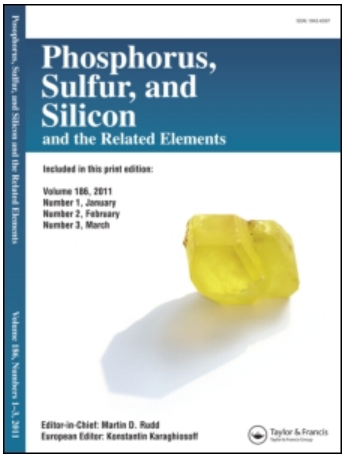

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SYNTHESIS AND ABSOLUTE CONFIGURATIONS OF OPTICALLY ACTIVE OXOSULFONIUM SALTS

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SYNTHESIS AND ABSOLUTE CONFIGURATIONS OF OPTICALLY ACTIVE OXOSULFONIUM SALTS

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The optically active arylethylmethyloxosulfonium perchlorates (**2a–c**) were prepared by the oxidation of the corresponding sulfonium salts (**1a–c**) with sodium perbenzoate. The absolute configurations of oxosulfonium salts were determined by converting them into aryl ethyl sulfoxides (**3a–c**). From the relationship of the absolute configurations of ethylmethylphenylsulfonium perchlorate (**1a**) and ethylmethylphenyloxosulfonium perchlorate (**2a**), it was found that the oxidation of sulfonium salt (+)-(S)-**1a** with sodium perbenzoate proceeded with retention of configuration around the sulfur atom to afford oxosulfonium salt (+)-(R)-**2a**. The circular dichroism (CD) spectra of optically active oxosulfonium perchlorates (**2**) with (+)-(R) configuration show a positive strong Cotton effect at ca. 230 nm and a positive weak one at ca. 260 nm. Whereas, the CD spectra of optically active oxosulfonium perchlorates (**2**) with (−)-(S) configuration show a negative strong Cotton effect at ca. 230 nm and a negative one at ca. 260 nm.

Key words: Optically active oxosulfonium salts; oxidation of optically active sulfonium salts; optically active aryl ethyl sulfoxide; sodium perbenzoate; circular dichroism (CD) spectra.

INTRODUCTION

Although extensive studies on the asymmetric synthesis using enantiomerically pure sulfoxides have been reported,[1] a little has been studied on the use of optically active sulfonium and oxosulfonium salts in asymmetric synthesis, except for the use of optically active sulfonium and oxosulfonium ylides prepared by deprotonation of sulfonium salts (or azaoxosulfonium salts) with strong bases.[2,3] In a preceding paper, we reported a general synthetic route to oxosulfonium salts by the oxidation of sulfonium salts with sodium perbenzoate.[4] It is of interest to investigate the methods for synthesizing optically active oxosulfonium salts. We report herein on the synthesis of optically active arylethylmethyloxosulfonium perchlorates by the oxidation of the corresponding optically active sulfonium salts with sodium perbenzoate and on the absolute configurations of oxosulfonium salts.

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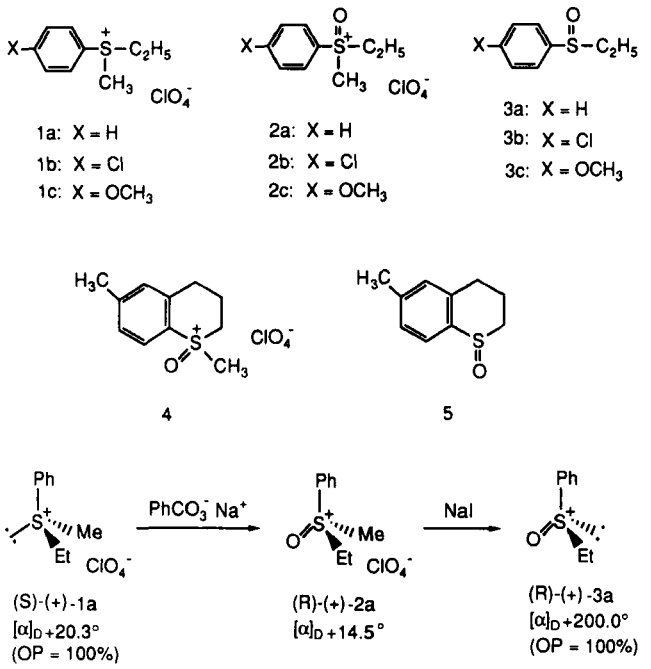
RESULTS AND DISCUSSION

