Dimethyldioxirane Oxidation of the Epoxides of (*Z*)-3-Arylidene-1-thioflavanones

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Dedicated to Professor Dr. Waldemar Adam on the occasion of his 65th birthday.

Sulfur atom of the *trans,cis*- and *trans,trans*-epoxides **1** of (*Z*)-3-arylidene-1-thioflavanones have been oxidized with dimethyldioxirane to afford the appropriate sulfoxides **2** and sulfones **3** depending on the amount of oxidant used.

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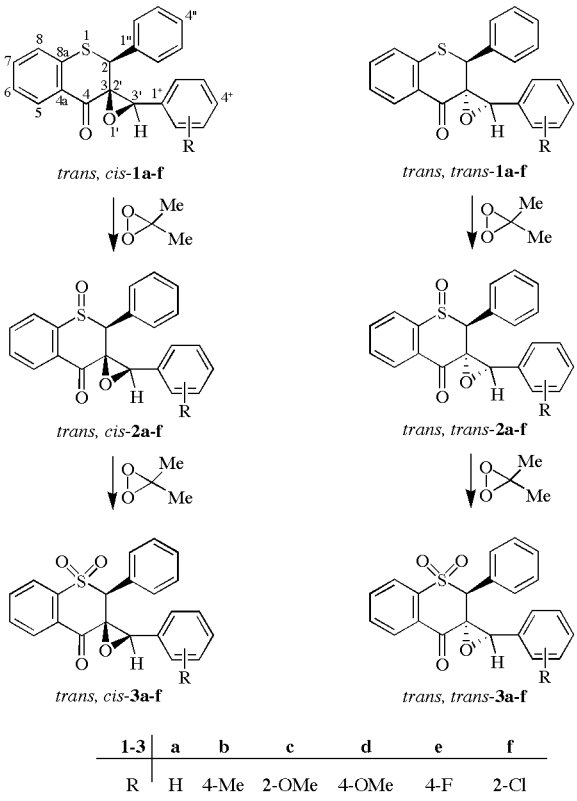
3-Arylideneflavanones (also termed flavindogenides) are well-known exocyclic α,β-unsaturated ketones. Their synthesis and chemical transformations were thoroughly investigated by several research groups [1-14]. However, the related 3-arylidene-1-thioflavanones have hitherto received less attention. (*Z*)-3-Arylidene-1-thioflavanones, where the carbonyl and aryl moieties are on opposite sides of the carbon-carbon double bond, were obtained by acid- [15-17] and base-catalyzed condensation [18] of 1-thioflavanones and aromatic aldehydes. Their (*E*)-isomers, where the aryl and carbonyl groups are on the same side of the carbon-carbon double bond were prepared by the photoisomerization of the appropriate (*Z*)-3-arylidene-1-thioflavanones [19,20]. Previously, we have studied several chemical transformations of the 3-arylidene-1-thioflavanones including their oxidation with dioxiranes [10,21-26].

It has been found that, depending on the amount of the oxidant, dimethyldioxirane oxidation of (*Z*)-3-arylidene-1-thioflavanones afforded sulfoxides and/or sulfones which could not be epoxidized to their corresponding epoxides either with a high excess of dimethyldioxirane or with the much more effective methyl(trifluoromethyl)dioxirane [24]. 3-Arylidene-1-thioflavanones gave sulfones with *m*-chloroperbenzoic acid as another electrophilic oxidant [17]. Thus, these electrophilic oxidants oxidize only the sulfur atom of the 3-arylidene-1-thioflavanones in a chemoselective reaction which may be a consequence of the strongly electron deficient character of the carbon-carbon double bond. For this reason, the nucleophilic oxidants alkaline hydrogen peroxide and sodium hypochlorite proved to be the reagents of choice for the epoxidation of 3-arylidene-1-thioflavanones [17,25,26]. Although the use of these oxidants afforded a diastereomeric mixture of the *trans,cis*- and *trans,trans*-epoxides, the two diastereomeric epoxides could easily be separated by silica gel column chromatography. Therefore, these stereohomogeneous epoxides are now available for further chemical transformations.

