically active allyl sulfinates, (*S*)-(−)-**3b**—**g** with phenylmagnesium bromide were carried out in the same way, and the results are summarized in Table III. The optical rotations of optically pure (*S*)-(−)-**3a**—**g** are calculated on the basis of complete inversion of configuration in this transformation and are also listed in Table III.

Studies on Solvent Effects in Thermolysis of Sulfinates

Thermolysis of (±)-3a——A solution of 100 mg of (±)-**3a** in 2 ml of the solvent was heated under the reaction conditions described in Table IV. The solvent was evaporated off under reduced pressure and the residue was subjected to preparative TLC (ether–hexane 1 : 2) to give (±)-1-buten-3-yl *p*-tolyl sulfone (**5**). The results are summarized in Table IV. This product was identical with the authentic sulfone described below, on the basis of a comparison with the spectral properties. (±)-**5**: colorless needles of mp 66.5 °C (recryst. from hexane). IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1590 (aromatic), 1290, 1130 (SO_2). NMR (CCl_4) δ: 1.36 (3H, d, J = 6 Hz, CH_3), 2.43 (3H, s, $CH_3C_6H_4$), 3.23—3.83 (1H, m, CH–SO_2), 4.73—6.10 (3H, m, CH=CH_2), 7.10—7.80 (4H, m, C_6H_4). MS *m/e*: 210 (M^+). Exact mass determination: 210.0730 (Calcd for $C_{11}H_{14}O_2S$: 210.0715).

Thermolysis of (±)-*trans*-2-Hexenyl *p*-Toluenesulfinate (3c)——A solution of 100 mg of (±)-**3c** in 2 ml of DMF was heated at 110 °C for 18 h. The same work-up as described above gave 84 mg (84% yield) of (±)-1-hexen-3-yl *p*-tolyl sulfone (**6**). (±)-**6**: colorless needles of mp 78 °C (recryst. from hexane). IR ν_{max}^{film} cm^{-1}: 1630 (C=C), 1600 (aromatic), 1290, 1140 (SO_2). NMR (CCl_4) δ: 0.83 (3H, t, J = 6 Hz, CH_3CH_2), 1.00—2.16 (4H, m, $(CH_2)_2$), 2.33 (3H, s, $CH_3C_6H_4$), 3.00—3.50 (1H, m, CH–SO_2), 4.60—5.83 (3H, m, CH=CH_2), 7.00—7.73 (4H, m, C_6H_4). MS *m/e*: 238 (M^+). Exact mass determination: 238.1031 (Calcd for $C_{13}H_{18}O_2S$: 238.1028). The results obtained under other reaction conditions are summarized in Table IV.

Thermolysis of (±)-Cinnamyl *p*-Toluenesulfinate (3g) in Dioxane——A solution of 400 mg of (±)-**3g** in 8 ml of dioxane was refluxed for 18 h. The solvent was evaporated off under reduced pressure and the residue was subjected to preparative TLC (ether–hexane 1 : 1) to give 256 mg (64% yield) of cinnamyl *p*-tolyl sulfone (**9**); colorless needles of 122—124 °C (recryst. from hexane) [lit. mp 118—119 °C[18a] and mp 126—126.5 °C[18b]]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640 (C=C), 1600 (aromatic), 1300, 1240 (SO_2). NMR ($CDCl_3$) δ: 2.40 (3H, s, $CH_3C_6H_4$), 2.90 (2H, d, J = 6 Hz, CH_2–CH=C), 5.73—6.60 (2H, m, CH=CH), 7.10—7.90 (9H, m, C_6H_4 and C_6H_5). MS *m/e*: 272 (M^+). Exact mass determination: 272.0882 (Calcd for $C_{16}H_{16}O_2S$: 272.0877).

