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Optically active cyclic diaryl(alkoxy)sulfonium salts with intramolecular S···O interaction: synthesis, absolute configuration and stereoselective hydrolysis

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Abstract

Optically active cyclic sulfonium salts {(*S*)-(–)-1-[2′-(methoxycarbonyl)phenyl]-3*H*-2,1-benzoxathiol-1-ium tetrafluoroborate (*S*)-(–)-**2**, (*R*)-(–)-1-[8′-(methoxycarbonyl)-1′-naphthyl]-3*H*-2,1-benzoxathiol-1-ium tetrafluoroborate (*R*)-(–)-**4** and (*R*)-(–)-1-[2′-(methoxycarbonyl)phenyl]-3*H*-2,1-naphtho[1,8-*d*,*e*]-oxathiin-1-ium tetrafluoroborate (*R*)-(–)-**6**} were prepared from optically active diaryl(acyloxy)(alkoxy)spiro-λ^4-sulfanes (*R*)-(+)-**1**, (*S*)-(–)-**3** and (*S*)-(+)-**5**, respectively. The molecular structures determined by ^{1}H and ^{13}C NMR measurements can be described with spiro-λ^4-sulfane-like trigonal bipyramidal geometry about the central sulfur owing to the S···O(carbonyl) intramolecular interaction in the axial position. The stereochemistry of the hydrolysis reactions of sulfonium salts **2**, **4**, **6** and spiro-λ^4-sulfanes **1**, **3**, **5** depending on pH is discussed in detail.

1. Introduction

Recently we described the stereospecific synthesis of optically active diaryl(acyloxy)(alkoxy)-spiro-λ^4-sulfanes **1**, **3** and **5** starting from optically active precursor sulfoxides (see e.g. **7**→**1** in Scheme 2).[1] The absolute configurations were determined by X-ray diffraction method and a comparative analysis of CD spectra.[2] It has also been published that cyclic sulfonium salts with carbonyl oxygen atom in 1,5 or 1,6 position to sulfur (prepared in racemic form) show molecular structures of slightly distorted trigonal bipyramidal (TBP) geometry about the sulfonium centre similarly to those ones found in analogous spiro-λ^4-sulfanes.[3–6] In these cases the molecular arrangement is stabilized by intramolecular S···O(carbonyl) interaction with the oxygen atom in the axial position. To get more information about the stereochemistry and reactivity of compounds of such type, we decided to prepare optically active diaryl(alkoxy)sulfonium salts stabilized by

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intramolecular O(alkoxy)–S···O(carbonyl) interactions and to investigate their structure and reactivity including the determination of absolute configurations.

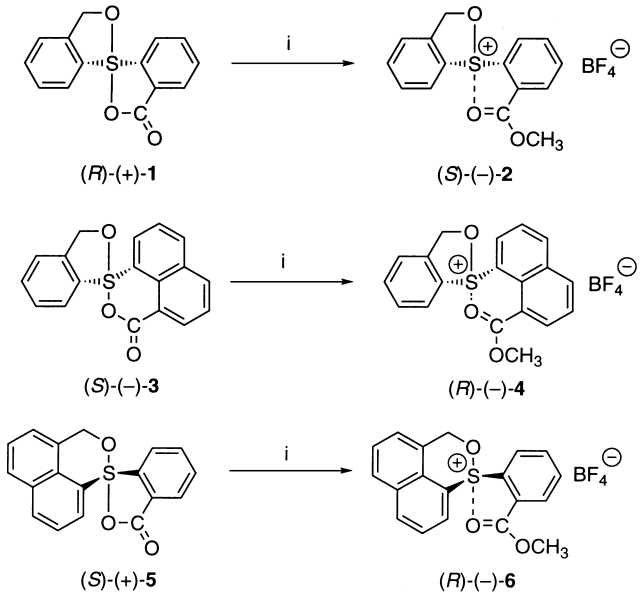
As a first part of this work we report now the stereospecific synthesis of diaryl(alkoxy)-sulfonium tetrafluoroborates (*S*)-(–)-**2**, (*R*)-(–)-**4** and (*R*)-(–)-**6**. In addition, the hydrolysis reactions of the above compounds and their optically active spiro-λ^4-sulfane precursors {(*R*)-(+)-**1**, (*S*)-(–)-**3** and (*S*)-(+)-**5**} leading to optically active sulfoxides are also described. From the results obtained one can reach some conclusions about the stereochemistry of nucleophilic reactions occurring at the four-coordinated sulfur atom of spiro-λ^4-sulfanes and sulfonium salts having an axial O(alkoxy)–S–O(acyloxy) and O(alkoxy)–S^+···O(carbonyl) part, respectively.