Oxidation of Optically Active Sulfonium Salt **1a**

Optically active sulfonium salts have been synthesized previously by treating alkoxysulfonium salts, derived from sulfoxides by alkylation, with organocadmium or Grignard reagents.[5] Andersen *et al.* established that the absolute configuration of (+)-ethylmethyl(*p*-tolyl)sulfonium tetra-fluoroborate was S form.[5] We obtained optically pure sulfonium salt, (+)-ethylmethylphenylsulfonium perchlorate (**1a**), by fractional recrystallization of the diastereomeric *d*-10-camphorsulfonate salts. The absolute configuration of (+)-**1a** was determined as S form because circular dichroism showed a strong positive Cotton effect at 223 nm and a weak negative Cotton effect at 266 nm.[5] When sulfonium salt (+)-**1a** was oxidized with sodium perbenzoate in aqueous solution, optically active (+)-ethylmethylphenyloxosulfonium perchlorate (**2a**) was obtained in 91% yield. The absolute configuration of oxosulfonium salt (+)-**2a** was determined by converting it into optically active (+)-ethyl phenyl sulfoxide (**3a**) treating with sodium iodide as shown in Scheme 1.[6]

Sulfoxide (+)-**3a** was assigned to be R configuration because Mislow *et al.* established that (+)-alkyl aryl sulfoxides have R configuration.[7] Since demethylation of the ethylmethylphenyloxosulfonium ion is known to proceed via SN2 attack by iodide ion on the methyl group, the stereochemistry of the sulfur atom is retained during the demethylation.[8] Therefore, (+)-oxosulfonium salt **2a** is assigned to be R configuration.[6] These findings show that the oxidation of



Scheme 1

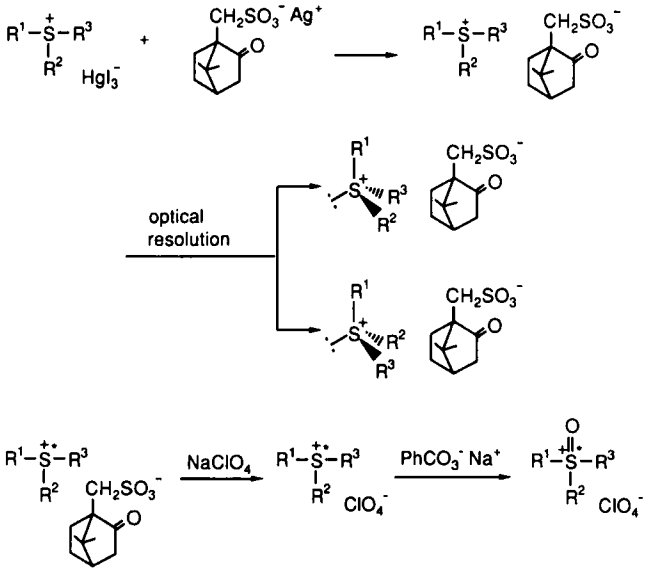
sulfonium salt (S)-(+)-**1a** with sodium perbenzoate proceeds with retention of configuration around the sulfur atom. The peracid anion may attack on the sulfur atom of (S)-(+)-**1a** giving a sulfurane intermediate which eliminates acid anion to produce the oxosulfonium salt (R)-(+)-**2a** as we reported in the preceding paper.[4]