Thermolysis of (±)-3g in DMF——A solution of 200 mg of (±)-**3g** in 4 ml of DMF was heated at 90 °C for 18 h. The same work-up as described above gave the γ-rearranged products, 72 mg (36% yield) of (±)-3-phenyl-1-propen-3-yl *p*-tolyl sulfone (**8a**) and 28 mg (14% yield) of 1-phenyl-1-propenyl *p*-tolyl sulfone (**8b**), together with the recovered starting sulfinate **3g** (80 mg, 40% recovered yield). (±)-**8a**: mp 120—121 °C (recryst. from hexane). IR ν_{max}^{film} cm^{-1}: 1630 (C=C), 1600 (aromatic), 1300, 1240 (SO_2). NMR ($CDCl_3$) δ: 2.37 (3H, s, $CH_3C_6H_4$), 4.63 (1H, d, J = 8 Hz, CH–C_6H_5), 5.00—6.70 (3H, m, CH=CH_2), 7.00—7.80 (9H, m, C_6H_4 and C_6H_5). MS *m/e*: 272 (M^+). Exact mass determination: 272.0883 (Calcd for $C_{16}H_{16}O_2S$: 272.0877). **8b**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 (C=C), 1600 (aromatic), 1300, 1240 (SO_2). NMR (CCl_4) δ: 1.67 (3H, d, J = 6 Hz, CH_3CH=C), 2.33 (3H, s, $CH_3C_6H_4$), 5.00—6.73 (1H, m, CH=C), 6.90—7.70 (9H, m, C_6H_4 and C_6H_5). MS *m/e*: 272 (M^+). The results obtained under other reaction conditions are summarized in Table V.

Thermolysis of Optically Active Sulfinates

Thermolysis of (*S*)-(−)-3a——A solution of 100 mg of (*S*)-(−)-**3a** ($[\alpha]_D^{19}$ −120.5° (*c* = 0.80, EtOH), 57.4% enantiomeric excess) in 2 ml of DMF was heated at 90 °C for 12 h. The solvent was evaporated off under reduced pressure and the residue was subjected to preparative TLC (ether–hexane 1 : 2) to give 86 mg (86% yield) of (*S*)-(+)-**5** ($[\alpha]_D^{18}$ +4.4° (*c* = 0.40, EtOH)) with 49.8% enantiomeric excess as determined by NMR analysis with a shift reagent [Eu(hfc)$_3$]. Recrystallization of this product from hexane afforded an analytically pure sample as colorless needles of mp 66.5 °C.

Thermolysis of (*S*)-(−)-**3b**—**g** was carried out in the same way, and the results are summarized in Table VI. The products **5**, **6**, **7**, and **8a** were identical with the corresponding racemic sulfones **5**, **6**, and **8a** and the authentic samples **5**, **6**, and **7** described below, on the basis of a comparison of the spectral data. (*S*)-(+)-1-Octen-3-yl *p*-tolyl sulfone (**7**): mp 92—94 °C (colorless needles, recryst. from hexane). IR ν_{max}^{film} cm^{-1}: 1630 (C=C), 1590 (aromatic), 1280, 1140 (SO_2). NMR (CCl_4) δ: 0.83 (3H, t, J = 6 Hz, CH_3CH_2), 1.00—2.16 (8H, m, $(CH_2)_4$), 2.40 (3H, s, $CH_3C_6H_4$), 3.00—3.53 (1H, m, CH–SO_2), 4.66—5.96 (3H, m, CH=CH_2), 7.06—7.76 (4H, m, C_6H_4). MS *m/e*: 266 (M^+). Exact mass determination: 266.1315 (Calcd for $C_{15}H_{22}O_2S$: 266.1340).

Preparation of (±)-5, 6, and 7 by Alkylation of Allyl *p*-Tolyl Sulfone

Allyl *p*-Tolyl Sulfone——Allyl chloride (0.36 ml, 4.40 mmol) was added to a suspension of 1.00 g (3.99 mmol) of sodium *p*-toluenesulfinate hydrate ($4H_2O$) in 10 ml of ethanol and the reaction mixture was refluxed for 18 h with stirring. The solvent was evaporated off under reduced pressure and the residue was diluted with ether. The ether solution was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The

residue was subjected to preparative TLC (ether–hexane 2 : 3) to give 608 mg (78% yield) of allyl *p*-tolyl sulfone; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620 (C=C), 1600 (tolyl), 1310, 1120 (SO_2). NMR (CCl_4) δ: 2.40 (3H, s, $CH_3C_6H_4$), 3.70 (2H, d, J= 8 Hz, CH_2), 4.80—6.10 (3H, m, CH=CH_2), 7.03—7.83 (4H, m, C_6H_4). MS *m/e*: 196 (M^+).