2. Results and discussion

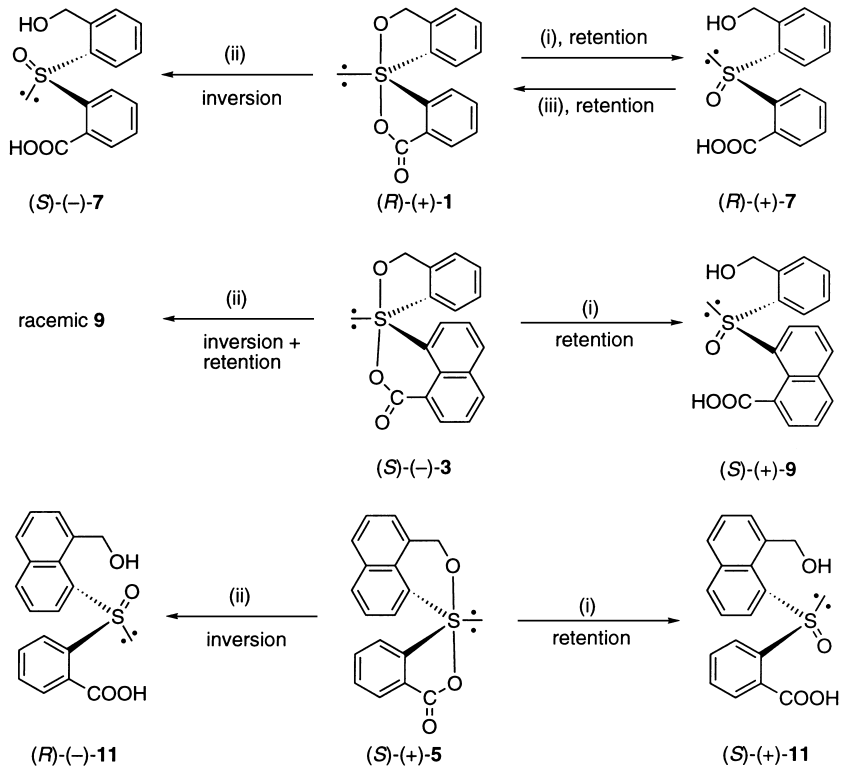
2.1. Synthesis (see Scheme 1)

(*R*)-(+)-1,1′-Spirobi[3*H*-2,1-benzoxathiol]-3-one, (*S*)-(–)-spiro[3*H*-2,1-benzoxathiol-1,1′-naphtho[1,8-*d*,*e*]-3*H*-2,1-oxathiin-3-one] and (*S*)-(+)-spiro[3*H*-2,1-benzoxathiol-3-one-1,1′-naphtho[1,8-*d*,*e*]-3*H*-2,1-oxathiin] {spiro-λ^4-sulfanes (*R*)-(+)-**1**, (*S*)-(–)-**3** and (*S*)-(+)-5[1]} were treated with trimethyloxonium tetrafluoroborate at room temperature in dichloromethane to give (*S*)-(–)-1-[2′-(methoxycarbonyl)phenyl]-3*H*-2,1-benzoxathiol-1-ium tetrafluoroborate, (*R*)-(–)-1-[8′-(methoxycarbonyl)-1′-naphthyl]-3*H*-2,1-benzoxathiol-1-ium tetrafluoroborate and (*R*)-(–)-1-[2′-(methoxycarbonyl)-phenyl]-3*H*-2,1-naphtho[1,8-*d*,*e*]-oxathiin-1-ium tetrafluoroborate {sulfonium salts (*S*)-(–)-**2**, (*R*)-(–)-**4** and (*R*)-(–)-**6**}.