General Synthesis of Optically Active Oxosulfonism Salts ***1***

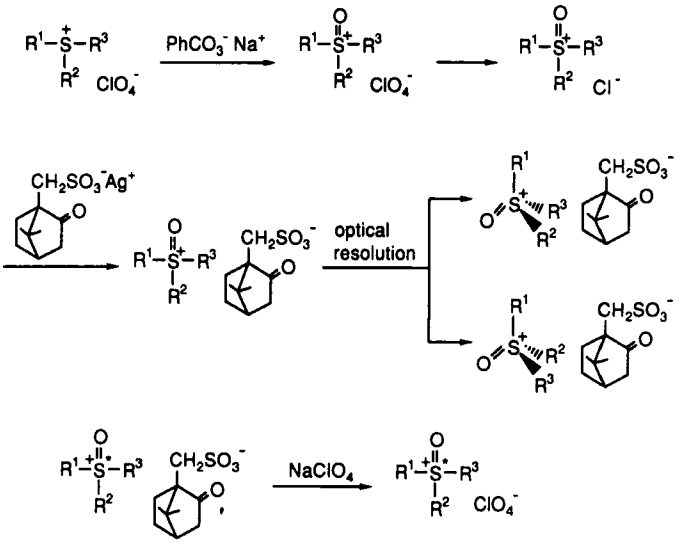
According to the reaction procedure as shown in Scheme 1, various optically active oxosulfonium salts can be prepared by the oxidation of the optically active sulfonium salts. Two synthetic procedures (Methods A and B) are possible for the synthesis of optically active oxosulfonium salt **2** as shown in Schemes 2 and 3. In the first method (A) the diastereomeric sulfonium *d*-10-camphorsulfonate salts are resolved and converted into perchlorate salts by ion exchange. The resulting sulfonium perchlorates **1** are oxidized with sodium perbenozate to optically active oxosulfonium salts **2**. In Method (B) one resolves the diastereomeric mixture of oxosulfonium *d*-10-camphorsulfonates followed by treating the oxosulfonium salts with sodium perchlorate to give the optically active oxosulfonium perchlorates **2**. According to the procedures as shown in Scheme 2 (Method A), the optically active arylethylmethyloxosulfonium salts, (+)-(R)-**2a**, (−)-(S)-**2b**, and (+)-(R)-**2c**, were obtained in good yields. The cyclic oxosulfonium salt, (−)-(S)-1-oxo-1,6-dimethyl-3,4-dihydro-2H-1-benzothiopyranium perchlorate (**4**), was also synthesized according to the procedure shown in Scheme 3 (Method B).

Absolute Configuration of Optically Active Oxosulfonium Salts ***2***

The absolute configurations of optically active oxosulfonium salts **2** prepared were determined by converting them into sulfoxides **3** by the selective demethylation of



SCHEME 2.



SCHEME 3.

2 with iodide ion according to the similar procedure as shown in Scheme 1. Optically active arylethylmethyloxosulfonium salts, (+)-(R)-**2a**, (−)-(S)-**2b**, and (+)-(R)-**2c**, were treated with sodium iodide to afford the corresponding optically active aryl ethyl sulfoxides, (+)-(R)-**3a**, (−)-(S)-**3b**, and (+)-(R)-**3c**, respectively.

*Circular Dichroism Spectra of Sulfonium Salts **1**, Oxosulfonium Salts **2** and Sulfoxides **3***

It is fruitful to investigate the relationship between Cotton effects on the circular dichroism spectra and the absolute configurations of the optically active arylethylmethylsulfonium salts **1**, aryldialkyloxosulfonium salts **2**, and aryl ethyl sulfoxides **3**. The UV and CD spectra of (+)-(S)-ethylmethylphenylsulfonium perchlorate (**1a**), (+)-(R)-ethylmethylphenyloxosulfonium perchlorate (**2a**), and (+)-(R)-ethyl phenyl sulfoxide (**3a**), are shown in Figure 1.

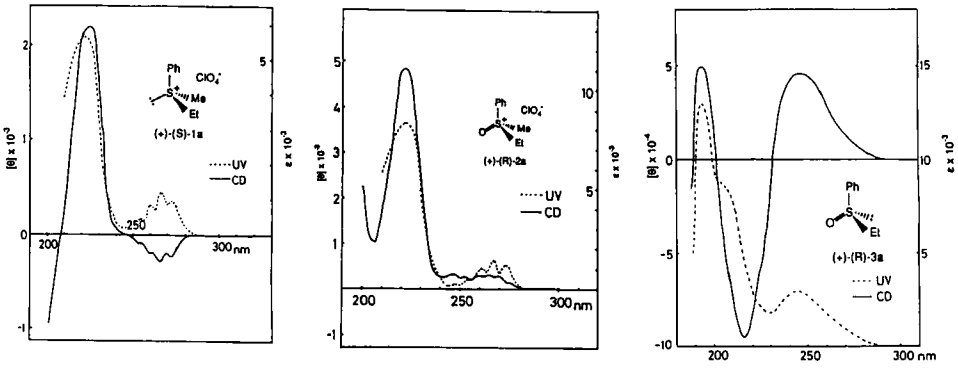


FIGURE 1 The UV and CD spectra of optically active compounds **1a**, **2a**, and **3a**.