Alkylation of Allyl *p*-Tolyl Sulfone——A dry 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar was flushed with nitrogen and maintained under a positive pressure of nitrogen. A solution of 100 mg (0.51 mmol) of allyl *p*-tolyl sulfone in 1 ml of THF was added to the flask, followed by the dropwise addition of a 1.5 N hexane solution of butyllithium (0.42 ml, 0.66 mmol) at −78 °C. After 30 min, a solution of 94 mg (0.66 mmol) of methyl iodide in 1 ml of THF was added at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, then quenched with 10% aqueous HCl, and extracted with ether. The ether extracts were combined, washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to preparative TLC (ether–hexane 2 : 3) to give 91 mg (85% yield) of (±)-**5**. (±)-**6** and -**7** were prepared by alkylation with propyl iodide and pentyl iodide in the same way as described above in 72 and 76% yields, respectively. The products obtained by thermolysis of (*S*)-(−)-**3a**—**f** were identical with the corresponding authentic samples (comparison of spectral data).

Preparation of Optically Active Sulfones, (*S*)-(−)-5—7, from Optically Active Alcohols 11a—c

Synthesis of Optically Active Alcohols 11a—c——(*R*)-(−)-2-Butanol (**11a**): l-Menthol (15.60 g, 99.86 mmol)[19] was added to an ice-cooled suspension of 1.89 g (49.93 mmol) of $LiAlH_4$ in 40 ml of diethyl ether (Et_2O) and the suspension was stirred at 0 °C for 1 h. Methyl ethyl ketone (**10a**) (3.72 ml, 41.60 mmol) was added to the above suspension at 0 °C and the mixture was stirred at 0 °C for 6 h, and then quenched subsequently with 2 ml of H_2O, 2 ml of 10% aqueous NaOH, and 2 ml of H_2O. After being refluxed for 30 min, the mixture was filtered and the filtrate was concentrated *in vacuo*. The residual liquid was distilled to give 1.50 g of (*R*)-(−)-**11a**; bp 98 °C [lit.[21] bp 99 °C (758 mmHg)]. $[\alpha]_D^{20}$ −1.4° (*c*=5.4, EtOH).

(*S*)-(+)-3-Hexanol (**11b**): *N*-Ethylaniline (3.15 ml, 24.9 mmol) and (1*R*,2*S*)-(−)-*N*-methylephedrine (2.20 g, 12.5 mmol) were added to a suspension of 473 mg (12.5 mmol) of $LiAlH_4$ in 10 ml of Et_2O and the mixture was heated at 50 °C for 1 h with stirring. A solution of 960 mg (9.60 mmol) of 3-hexanone (**10b**) in 6 ml of Et_2O was added to the above mixture at −78 °C. The whole was stirred at −78 °C for 4 h, then diluted with Et_2O (10 ml), and quenched with 0.5 ml of 10% aqueous NaOH and 0.5 ml of H_2O. The mixture was heated under reflux for 30 min, then cooled to room temperature, and filtered. The filtrate was washed with 10% aqueous HCl and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give 560 mg (58% yield) of (*S*)-(+)-**11b**; bp 55—58 °C (10 mmHg) [lit.[22] bp 133—134 °C (733 mmHg)]. $[\alpha]_D^{19}$ +1.3° (*c*=21.1, EtOH).

(*R*)-(−)-3-Octanol (**11c**): Reduction of 3-octanone (**10c**) (1.00 g, 7.81 mmol) was carried out by using a complex prepared from $LiAlH_4$ (358 mg, 10.15 mmol), *N*-ethylaniline (2.56 ml, 20.31 mmol), and (1*R*,2*S*)-*N*-methylephedrine (1.81 g, 10.15 mmol) under the same reaction conditions as above to give 600 mg (60% yield) of (*R*)-(−)-**11c**; bp 78—81 °C (15 mmHg) [lit.[23] bp 52—53 °C (2.2 mmHg)]. $[\alpha]_D^{20}$ −0.4° (*c*=20.1, $CHCl_3$).