Formerly, we have investigated the utility of the dimethyldioxirane (DMD), as a versatile electrophilic oxidant, for the oxidation of the sulfur atom of sulfur-containing six- and seven-membered heterocyclic compounds, *viz.* 4*H*-1-benzothiopyran-4-ones [27] and 2,3-dihydro-1,5-benzothiazepin-4(5*H*)-ones [28]. Depending on the amount of the oxidant, sulfoxides or sulfones were obtained. Moreover, in the case of the sulfoxidation of the 2-substituted 1,5-benzothiazepine derivatives a high *trans* diastereoselectivity was observed. All these results prompted us to study the dimethyldioxirane oxidation of the (*Z*)-3-arylidene-1-thioflavanone epoxides described in our previous papers [25,26]. It should also be mentioned that no example has hitherto been published concerning the oxidation of the sulfur atom of 3-arylidene-1-thioflavanone epoxides.

3-Arylidene-1-thioflavanone epoxides *trans,cis*-**1a-f** and *trans,trans*-**1a-f** were allowed to react with a slight excess of isolated dimethyldioxirane (DMD) in acetone (0.05-0.1 *M*) [29] at room temperature for 18 hours. Under these reaction conditions 80-90% conversion of the starting epoxides **1** was detected and the formed sulfoxides **2** were separated by column chromatography. This protocol made possible the preparation of sulfone free sulfoxides *trans,cis*-**2a-f** and



trans,trans-**2a-f** in moderate (27-64%) yields. If a complete conversion was reached, 5-10% sulfones were detected in the crude reaction mixtures. In case 5 or 6 equivalents of DMD was used for the oxidation of compounds *trans,cis*-**1a-f** and *trans,trans*-**1a-f** under the same reaction conditions, sulfones *trans,cis*-**3a-f** and *trans,trans*-**3a-f** were detected, on a complete conversion of the starting epoxides **1,** and isolated as sole products in high (70-90%) yields. Structure and stereochemistry of the prepared sulfoxides **2** and sulfones **3** have been elucidated by mass spectroscopy and nmr spectroscopic measurements.

In the TSP mass spectra, molecular ions of sulfoxides **2** and sulfones **3** were detected which unequivocally prove the types of the oxidized products. Results of the microanalyses (*cf.* Experimental) corroborate the sulfoxide or sulfone character of all new isolated compounds.

Recently we have reported the stereochemistry and ^{1}H and ^{13}C nmr data of the starting *trans,cis*- and *trans,trans*-2,3'-diarylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-ones **1** [26]. Comparison of the corresponding nmr data of the starting materials **1** with the sulfoxides **2** and sulfones **3** (δH-3' = 4.70-5.12, δC-3' = 58.9-67.9 and $^{1}J_{C\text{-}3',H\text{-}3'} \approx 181$-182 Hz) unequivocally proves that the epoxide moiety has remained intact on the dimethyldioxirane oxidation of compounds **1**. Due to the anisotropic effect of the C(4)=O group, an upfield shift (*ca*. 0.2 ppm) of the H-3' signal was found in the *trans,cis* products **2** and **3** if compared to the corresponding *trans,trans* isomers. The –M effect of the SO and SO_2 groups, induced a shielding effect on the H-6 (δH-6 *ca*. 7.2) and on the C-6 (δC-6 *ca*. 126) of **1** as reflected in the corresponding signals at *ca*.7.7 and 133 for **2** and at *ca*. 7.8 and 134 for **3**. A comprehensive conformational analysis of the starting *trans,cis*-**1** and *trans,trans*-**1** proved the axial arrangement of the 2-phenyl group in the preferred conformers. As a consequence, the quite bulky dimethyldioxirane may preferably attack the sulfur atom from the opposite side resulting in the formation of sulfoxide isomer in which the oxygen atom and the 2-phenyl group are *trans* oriented. A detailed stereochemical study sulfoxides **2** and sulfones **3**, together with related sulfur-containing compounds, by various physical methods and quantum-chemical calculations are in progress and the results will be published in a separate paper.

In summary, it can be concluded that, as results of our previous [24-26] and present investigations, we managed to oxidize both the carbon-carbon double bond and the sulfur atom of the (*Z*)-3-arylidene-1-thioflavanones by using either nucleophilic or electrophilic oxidants. All oxidized derivatives of the (*Z*)-3-arylidene-1-thioflavanones are now easily accessible.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C nmr spectra were recorded with a Bruker Avance DRX-500 spectrometer (at 500 MHz for ^{1}H, 125 MHz for ^{13}C) at ambient temperature in chloroform-d. Chemical shifts are given on the δ scale ($\delta_{TMS} = 0.00$). Elemental analyses were measured in house on a Carlo Erba 1106 EA instrument. Mass spectra were recorded on a VG TRIO-2 instrument with thermospray technique. Samples were analyzed in the by-pass mode. 20 µl of the sample solutions in methanol was introduced *via* the thermospray interface. The mobile phase was methanol and water (1:1 v/v) mixture containing 0.1 *M* ammonium acetate. The capillary tip temperature was 230°, the electrode voltage was 180 V and the source temperature was 210°. The tlc was performed on Kieselgel 60 F_{254} (Merck) layer and Merck silica gel was used for column chromatography both with 1,2-dichloroethane as eluent. The starting materials **1a-f** were synthesized as described in our previous paper [25]. Dimethyldioxirane (DMD, as 0.05-0.1 *M* acetone solution) was prepared as published [29] and its peroxide content was determined iodometrically. Curox (potassium monopersulfate), the triple salt $2KHSO_5.KHSO_4.K_2SO_4$, was used as received, a generous gift from the Peroxid-Chemie GmbH (München, Germany).