The formation of sulfonium salts can be explained by the structure of the precursor spiro-λ^4-sulfanes. X-Ray determinations revealed that in asymmetrically substituted (acyloxy)(alkoxy)-



Scheme 1. Conversion of spiro-λ^4-sulfanes into sulfonium tetrafluoroborates. *Reagents and conditions:* (i) $Me_3O^+BF_4^-$, CH_2Cl_2, 20°C, 4 h

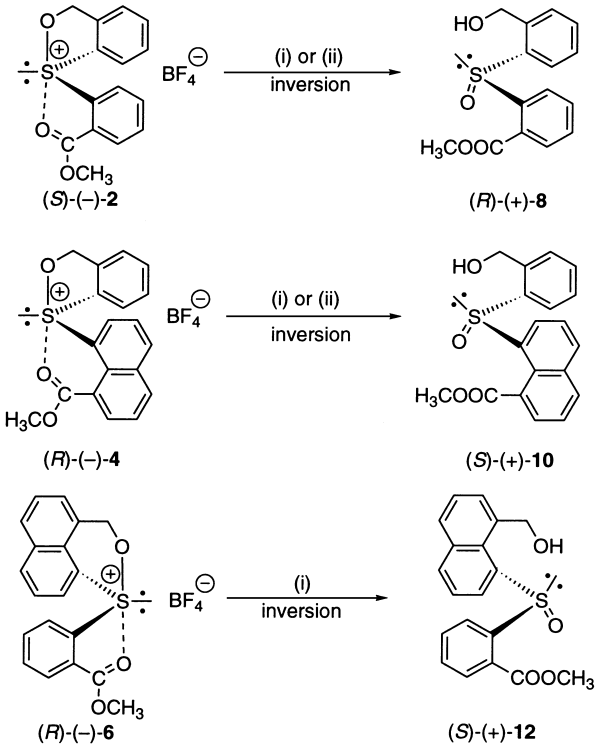


Scheme 2. Stereospecific conversion of spiro-λ^4-sulfanes to sulfoxide-carboxylic acids by hydrolysis. *Reagents and conditions*: (i) $KHCO_3$ aq., 20°C, 30 min; (ii) H_2SO_4 aq., 20°C, 30 min–48 h; (iii) AcCl, 1 equiv. Et_3N, DMF, –60°C, then 1,2-dichloroethane, 83°C, 20 min

spiro-λ^4-sulfanes the axial S–O bonds differ markedly. The S–O(alkoxy) bond is a usual covalent bonding (1.71, 1.66 and 1.69 Å in (*R*)-(+)-**1**, (*R*)-(+)-**3**[1] and racemic **5**,[5] respectively), whereas the S–O(acyloxy) bond lengths (2.05, 2.13 and 2.11 Å in (*R*)-(+)-**1**, (*R*)-(+)-**3**[1] and racemic **5**,[5] respectively) point to a weak hypervalent bond, which results in a sulfonium-carboxylate zwitterion structure. Trimethyloxonium tetrafluoroborate can methylate the carboxylate-like oxygen, thus leading to the formation of diaryl(alkoxy)sulfonium salts carrying an *o*-methoxycarbonyl substituent on one of the aromatic rings.

2.2. Enantiomeric excess

Sulfonium salts **2**, **4** and **6** can be hydrolysed in $KHCO_3$ aq. into diaryl sulfoxides **8**, **10** and **12**, respectively (cf. Scheme 3). Because this reaction is stereospecific, the hydrolysis of the enantiomers of **2**, **4** and **6** leads to optically active sulfoxide-methyl esters **8**, **10** and **12**, respectively. Measuring the optical activity of the latter compounds the minimal ee of the starting sulfonium salts can be calculated (for determining the ee of **8**, **10** and **12**, see Ref. 7). The following minimal enantiomeric excess data were obtained: $>86\%$ for (–)-**2**, $>89\%$ for (–)-**4** and $>99\%$ for (–)-**6**.



Scheme 3. Stereospecific conversion of sulfonium salts to sulfoxide-methyl esters by hydrolysis. *Reagents and conditions*: (i) $KHCO_3$ aq., 0°C, 30 min; (ii) H_2SO_4 aq., 20°C, 48 h. No reaction with (*R*)-(–)-**6**