The UV spectrum of sulfonium salt (+)-(S)-**1a** shows the absorption maxima due to $\pi - \pi^*$ transition in the phenyl group at 222 and 266 nm. The absorption at 266 nm, so called "benzenoid band", showed the vibrational fine structure. The CD spectrum of (+)-(S)-**1a** has a positive strong Cotton effect at 223 nm and a negative weak Cotton effect at 266 nm. The UV spectrum of oxosulfonium salt (+)-(R)-**2a** has a strong absorption at 222 nm and a weak one at 261–274 nm. The CD spectrum of (+)-(R)-**2a** showed a positive strong absorption at 220 nm and a positive weak one at 250–275 nm. The UV spectrum of sulfoxide (+)-(R)-**3a** has absorptions at 193, 203, and 245 nm, and the CD spectrum shows the Cotton effects at 194, 216, and 246 nm region. The CD spectrum of alkyl aryl sulfoxide with (+)-R configuration shows a positive Cotton effect at ca. 250 nm, and these observations are in consistent with the results reported by Mislow *et al.*[7]

Similarly, the UV and CD spectra of (−)-(R)-(*p*-chlorophenyl)ethylmethylsulfonium perchlorate (**1b**), (−)-(S)-(*p*-chlorophenyl)ethylmethyloxosulfonium perchlorate (**2b**), and (−)-(S)-*p*-chlorophenyl ethyl sulfoxide (**3b**), are determined and shown in Figure 2.

The CD spectrum of sulfonium salt (−)-(R)-**1b** showed a negative strong Cotton effect at 233 nm and a positive weak one at 255–276 nm. The UV spectrum of oxosulfonium salt (−)-(S)-**2b** shows a strong absorption maximum (^1L_a band) at 237 nm and weak ones (benzenoid band) at 269 and 277 nm. The CD spectrum of (−)-(S)-**2b** shows a negative strong Cotton effect at 232 nm and positive weak Cotton effects at 267 and 274 nm. The CD spectrum was different from that of oxosulfonium salt (+)-(R)-**2a**. It is expected from the CD spectrum of (+)-(R)-**2a** that the CD spectrum of (−)-(S)-**2b** would show a negative strong Cotton effect at ca. 230 nm and a negative weak one at ca. 270 nm. The Cotton effect at 232 nm is the expected one, however, the absorptions at 267 and 274 nm were opposite to the expected one. The UV spectrum of (−)-(S)-**3b** has absorption maxima at 195, 219, and 250 nm. The CD spectrum of sulfoxide (−)-(S)-**3b** shows the Cotton effects at 196, 221, and 250 nm. The UV and CD spectra of (+)-(S)-ethyl(*p*-methoxyphenyl)methylsulfonium perchlorate (**1c**), (+)-(R)-ethyl(*p*-methoxyphenyl)methyloxosulfonium perchlorate (**2c**), and (+)-(R)-ethyl *p*-methoxyphenyl sulfoxide (**3c**), were also determined.

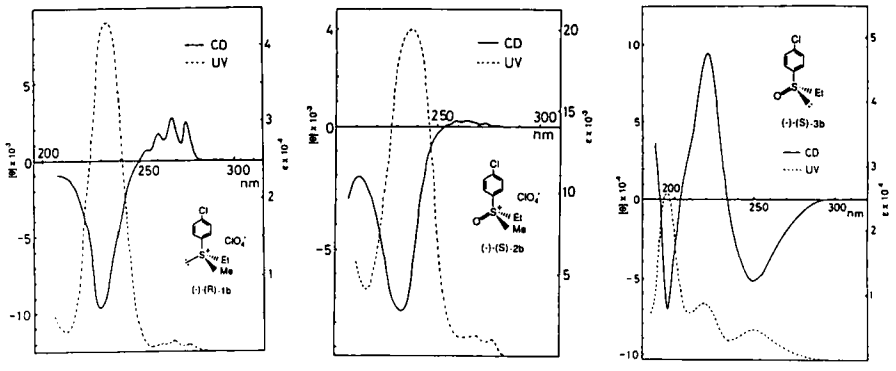


FIGURE 2 The UV and CD spectra of optically active compounds **1b**, **2b**, and **3b**.