Synthesis of Optically Active Sulfides 13a—c from (*R*-(−)-11a, (*S*)-(+)-11b, and (*R*)-(−)-11c[24]——(*S*)-(+)-2-Butyl *p*-Tolyl Sulfide (**13a**): Methanesulfonyl chloride (1.50 ml, 19.43 mmol) was added to a solution of 1.20 g (16.19 mmol) of (*R*)-(−)-**11a** ($[\alpha]_D^{20}$ −1.4° (*c*=5.4, EtOH)) in 4 ml of pyridine at 0 °C. The reaction mixture was stirred at 0 °C for 3 h, and then diluted with ether. The ether solution was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, then dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give 1.80 g of (*S*)-2-butyl methanesulfonate (**12a**); IR ν_{max}^{film} cm^{-1}: 1350, 1178 (OSO_2). NMR (CCl_4) δ: 0.97 (3H, t, J= 6 Hz, CH_3CH_2), 1.35 (3H, d, J=6 Hz, CH_3CH), 1.50—1.97 (2H, m, CH_2), 2.97 (3H, s, CH_3–OSO_2), 4.33—4.90 (1H, m, CH–O).

Anhydrous ethanol (30 ml) was added to 1.42 g (29.60 mmol) of sodium hydride (50% in oil, washed with hexane before use) at 0 °C. After 30 min, 3.67 g (29.60 mmol) of *p*-thiocresol was added to the above solution at 0 °C. The mixture was stirred at 0 °C for 1 h, and then 1.50 g (9.81 mmol) of (*S*)-**12a** in 6 ml of ethanol was added. The reaction mixture was heated at 40 °C for 1 h, then concentrated to dryness under reduced pressure, and the residue was dissolved in ether. The ether solution was washed with 10% aqueous NaOH and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual oil was distilled to give 900 mg (51% yield) of (*S*)-(+)-**13a**; bp 75 °C (4 mmHg) [lit.[27] bp 175—178 °C (15 mmHg)]. $[\alpha]_D^{18}$ +0.2° (*c*=8.0, EtOH). NMR (CCl_4) δ: 1.00 (3H, t, J=7 Hz, CH_3CH_2), 1.23 (3H, d, J=8 Hz, CH_3CH), 1.23—1.90 (2H, m, CH_2), 2.30 (3H, s, $CH_3C_6H_4$), 2.70—3.30 (1H, m, CH–S), 6.90—7.50 (4H, m, C_6H_4). MS *m/e*: 180 (M^+).

(*R*)-(−)-3-Hexyl *p*-Tolyl Sulfide (**13b**): Mesylation of 343 mg (3.37 mmol) of (*S*)-(+)-**11b** ($[\alpha]_D^{22}$ +1.3° (*c*=21.2, EtOH)) with methanesulfonyl chloride (0.30 ml, 4.00 mmol)–pyridine (1 ml) was carried out in the same way as described above. The crude mesylate **12b** (343 mg) thus obtained was reacted with 473 mg (3.80 mmol) of *p*-thiocresol in the same manner, and purification by preparative TLC (ether–hexane 1 : 1) gave 110 mg (30% yield) of (*R*)-(−)-**13b**; $[\alpha]_D^{20}$ −1.6° (*c*=6.4, EtOH). IR ν_{max}^{film} cm^{-1}: 1600 (aromatic). NMR (CCl_4) δ: 1.00 (6H, t, J=6 Hz, $2CH_3$), 1.20—2.00 (6H, m, $3CH_2$), 2.33 (3H, s, $CH_3C_6H_4$), 2.60—3.10 (1H, m, CH–S), 6.70—7.40 (4H, m, C_6H_4). MS *m/e*: 208 (M^+).

(*S*)-(−)-3-Octyl *p*-Tolyl Sulfide (**13c**): Mesylation of 600 mg (4.62 mmol) of (*R*)-(−)-**11c** ($[\alpha]_D^{22}$ −0.4° (*c*=19.9, $CHCl_3$)) with 0.40 ml (5.50 mmol) of methanesulfonyl chloride in 1.5 ml of pyridine produced 3-octyl methanesul-

fonate (**12c**) (728 mg). This crude mesylate was reacted with 956 mg (7.70 mmol) of *p*-thiocresol in the same manner as described above, and purification by preparative TLC (ether–hexane 1 : 1) gave 564 mg (62% yield) of (*S*)-(−)-**13c**; $[\alpha]_D^{19}$ −0.3° (*c* = 30.2, EtOH). IR ν_{max}^{film} cm^{-1}: 1600 (aromatic). NMR (CCl_4) δ: 0.97 (6H, t, *J* = 6 Hz, $2CH_3$), 1.00—1.80 (10H, m, $5CH_2$), 2.27 (3H, s, $C\underline{H}_3C_6H_4$), 2.60—3.00 (1H, m, CH–S), 6.73—7.33 (4H, m, C_6H_4). MS *m/e*: 236 (M^+).