2.3. Molecular structures

NMR measurements showed that optically active compounds **2**, **4** and **6** exhibit sulfonium structure with a spiro-λ^4-sulfane-like trigonal bipyramidal arrangement about sulfur. This means that the nearly linear O(alkoxy)–S^+···O(carbonyl) moieties occupy the axial position as was expected from the structures of analogous diaryl(alkoxy) and diaryl(acylamino) sulfonium salts.[3–6] Owing to the close contact between sulfonium centre and the methoxycarbonyl oxygen, the *endo* methylene hydrogen and the aromatic hydrogen attached in *ortho* position to sulfur on the aromatic ring carrying the methoxycarbonyl group come into steric proximity in the rigid ring systems of the investigated sulfonium salts **2**, **4** and **6.** This conformation is unambiguously evidenced in DMSO-d_6 by mutual NOE interaction between these hydrogens (6.5% for **2**, 5.8% for **4** and 4.1% for **6**). On the other hand the proximity of the carbonyl oxygen fixed in close contact and the hydrogen atom bonded to the other aromatic ring in *ortho* position relative to the sulfonium centre is clearly revealed by their characteristic downfield shifts (8.07 ppm for **2**, 8.27 ppm for **4** and 8.42 ppm for **6**).[†]

[†] Each ^1H and ^{13}C NMR assignment based on 2D-COSY, 2D-HSQC, 2D-HMBC and DNOE measurements is provided in supplementary material.

2.4. Absolute configurations

Knowing the absolute configurations of precursor spiro-λ^4-sulfanes (*R*)-(+)-**1**, (*S*)-(–)-**3** and (*S*)-(+)-**5**,[1,2] we may attribute the configurations to the sulfonium salts (*S*)-(–)-**2**, (*R*)-(–)-**4** and (*R*)-(–)-**6**, because the sulfonyl moiety of spiro-λ^4-sulfanes does not take part in the methylating reaction, which converts only the oxycarbonyl part of the molecule (see e.g. **1**→**2** in Scheme 1).

The similar CD spectra of spiro-λ^4-sulfanes (*R*)-(+)-**1**, (*S*)-(–)-**3**‡ and (*S*)-(+)-**5**,[1,2] and the corresponding sulfonium salts (*S*)-(–)-**2**, (*R*)-(–)-**4** and (*R*)-(–)-**6** (Fig. 1), gave convincing evidence for both the same absolute configurations and the similar TBP geometry of the compounds mentioned. A comparative analysis of CD spectra for the enantiomers of **2**, **4**, **6** and other sulfonium salts as well as their precursor compounds will be published in detail elsewhere.[8]

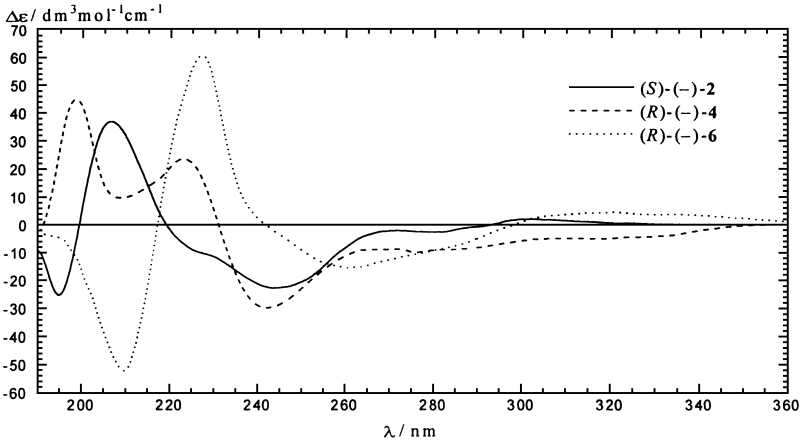


Figure 1. CD spectra of sulfonium salts (*S*)-(–)-**2**, (*R*)-(–)-**4** and (*R*)-(–)-**6**

It should be pointed out that the spatial arrangement of the above mentioned spiro-λ^4-sulfanes and corresponding sulfonium salts {(*R*)-(+)-**1** and (*S*)-(–)-**2**; (*S*)-(–)-**3** and (*R*)-(–)-**4**; (*S*)-(+)-**5** and (*R*)-(–)-**6**} are analogous although the designations of configuration are different. The configuration of sulfur in spiro-λ^4-sulfanes was designated by the convention proposed by Martin and Balthazor[9] for compounds with pentacoordinated stereogenic atom, while the Cahn–Ingold–Prelog convention was used for sulfonium salts.