TABLE I

The relationship between the absolute configuration and CD spectra of compound **1**, **2**, and **3**

Compound	Absolute configuration	Cotton effect 230 nm	Cotton effect 260 nm
Sulfonium salt **1**	(+)-S	+ (strong)	− (weak)
	(−)-R	− (strong)	+ (weak)
Oxosulfonium salt **2**	(+)-R	+ (strong)	+ (weak)
	(−)-S	− (strong)	− (weak)
Sulfoxide **3**	(+)-R	− (strong)	+ (medium)
	(−)-S	+ (strong)	− (medium)

Then, the UV and CD spectra of the oxosulfonium salt **4** whose benzene ring consists of a part of the ring structure and its free rotation is completely suppressed were measured. The UV spectrum of oxosulfonium salt (−)-(S)−**4** has the absorption maxima due to π–π^* transition in the phenyl group at 237, 274, and 282 nm. The CD spectrum shows a negative strong Cotton effect at 234 nm and negative weak ones at 273 and 281 nm. The CD spectrum were similar to that of CD spectrum of (−)-(S)-(*p*-chlorophenyl)ethylmethylphenyloxosulfonium perchlorate (**2b**), whose benzene ring may rotate freely. Treatment of (−)-(S)-**4** with sodium iodide gave (−)-(S)-6-methyl-3,4-dihydro-2H-1-benzothiopyran-1-oxide (**5**). The UV spectrum of (−)-(S)-**5** has absorption maxima at 200, 225, and 253 nm. The CD spectrum of (−)-(S)-**5** showed the Cotton effects at 203, 223, 254, 271, and 280 nm.

In conclusion, the relationship between the absolute configurations and CD spectra of optically active sulfonium salts **1**, oxosulfonium salts **2**, and sulfoxides **3**, are clarified as summarized in Table I.

EXPERIMENTAL

Melting points were determined on a Yamato Model MP-21 melting point apparatus and are uncorrected. The ^{1}H NMR spectra were measured on a Hitachi R 20B (60 MHz) spectrometer using TMS as internal standard. Chemical shifts and coupling constants were recorded in δ (ppm) and Hertz units. The IR spectra were recorded on a Hitachi Model 260-10 spectrometer. The UV spectra were obtained on a Hitachi EPS-3T or 220A spectrometer. The CD spectra were recorded on a JASCO J-40A automatic recording spectropolarimeter. The specific rotations were determined with a JASCO DIP-140 digital polarimeter.

Preparation of (+)-(*S*)-*Ethylmethylphenylsulfonium Perchlorate* (**1a**). Sulfonium salt **1a** was prepared according to modified procedures described in the literature as follows.[6] Racemic ethylmethylphenylsulfonium mercuritriiodide was prepared from ethyl phenyl sulfide (25 g, 0.18 mol), methyl iodide (129 g, 0.90 mol), and mercury(II) iodide (82 g, 0.18 mol). To an acetonitrile solution of silver *d*-10-camphorsulfonate, which was prepared in situ from *d*-10-camphorsulfonic acid (38 g, 0.16 mol) and silver oxide (38 g, 0.16 mol) in acetonitrile (200 ml), was added an acetonitrile solution (200 ml) of the ethylmethylphenylsulfonium mercuritriiodide (119 g, 0.16 mol) at room temperature. The mercury(II) iodide and silver iodide formed in the above reaction were filtered off and the solution was evaporated. Water was added to the residue and the insoluble materials were filtered off. Evaporation of the water under reduced pressure gave diastereomeric ethylmethylphenylsulfonium *d*-10-camphorsulfonate: 55 g (87%); $[\alpha]_D^{25}$ + 22.6°(c 4.3, MeOH). The crystals of sulfonium salt (55 g, 0.143 mol) were dissolved in acetone (500 ml) at 50°C. The solution was cooled to room temperature and ether was added until the solution became cloudy. The solution was allowed to cool in a freezer