Preparation of Optically Active Sulfones 14a—c by Oxidation of Optically Active Sulfides 13a—c

(*S*)-(−)-2-Butyl *p*-Toyl Sulfone (14a)——A mixture of 500 mg (2.78 mmol) of (*S*)-(+)-**13a** ($[\alpha]_D^{18}$ +0.2° (*c* = 8.0, EtOH)) 1.78 g (8.33 mmol) of $NaIO_4$, 20 ml of methanol, and 3 ml of H_2O was heated at 70 °C for 18 h with vigorous stirring.[25] The solvent was evaporated off under reduced pressure. The residue was triturated with $CHCl_3$ and the suspension was filtered. The filtrate was concentrated *in vacuo* and the crude product was subjected to preparative TLC (ether–hexane 2 : 1) to give 491 mg (83% yield) of (*S*)-(−)-**14a**;[28] $[\alpha]_D^{20}$ −0.5° (*c* = 7.6, EtOH). IR ν_{max}^{film} cm^{-1}: 1600 (aromatic), 1300, 1140 (SO_2). NMR (CCl_4) δ: 0.90 (3H, t, *J* = 7 Hz, $C\underline{H}_3CH_2$), 1.70 (3H, d, *J* = 8 Hz, $C\underline{H}_3CH$), 1.30—2.30 (2H, m, $C\underline{H}_2CH_3$), 2.40 (3H, s, $C\underline{H}_3C_6H_4$), 2.47—3.03 (1H, m, CH–S), 7.00—7.83 (4H, m, C_6H_4). MS *m/e*: 212 (M^+). Exact mass determination: 212.0876 (Calcd for $C_{11}H_{16}O_2S$: 212.0871).

(*R*)-(+)-3-Hexyl *p*-Tolyl Sulfone (14b)——(*R*)-(−)-**13b** (115 mg, 0.50 mmol, $[\alpha]_D^{20}$ −1.6° (*c* = 6.4, EtOH)) was oxidized with 355 mg (1.66 mmol) of $NaIO_4$ under the same reaction conditions as described above, and purification by preparative TLC (ether–hexane 1 : 1) gave 105 mg (79% yield) of (*R*)-(+)-**14b**; $[\alpha]_D^{21}$ +0.8° (*c* = 9.0, EtOH). IR ν_{max}^{film} cm^{-1}: 1600 (aromatic), 1300, 1140 (SO_2). NMR (CCl_4) δ: 0.93 (6H, t, *J* = 7 Hz, $2CH_3$), 1.13—2.10 (6H, m, $3CH_2$), 2.43 (3H, s, $C\underline{H}_3C_6H_4$), 2.43—2.90 (1H, m, CH–S), 7.06—7.80 (4H, m, C_6H_4). MS *m/e*: 240 (M^+). Exact mass determination: 240.1158 (Calcd for $C_{13}H_{20}O_2S$: 240.1183).

(*S*)-(−)-3-Octyl *p*-Tolyl Sulfone (14c)——(*S*)-(−)-**13c** (300 mg, 1.20 mmol, $[\alpha]_D^{19}$ −0.3° (*c* = 30.2, EtOH)) was oxidized with 813 mg (3.80 mmol) of $NaIO_4$ in the same way as described for **14a** to give 300 mg (88% yield) of (*S*)-(−)-**14c**; $[\alpha]_D^{20}$ −0.2° (*c* = 12.2, EtOH). IR ν_{max}^{film} cm^{-1}: 1600 (aromatic), 1300, 1140 (SO_2). NMR (CCl_4) δ: 0.97 (6H, t, *J* = 6 Hz, $2CH_3$), 1.00—2.00 (10H, m, $5CH_2$), 2.43 (3H, s, $C\underline{H}_3C_6H_4$), 2.30—2.80 (1H, m, CH–S), 7.00—7.80 (4H, m, C_6H_4). MS *m/e*: 268 (M^+). Exact mass determination: 268.1494 (Calcd for $C_{15}H_{24}O_2S$: 268.1496).