2.5. Hydrolysis

By using kinetic methods the mechanism of hydrolysis of racemic spiro-λ^4-sulfanes and related sulfonium salts has been investigated extensively in our laboratory by Ruff et al.[10–13] In contrast, only a few λ^4-sulfanes were prepared in optically active form, thus the stereochemistry of their nucleophilic reactions has been slightly studied. Martin et al. investigated the basic hydrolysis of an optically active chloro-λ^4-sulfane.[9] Zhang et al. found that the basic and acidic hydrolysis of optically active spiro-λ^4-sulfanes leads to sulfoxide diastereomers with opposite configurations of the sulfur atom, therefore they suggested different stereomechanisms depending on pH.[14]

‡ In Refs. 1 and 2 the CD spectrum of (*R*)-(+)-**3** is given. The spectrum of (*S*)-(–)-**3** was also recorded and shows the mirror image of (*R*)-(+)-**3**.

Having a set of optically active sulfonium salts, (*S*)-(–)-**2**, (*R*)-(–)-**4**, (*R*)-(–)-**6**, and the corresponding optically active precursor spiro-λ^4-sulfanes, (*R*)-(+)-**1**, (*S*)-(–)-**3**, (*S*)-(+)-**5**, of known absolute configurations, we submitted them to hydrolysis under different conditions (in 1N $KHCO_3$ and 1N H_2SO_4 solutions). Experimental results are summarized in Schemes 2 and 3.

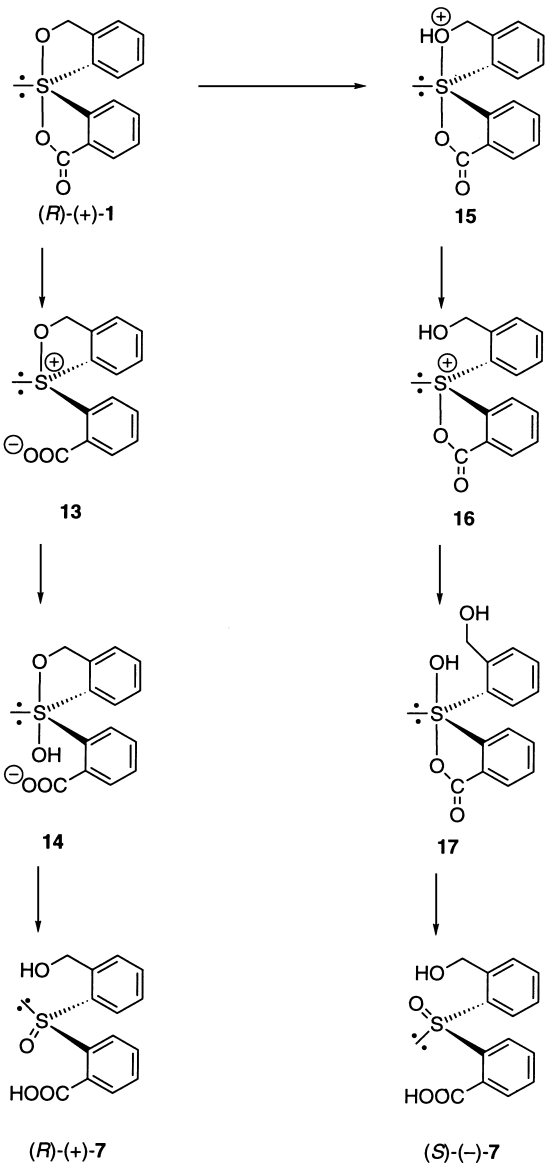
In a previous paper[1] we showed that the stereospecific dehydration of sulfoxide (*R*)-(+)-**7** yielding spiro-λ^4-sulfane (*R*)-(+)-**1** (see Scheme 2) proceeds with 'retention of configuration' because the C_{ar}(acyl–O)→C_{ar}(alkyl–O)→lone pair sequence of substituents attached to the stereogenic sulfur traces the same direction both in the case of sulfoxide (*R*)-(+)-**7** (Cahn–Ingold–Prelog convention) and in spiro-λ^4-sulfane (*R*)-(+)-**1** (Martin–Balthazor convention[9]). Thus, the reverse reaction, e.g. the hydrolysis of (*R*)-(+)-**1** into (*R*)-(+)-**7**, may be assumed to proceed with retention. However, this is true for reaction **1**→**7** only if it is conducted in aqueous $KHCO_3$ solution, whereas in acidic media inversion does occur (e.e. 84%). To exclude racemization as a contributing factor in the above experiments, we treated optically active sulfoxide **7** under the conditions as employed for the acidic hydrolysis of spiro-λ^4-sulfane (*R*)-(+)-**1** (1N H_2SO_4, 30 min, 25°C, cf. Exp.), which resulted in ca. 16% of racemization, while total racemization took ca. 60 h (for racemization of sulfoxides including the effect of acid catalysis and neighbouring participation of carboxylic group, see Ref. 15). Under basic conditions 10% of racemization was observed for sulfoxide (*R*)-(+)-**7**, while stirring the solution of the methyl ester (*R*)-(+)-**8** with aqueous $KHCO_3$ or H_2SO_4 afforded only the starting enantiomer.