(−20°C) and the separated crystals of salt were collected by filtration. This recrystallization procedure was repeated for 7 times to afford crystals of the *d,d*-isomer salt, (+)-(S)-ethylmethylphenylsulfonium *d*-10-camphorsulfonate, were obtained: yield 9.1 g (33% from 0.072 mol of the salt); $[\alpha]_D^{25}$ + 44.6° (c 2.8, MeOH); mp 113–115°C (MeOH-ether); ^{1}H NMR (acetone-d_6) δ = 0.81 (3H, s), 1.10 (3H, s), 1.40 (3H, t, J = 7.2 Hz), 1.12–2.10 (4H, m), 2.33–3.30 (5H, m), 3.52 (3H, s), 3.91 (1H, q, J = 7.2 Hz), 3.93 (1H, q, J = 7.2 Hz), 7.76–8.33 (5H, m); CD (MeOH) $[\theta]_{273}$ + 3900, $[\theta]_{292}$ + 5760. Anal. Calcd for $C_{19}H_{28}O_4S_2$: C, 59.33; H, 7.35. Found: C, 58.91; H, 7.64. The crystals of *d,d*-isomer salt (9.1 g, 23.7 mmol) was added to an aqueous solution (200 ml) of sodium perchlorate (29 g, 240 mmol), and then the oil separated was extracted with dichloromethane (200 ml × 2). Evaporation of the solution gave crystals of (+)-(S)-**1a**: yield 5.0 g (83%); $[\alpha]_D^{28}$ + 20.3° (c 1.03, acetone); mp 104–105.5°C (acetone-ether); ^{1}H NMR (acetone-d_6) δ = 1.40 (3H, t, J = 7.2 Hz), 3.52 (3H, s), 3.91 (1H, q, J = 7.2 Hz), 3.93 (1H, q, J = 7.2 Hz), 7.76–8.33 (5H, m); UV (MeOH) λ_{max} 222 (ε 5600), 247 (200), 254 (470), 260 (840), 266 (1200), 273 nm (970); CD (MeOH) $[\theta]_{223}$ + 2200, $[\theta]_{266}$ −290. Anal. Calcd for $C_9H_{13}ClO_4S$: C, 42.77; H, 5.18. Found: C, 42.83; H, 5.31.

Preparation of (+)-(*R*)-*Ethylmethylphenyloxosulfonium Perchlorate* (**2a**). Sulfonium salt (+)-(S)-**1a** (3.00 g, 11.9 mmol) ($[\alpha]_D^{28}$ +20.3° (c 1.3, acetone)) (op 100%) was oxidized with a 0.2 M (1 M = 1 mol dm^{-1}) aqueous solution of sodium perbenzoate[8] (180 ml, 35.6 mmol) to afford (+)-(R)-**2a**: yield 2.91 g (91%); mp 79.0–79.5°C; IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); $[\alpha]_D^{29}$ + 14.5°(c 1.84, acetone) (lit.[6] $[\alpha]_D^{32}$ + 14.5° (c 5.52, acetone)); ^{1}H NMR (acetone-d_6) δ = 1.55 (3H, t, J = 7.2 Hz), 4.39 (3H, s), 4.54 (1H, q, J = 7.2 Hz), 4.57 (1H, q, J = 7.2 Hz), 7.95–8.50 (5H, m); UV (MeOH) λ_{max} 222 (ε 8500), 261 (1100), 267 (1500), 274 nm (1600); CD (MeOH) $[\theta]_{220}$ (+4900), $[\theta]_{265}$ (+310). Anal. Calcd for $C_9H_{13}ClO_5S$: C, 40.23; H, 4.88. Found: C, 40.21; H, 4.75.

(+)-(*R*)-*Ethyl Phenyl Sulfoxide* (**3a**). A mixture of (+)-ethylmethylphenyloxosulfonium perchlorate (**2a**) ($[\alpha]_D^{29}$ +14.5° (c 20.5, acetone)) (0.276 g, 1.09 mmol) and NaI (0.327 g, 2.18 mmol) in 5 ml of acetone was refluxed for 1 h. Water was added to the mixture, and the sulfoxide was extracted with ether. After the ether extracts were dried over $MgSO_4$ and ether was removed under reduced pressure, (+)-ethyl phenyl sulfoxide was obtained in pure form: yield 86.7 mg (51%); $[\alpha]_D^{25}$ + 200.0° (c 1.68, $CHCl_3$); $[\alpha]_D^{25}$ + 185.6° (c 0.71, acetone) (op 100%);[9] IR (neat) 1040 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ = 1.14 (3H, t, J = 7.2 Hz), 2.70 (4H, q, J = 7.2 Hz), 7.49 (5H, m); UV (MeOH) λ_{max} 193 (ε 13000), 203 (88000), 245 nm (3000); CD (MeOH) $[\theta]_{194}$ (+50000), $[\theta]_{216}$ (−95000), $[\theta]_{246}$ (+46000).