Preparation of (*S*)-(−)-14a and (*R*)-(+)-14b, c from (*S*)-(+)-5, -6, and -7[26]

(*S*)-(−)-14a——Two drops of saturated aqueous $CuSO_2$ and acetic acid were added with a syringe to a solution of 100 mg (0.48 mmol) of (*S*)-(+)-**5** ($[\alpha]_D^{19}$ +1.2° (*c* = 50.0, EtOH)) in 2 ml of dioxane. Hydrazine hydrate (715 mg, 14.3 mmol) was added to the above mixture at 0 °C, followed by the dropwise addition of a suspension of 1.02 g (4.76 mmol) of $NaIO_4$ in 4 ml of H_2O. The reaction mixture was stirred at room temperature for 30 h, and then extracted with ether. The ether extract was washed with saturated aqueous Na_2CO_3 and saturated aqueous NaCl, then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was subjected to preparative TLC (ether–hexane 2 : 3) to give 57 mg (56% yield) of (*S*)-(−)-**14a**;[28] $[\alpha]_D^{20}$ −0.8° (*c* = 4.0, EtOH).

(*R*)-(+)-14b——(*S*)-(+)-**6** (126 mg, 0.52 mmol, $[\alpha]_D^{20}$ +6.4° (*c* = 15.5, EtOH)) was reduced with diimide in the same way as described above to give (*R*)-(+)-**14b** (50 mg, 40% yield, $[\alpha]_D^{18}$ +3.0° (*c* = 4.3, EtOH).

(*R*)-(+)-14c——(*S*)-(+)-**7** (80 mg, 0.30 mmol, $[\alpha]_D^{25}$ +8.3° (*c* = 12.4, EtOH)) was reduced with diimide in the same way as described above to give (*R*)-(+)-**14c** (30 mg, 38% yield, $[\alpha]_D^{20}$ +2.7° (*c* = 1.1, EtOH)). The spectral data for the saturated sulfones **14a—c** thus obtained were identical with those of the authentic samples mentioned above.

References and Notes

1) Part I: K. Hiroi, S. Sato, and R. Kitayama, *Chem. Pharm. Bull.*, **31**, 3471 (1983).
2) For preliminary reports of parts of this work see *a*) K. Hiroi, R. Kitayama, and S. Sato, *Chem. Commun.*, **1983**, 1740; *b*) *Idem*, *Synthesis*, **1983**, 1040.
3) *a*) K. Hiroi, *Yukigosei Kyokaishi*, **41**, 925 (1983); *b*) K. Drauz, A. Kleeman, and J. Martens, *Angew. Chem. Int. Ed. Engl.*, **21**, 584 (1982); *c*) J. W. Apsimon and R. P. Sequin, *Tetrahedron*, **35**, 2797 (1979); *d*) D. Valentine, Jr. and J. W. Scott, "Annual Reports in Medicinal Chemistry," Vol. 13, Academic Press, New York, 1978, p. 282; *e*) *Idem, Synthesis*, **1978**, 329; *f*) J. W. Scott and D. Valentine, Jr., *Science*, **184**, 943 (1974).
4) K. Hiroi, *Yukigosei Kyokaishi*, **35**, 265 (1977); L. Field, *Synthesis*, **1978**, 713; B. M. Trost, *Chem. Rev.*, **78**, 363 (1978).
5) K. Hiroi, *Tohoku Yakka Daigaku Kenkyu Nempo*, **26**, 1 (1979); G. Solladie, *Synthesis*, **1981**, 185; S. Colonna, R. Annuziata, and M. Cinquini, *Phosphorus and Sulfur*, **10**, 197 (1981); M. Mikolajczyk and J. Drabowitz, "Topics in Stereochemistry," Vol. 13, ed. by N. Allinger, E. Eliel, and S. H. Wilen, John Wiley & Sons, Inc., New York, 1982, pp. 333—468.
6) K. Hiroi, *Tohoku Yakka Daigaku Kenkyu Nempo*, **27**, 1 (1980); R. W. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **18**, 563 (1979); G. B. Bennett, *Synthesis*, **1977**, 589; F. E. Ziegler, *Acc. Chem. Res.*, **1977**, 227; T. Hayashi, *Yukigosei Kyokaishi*, **34**, 396 (1976); S. J. Rhoads and N. R. Raulins, *Org. React.*, **22**, 1 (1975).
7) G. Stork and A. F. Kreft, *J. Am. Chem. Soc.*, **99**, 3851 (1977); G. Stork and A. R. Schoofs, *ibid.*, **101**, 5081 (1979).
8) *a*) A. C. Cope, D. E. Morrison, and I. Field, *J. Am.Chem. Soc.*, **72**, 59 (1950); *b*) A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, **1958**, 3603; *c*) D. Darwish and R. A. McLaren, *Tetrahedron Lett.*, **1962**, 1231;