Thus we may assume that the hydrolysis of (*R*)-(+)-**1** is stereospecific and can follow two different pathways depending on pH. This assumption is in accordance with the results of Zhang et al.[14] obtained for the hydrolysis of other five-membered (acyloxy)(alkoxy)spiro-λ^4-sulfanes. The proposed mechanisms are shown in Scheme 4.

Owing to the polar and weak S–O(acyloxy) hypervalent bond, the acyloxy-ring of diaryl(acyloxy)-(alkoxy)spiro-λ^4-sulfanes splits easily, and hydroxide ion can attack the sulfonium centre from the 'acyloxy-side' of the monocyclic alkoxy-sulfonium salt **13**. A monocyclic (alkoxy)(hydroxy)-λ^4-sulfane intermediate **14** is formed, which transforms into sulfoxide-carboxylic acid (*R*)-(+)-**7** by splitting of the 'alkoxy-ring' and by proton-transfer. The reaction proceeds with retention, e.g. the configuration of sulfur is preserved.

In acidic media the alkoxy ring may open after protonation and water molecule can hydrolyse the acyloxy-sulfonium intermediate **16** through the formation of the monocyclic (acyloxy)(hydroxy)-λ^4-sulfane **17** intermediate. In compounds **14** and **17** sulfur atoms have opposite configurations, thus the ring-splitting and proton-transfers convert **17** to the enantiomeric sulfoxide–carboxylic acid (*S*)-(–)-**7**. This mechanism is supported by the following data: (i) isotopically labelled H_2O experiments proved that the water molecule attacks the sulfur during hydrolysis;[14,16] therefore, regarding the inversion of sulfur the attack of water takes place from the 'alkoxy-side'; (ii) the basicity of ethers is stronger than that of esters[17] ($pK_{BH+} = -3.5$ and –6.5, respectively); (iii) kinetic investigations revealed that water as a poor nucleophile can hydrolyse asymmetrically substituted spiro-λ^4-sulfanes in a slow reaction,[11] but even water can hydrolyse the very unstable acyloxy-sulfonium intermediate **16** formed by the splitting of the S–O^+H(alkoxy) bond.

In alkaline media the hydrolysis of spiro-λ^4-sulfanes (*S*)-(–)-**3** and (*S*)-(+)-**5** containing naphthalene rings (see path i in Scheme 2) proceeds in a similar way as that of compound (*R*)-(+)-**1**, yielding the expected stereoisomer of sulfoxide-carboxylic acids (*S*)-(+)-**9** and (*S*)-(+)-**11.** The formation of a nearly racemic product (**9**) {$[\alpha]^{25}_{546} = -23$; $[\alpha]^{25}_{546} = 673$ (c = 0.5, DMF) for the pure enantiomer[7]} from (*S*)-(–)-**3** in acidic media indicates, however, that two parallel mechanisms are operative in this case. A water molecule can attack the sulfonium centre after the



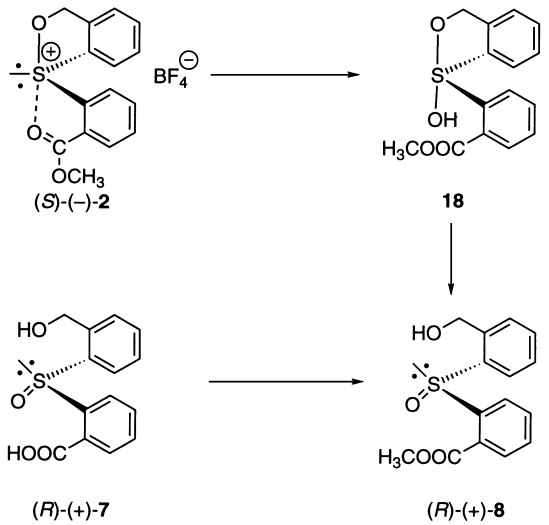
Scheme 4. The stereospecific hydrolysis of spiro-λ^4-sulfane (*R*)-(+)-**1** in basic (1N $KHCO_3$) and acidic (1N H_2SO_4) media

cleavage of the S–OH^+(alkoxy) bond (inversion), and from the side of the acyloxy group (retention), due to the very weak S–O(acyloxy) bond in the six-membered ring (cf. Ref. 11). In the acidic hydrolysis of (*S*)-(+)-**5** the ee of (*R*)-(–)-**11** was 66%. In control experiments sulfoxide-carboxylic acid enantiomers **9** and **11** were treated with H_2SO_4 and $KHCO_3$ and only in the case of **9** was ca. 10% of racemization observed.