(−)-(*R*)-(*p-Chlorophenyl*)*ethylmethylsulfonium Perchlorate* (**1b**). According to the similar procedure described in the synthesis of (+)-(S)-**1a**, (+)-(*p*-chlorophenyl)ethylmethylsulfonium *d*-10-camphorsulfonate was prepared: yield 35%; mp 128.5–130°C (acetone-ether); $[\alpha]_D^{30}$ + 6.2° (c 2.3, MeOH); CD (MeOH) $[\theta]_{233}$ −6200, $[\theta]_{293}$ +5400. Sulfonium perchlorate **1b** was obtained by ion exchange with sodium perchlorate in aqueous solution: 80% yield; mp 93–94.5°C (MeOH-ether); $[\alpha]_D^{27}$ −23.3° (c 1.2, MeOH); ^{1}H NMR (acetone-d_6) δ = 1.42 (3H, t, J = 7.2 Hz), 3.50 (3H, s), 3.73–4.10 (2H, m), 7.85 and 8.23 (4H, AA'BB', J = 8.4 Hz); UV (MeOH) λ_{max} 234 (ε 43000), 269 (1100), 277 nm (900); CD (MeOH) $[\theta]_{232}$ −9400, $[\theta]_{255}$ +1200, $[\theta]_{261}$ +2200. Anal. Calcd for $C_9H_{12}Cl_2O_4S$: C, 37.64; H, 4.21. Found: C, 37.68; H, 4.31.

(−)-(*S*)-(*p-Chlorophenyl*)*ethylmethylsulfonium Perchlorate* (**2b**). Sulfonium salt (−)-(R)-**1b** was oxidized with sodium perbenzoate to give oxosulfonium salt (−)-(S)-**2b**: yield 64%; mp 121.5–122°C (MeOH-ether); $[\alpha]_D^{30}$ −10.7° (c 1.5; acetone); IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ = 1.57 (3H, t, J = 7.2 Hz), 4.33–4.82 (2H, m), 4.40 (3H, s), 8.04 and 8.36 (4H, AA'BB', J = 9.0 Hz); UV (MeOH) λ_{max} 237 (ε 20000), 269 (1300), 277 nm (970); CD (MeOH) $[\theta]_{232}$ −7400, $[\theta]_{267}$ +200, $[\theta]_{274}$ +170. Anal. Calcd for $C_9H_{12}Cl_2O_5S$: C, 35.66; H, 3.99. Found: C, 36.39; H, 3.70.

(−)-(*S*)-*Ethyl p-Chlorophenyl Sulfoxide* (**3b**). The reaction of oxosulfonium salt (−)-(S)-**2b** (280 mg, 0.92 mmol) and NaI (227 mg, 1.9 mmol) afforded (−)-(S)-ethyl *p*-chlorophenyl sulfoxide (**3b**): yield 58 mg (34%); oil; $[\alpha]_D^{30}$ −142.5° (c 0.47, MeOH); IR (neat) 1050 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ = 1.20 (3H, t, J = 7.2 Hz), 2.82 (1H, q, J = 7.2 Hz), 2.86 (1H, q, J = 7.2 Hz), 7.56 (4H, s); UV (CH_3CN) λ_{max} 195 (ε 26000), 219 (89000), 250 nm (47000); CD (c 0.037, CH_3CN) $[\theta]_{196}$ −72000, $[\theta]_{221}$ +94000, $[\theta]_{250}$ −53000.

(+)-(*S*)-*Ethyl*(*p-methoxyphenyl*)*methylsulfonium Perchlorate* (**1c**). *d,d*-Isomer salt of ethyl(*p*-methoxyphenyl)methylsulfonium *d*-10-camphorsulfonate was prepared according to the similar procedure described in the preparation of **1a**: yield 35%; mp 144–146°C (acetone-MeOH); $[\alpha]_D^{25}$ +50.1° (c 2.7, MeOH); UV (MeOH) λ_{max} (ε 17000), 270 (3100), 280 nm (2000); CD (MeOH) $[\theta]_{248}$

+4600, $[\theta]_{291}$ +7500. *d,d*-Isomer salt was treated with sodium perchlorate to give (+)-(S)-**1c**: 73% yield; mp 81.5–82.5°C (MeOH-ether); $[\alpha]_D^{30}$ +26.0° (c 2.6, acetone); ^{1}H NMR (acetone-d_6) δ = 1.39 (3H, t, J = 7.2 Hz), 3.47 (3H, s), 3.65–4.10 (2H, m), 3.99 (3H, s), 7.33 and 8.11 (4H, AA'BB', J = 9.0 Hz); UV (MeOH) λ_{max} 245 (ε 30000), 270 (5800), 279 nm (3600); CD (MeOH) $[\theta]_{250}$ +2800, $[\theta]_{272}$ −930, $[\theta]_{278}$ −930.