d) D. Darwish and E. A. Preston, *ibid.*, **1964**, 113; *e*) E. Ciuffarin, M. Isola, and A. Fava, *J. Am. Chem. Soc.*, **90**, 3594 (1968); *f*) S. Braverman, *Int. J. Sulfur Chem., Part C*, **6**, 149 (1971).
9) H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).
10) L. Sogramora, P. Koch, A. Garbesi, and A. Fava, *Chem. Commun.*, **1967**, 985.
11) M. Mikolajczyk and J. Drabowicz, *Chem. Commun.*, **1974**, 547.
12) M. Mikolajczyk, J. Drabowicz, and B. Bujnicki, *Chem. Commun.*, **1976**, 568.
13) W. H. Pirkle and M. S. Hoekstra, *J. Am. Chem. Soc.*, **98**, 1832 (1976).
14) M. Mikolajczyk and J. Drabowicz, *Tetrahedron Lett.*, **1972**, 2379.
15) S. Colonna, R. Giovini, and F. Montanari, *Chem. Commun.*, **1968**, 865.
16) D. N. Harpp, S. M. Vines, J. P. Montillier, and T. H. Chan, *J. Org. Chem.*, **41**, 3987 (1976).
17) *a*) K. K. Andersen, *Tetrahedron Lett.*, **1962**, 93; *b*) *Idem, J. Org. Chem.*, **29**, 1953 (1964); *c*) K. K. Andersen, W. Gaffield, N. E. Papanidolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**, 5637 (1964); *d*) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965); *e*) J. G. Tillett, *Chem. Rev.*, **76**, 747 (1976).
18) *a*) T. Sato and I. Homma, *Bull. Chem. Soc. Jpn.*, **44**, 1885 (1971); *b*) V. Balish and S. Shanmuganathan, *J. Indian Chem. Soc.*, **35**, 31 (1958).
19) A. Horeau, H. B. Kagan, and V. P. Vigneron, *Bull. Soc. Chim. Fr.*, **1968**, 3795.
20) S. R. Landor and A. R. Tatchell, *J. Chem. Soc., (C)*, **1966**, 2280; N. Tanno and S. Terashima, *Chem. Pharm. Bull.*, **31**, 837 (1983).
21) M. M. Sprung and E. S. Wallis, *J. Am. Chem. Soc.*, **56**, 1717 (1934).
22) H. C. Brown, H. R. Ayyanger, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 1839; R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **1913**, 1923.
23) Y. R. Naves, *Helv. Chim. Acta*, **26**, 1034 (1943).
24) H. M. R. Hoffmann, *J. Chem. Soc.*, **1964**, 1249.
25) L. L. Replogle and J. R. Maynard, *J. Org. Chem.*, **32**, 1901 (1967).
26) J. M. Hoffman, Jr. and R. H. Schlessinger, *Chem. Commun.*, **1971**, 1245.
27) E. Profft, *Chem. Tech.* (Berlin), **6**, 366 (1954).
28) A. Dondoni, G. Modena, and G. Scorrano, *Boll. Sci. Fac. Chim. Ind. Bologna*, **22**, 26 (1964) [*Chem. Abstr.*, **61** 10613*h* (1964)].