As shown in Scheme 3, the hydrolyses of diaryl(alkoxy)sulfonium salts (*S*)-(–)-**2** and (*R*)-(–)-**4** gave the corresponding diaryl sulfoxide-methyl esters (*R*)-(+)-**8** and (*S*)-(+)-**10** with opposite sulfur configurations both in 1N $KHCO_3$ and 1N H_2SO_4 solutions. It should be mentioned that (*R*)-(–)-**6** gives (*S*)-(+)-**12** in basic media but did not hydrolyse under acidic conditions, which may

be attributed to the slight reactivity of water toward the six-membered alkoxy-ring, which can be cleaved by hydroxide.[11] In reference experiments sulfoxide-methyl ester enantiomers **8**, **10** and **12** were treated with H_2SO_4 and $KHCO_3$ and all of them were isolated in enantiomerically pure form.

The detailed mechanism proposed for the hydrolysis of the sulfonium salt (*S*)-(–)-**2** is illustrated in Scheme 5. We may assume that the sulfonium centre is attacked by hydroxide ion (in $KHCO_3$ aq.) or by a water molecule (in H_2SO_4 aq.), which gives the monocyclic (alkoxy)-(hydroxy)-λ^4-sulfane **18** intermediate, from which (*R*)-(+)-**8** sulfoxide-methyl ester is formed by cleavage of the alkoxy-ring and by proton-transfer, involving inversion of the configuration of the sulfonium centre. (*R*)-(+)-**8** can also be obtained from (*R*)-(+)-**7** by methylation with diazomethane.



Scheme 5. The stereospecific hydrolysis of sulfonium salt (*S*)-(–)-**2** in basic (1N $KHCO_3$) or in acidic (1N H_2SO_4) media

3. Experimental

Melting points were determined on a Boetius micro melting point apparatus. IR spectra were taken on a Specord IR 75 (Zeiss, Jena) spectrophotometer. ^1H and ^{13}CNMR spectra were recorded in DMSO-d_6 solution at room temperature on a Bruker DRX 500 spectrometer at 500.13 (^1H) and 125.76 (^{13}C) MHz with the deuterium signal of the solvent as the lock and TMS as internal reference. The standard Bruker microprogram NOEMULT.AU to generate NOE was used with a selective preirradiation time. The 2D-COSY, 2D-HSQC and 2D-HMBC spectra were obtained by using the standard Bruker pulse programs COSYGS, INV4GS and INV4GSLPLRND.

*3.1. General procedure for the preparation of sulfonium tetrafluoroborates (*S*)-(–)-**2**, (*R*)-(–)-**4** and (*R*)-(–)-**6***

To a stirred solution of spiro-λ^4-sulfanes (*R*)-(+)-**1**, (*S*)-(–)-**3** and (*S*)-(+)-**5**[1] (3 mmol) in dichloromethane (40 mL) was added trimethyloxonium tetrafluoroborate (0.46 g, 3.03 mmol).

The stirring continued for 4 h at room temperature then ether (100 mL) was poured into the mixture. The precipitate was filtered off, washed with ether and dried over P_2O_5.

3.1.1. Selected data for sulfonium tetrafluoroborates

*3.1.1.1. (S)-(–)-1-[2′-(Methoxycarbonyl)phenyl]-3*H*-2,1-benzoxathiol-1-ium tetrafluoroborate (S)-(–)-**2**.* Yield 84%; $[\alpha]_{546}^{25}=-204$, c = 0.5, DMF; mp 155–158°C; IR ν_{max} (KBr)/cm^{-1} 1662vs (C=O), 1050vs (BF_4); ^{1}H NMR δ 6.18 (d, 1H, J = 13.2 Hz), 6.54 (d, 1H, J = 13.2 Hz), 4.20 (s, 3H), 7.67–8.23 (m, ArH); ^{13}C NMR δ 169.1 (s, C=O), 84.2 (t, CH_2), 55.9 (q, CH_3), 124.5–140.4 (aromatic ring).