(+)-(*R*)-*Ethyl(p-methoxyphenyl)methyloxosulfonium Perchlorate* (**2c**). Sulfonium salt (+)-(S)-**1c** was oxidized with sodium perbenzoate to give (+)-(R)-**2c**: yield 80%; mp 117–118°C (MeOH-ether); $[\alpha]_D^{30}$ +11.1° (c 2.2, acetone); IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ = 1.51 (3H, t, J = 7.2 Hz), 4.06 (3H, s), 4.30 (3H, s), 4.23–4.70 (2H, m), 7.56 and 8.26 (4H, AA'BB', J = 9.0 Hz); UV (MeOH) λ_{max} 250 (ε 16000), 269 (4500), 277 nm (1200); CD (c 0.027, MeOH) $[\theta]_{250}$ +1300. Anal. Calcd for $C_{10}H_{15}ClO_6S$: C, 40.21; H, 5.06. Found: C, 40.32; H, 5.10.

(+)-(*R*)-*Ethyl p-Methoxyphenyl Sulfoxide* (**3c**). Oxosulfonium salt (+)-(R)-**2c** (0.68 g, 2.3 mmol) was treated with NaI (0.68, 4.6 mmol) to give sulfoxide (+)-(R)-**3c**: yield 0.41 g (98%); oil; $[\alpha]_D^{30}$ +130.0° (c 1.4, MeOH); IR (neat) 1020 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ = 1.19 (3H, t, J = 7.2 Hz), 2.82 (2H, q, J = 7.2 Hz), 3.89 (3H, s), 7.06 and 7.58 (4H, AA'BB', J = 9.0 Hz); UV (MeOH) λ_{max} 230 (ε 6500), 245 (9400), 273 (1500), 282 nm (900); CD (MeOH) $[\theta]_{223}$ −62000, $[\theta]_{247}$ +58000.

(−)-(*S*)-*1-Oxo-1,6-dimethyl-3,4-dihydro-2H-1-benzothiopyranium Perchlorate* (**4**). 6-Methyl-3,4-dihydro-2H-1-benzothiopyran was synthesized by the method in the literature:[10] bp 103–104°C/4 mmHg. (−)-(S)-**4** was prepared from 6-methyl-3,4-dihydro-2H-1-benzothiopyran by the method described in Scheme 3: mp 99.5–101°C (MeOH); $[\alpha]_D^{22}$ −5.0° (c 2.1, CH_3CN); IR (KBr) 1210 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ = 2.50 (3H, s), 2.58–2.97 (2H, m), 3.10–3.44 (2H, m), 4.30 (3H, s), 4.40–4.76 (2H, m), 7.53 (1H, s), 7.62 and 8.34 (2H, AB, J = 8.4 Hz); UV (MeOH) λ_{max} 237 (ε 16000), 274 (2000), 282 nm (1900), CD (MeOH) $[\theta]_{234}$ −9800, $[\theta]_{273}$ −2400, $[\theta]_{281}$ −2500. Anal. Calcd for $C_{11}H_{15}ClO_5S$: C, 44.83; H, 5.13. Found: C, 44.86; H, 5.11.

(−)-(*S*) − *6-Methyl-3,4-dihydro-2H-1-benzothiopyran-1-oxide* (**5**). Oxosulfonium salt (−)-(S)-**4** was treated with NaI to give (−)-(S)-**5**: mp 100–101°C (AcOEt); $[\alpha]_D^{22}$ −162.5° (c 1.2, MeOH); IR (KBr) 1040 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ = 1.76–2.67 (2H, m), 2.36 (2H, s), 2.67–3.25 (4H, m), 7.08 (1H, s), 7.18 and 7.62 (2H, AB, J = 8.3 Hz); UV (CH_3CN) λ_{max} 200 (ε 75000), 225 (14000), 253 (2300), 280 nm (900); CD (CH_3CN) $[\theta]_{203}$ +7900, $[\theta]_{223}$ +29000, $[\theta]_{254}$ − 26000, $[\theta]_{271}$ −21000, $[\theta]_{280}$ −17000. Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found: C, 66.55; H, 6.63.

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