*3.1.1.2. (R)-(–)-1-[8′-(Methoxycarbonyl)-1′-naphthyl]-3*H*-2,1-benzoxathiol-1-ium tetrafluoroborate (R)-(–)-**4**.* Yield 80%; $[\alpha]_{546}^{25}=-279$, c = 0.5, DMF; mp 183–193°C; IR ν_{max} (KBr)/cm^{-1} 1674vs (C=O), 1050vs (BF_4); ^{1}H NMR δ 6.06 (d, 1H, J = 12.8 Hz), 6.47 (d, 1H, J = 12.8 Hz), 4.16 (s, 3H), 7.79–8.53 (m, ArH); ^{13}C NMR δ 172.1 (s, C=O), 83.3 (t, CH_2), 55.1 (q, CH_3), 124.6–139.3 (aromatic ring).

*3.1.1.3. (R)-(–)-1-[2′-(Methoxycarbonyl)-phenyl]-3*H*-2,1-naphtho[1,8-d,e]-oxathiin-1-ium tetrafluoroborate (R)-(–)-**6**.* Yield 86%; $[\alpha]_{546}^{25}=-87$, c = 0.5, DMF; mp 198–204°C; IR ν_{max} (KBr)/cm^{-1} 1710vs (C=O), 1070vs (BF_4); ^{1}H NMR δ 5.13 (d, 1H, J = 12.8 Hz), 5.87 (d, 1H, J = 12.8 Hz), 4.08 (s, 3H), 6.91–8.59 (m, ArH); ^{13}C NMR δ 164.9 (s, C=O), 68.2 (t, CH_2), 53.8 (q, CH_3), 124.0–136.1 (aromatic ring).

*3.2. General procedure for the hydrolysis of spiro-λ^4-sulfanes (R)-(+)-**1**, (S)-(–)-**3** and (S)-(+)-**5***

(A) To the solution of 1N $KHCO_3$ (2 mL) was added a spiro-λ^4-sulfane (0.1 mmol) and the reaction mixture was stirred for 30 min at room temperature. The solution was acidified with 1N H_2SO_4 (pH 2) then the crystals were filtered, washed with water and dried. Yields: 88, 87 and 90% for sulfoxide-carboxylic acids (*R*)-(+)-**7**, (*S*)-(+)-**9** and (*S*)-(+)-**11**, respectively.

(B) To the solution of a spiro-λ^4-sulfane (0.1 mmol) in dichloromethane (2 mL) was added 1N H_2SO_4 (2 mL) and the mixture was stirred for 30 min {for (*R*)-(+)-**1**)} or 48 h {for (*S*)-(–)-**3** and (*S*)-(+)-**5**} at room temperature. Dichloromethane was removed in vacuo then the crystals were filtered, washed with water and dried. Yields: 93, 91 and 91% for sulfoxides (*S*)-(–)-**7**, racemic **9** and (*R*)-(–)-**11**, respectively.

*3.3. General procedure for the hydrolysis of sulfonium tetrafluoroborates (S)-(–)-**2**, (R)-(–)-**4** and (R)-(–)-**6***

(A) To the solution of a sulfonium salt (0.1 mmol) in dichloromethane (2 mL) was added 1N $KHCO_3$ (2 mL) then the mixture was stirred for 30 min at 0°C. The organic phase was separated, dried and then the solvent was removed in vacuo. Yields: 83, 87 and 88% for sulfoxide-methyl esters (*R*)-(+)-**8**, (*S*)-(+)-**10** and (*S*)-(+)-**12**, respectively.

(B) To the solution of a sulfonium salt (0.1 mmol) in dichloromethane (2 mL) was added 1N H_2SO_4 (2 mL) and the mixture was stirred for 48 h at room temperature. The organic phase was separated, dried and then the solvent was removed in vacuo. Yields: 94 and 89% for sulfoxide-methyl esters (*R*)-(+)-**8** and (*S*)-(+)-**10**; the unchanged (*R*)-(–)-**6** was isolated in the yield of 95%.

Physical data of sulfoxide-carboxylic acids and sulfoxide-methyl esters isolated by the hydrolysis reactions are identical with those given in Ref. 7.

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