General Procedure for the Preparation of Sulfoxides **2a-f.**

Epoxides **1a-f** (0.20 g, 0.50-0.60 mmoles) was dissolved in anhydrous methylene chloride (10.0 ml) and dimethyldioxirane (*ca*. 0.05-0.1 *M* acetone solution, 0.75 mmol) was added and the reaction mixture was left to stand at room temperature for 18 hours. The solvent was evaporated *in vacuo* and sulfoxides **2a-f** were isolated by silica gel chromatography with 1,2-dichloroethane as eluent.

trans,cis-(±)-2,3'-Diphenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,cis*-**2a**).

This compound was prepared as white needles in 27% yield, mp 217-218°; ^{1}H nmr: δ 4.66 (1H, s, H-2), 4.78 (1H, s, H-3'), 7.12-7.27 (5 arom H, m), 7.39-7.50 (4 arom H, m), 7.56 (1H, d, J=7.5 Hz, H-8), 7.64 (1H, t, J=7.6 Hz, H-7), 7.68 (1H, t, J=7.6 Hz, H-6), 8.36 (1H, d, J=7.6 Hz, H-5); ^{13}C nmr: δ 60.8 (C-3), 61.2 (C-2), 67.5 (C-3'), 189.5 (C-4); ms (TSP): m/z 361 $(M+H)^+$.

Anal. Calcd. for $C_{22}H_{16}O_3S$: C, 73.32; H, 4.48. Found: C, 73.35; H, 4.46.

trans,trans-(±)-2,3'-Diphenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,trans*-**2a**).

This compound was obtained as white needles in 39% yield, mp 213-214°; ^{1}H nmr: δ 4.70 (1H, s, H-2), 4.92 (1H, s, H-3'), 6.60 (2H, d, J=7.7 Hz, H-2",6"), 6.93 (2H, t, J=7.3 Hz, H-3",5"), 6.99 (1H, t, J=7.3 Hz, H-4"), 7.02-7.11 (3 arom H, m), 7.15 (2H, d, J=7.2 Hz, H-2$^+$,6$^+$), 7.48 (1H, d, J=7.4 Hz, H-8), 7.61 (1H, t, J=7.4 Hz, H-7), 7.77 (1H, t, J=7.6 Hz, H-6), 8.25 (1H, d, J=7.6 Hz, H-5); ^{13}C nmr: δ 59.1 (C-3), 60.9 (C-3'), 65.3 (C-2), 190.1 (C-4); ms (TSP): m/z 361 $(M+H)^+$.

Anal. Calcd. for $C_{22}H_{16}O_3S$: C, 73.32; H, 4.48. Found: C, 73.28; H, 4.50.

trans,cis-(±)-3'-(4-Methylphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,cis*-**2b**).

This substance was isolated as white needles in 66% yield, mp 210-211º; ^{1}H nmr: δ 4.68 (1H, s, H-2), 4.75 (1H, s, H-3'), 7.18 (2H, d, J=7.3 Hz, H-2",6"), 7.20-7.27 (5 arom H, m), 7.34 (2H, d, J=7.7 Hz, H-2$^+$,6$^+$), 7.56 (1H, d, J=7.5 Hz, H-8), 7.64 (1H, t, J=7.5 Hz, H-7), 7.69 (1H, t, J=7.6 Hz, H-6), 8.37 (1H, d, J=7.6 Hz, H-5); ^{13}C nmr: δ 60.9 (C-3), 61.2 (C-2), 67.7 (C-3'), 189.6 (C-4); ms (TSP): m/z 375 $(M+H)^+$.

Anal. Calcd. for $C_{23}H_{18}O_3S$: C, 73.78; H, 4.84. Found: C, 73.75; H, 4.86.

trans,trans-(±)-3'-(4-Methylphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,trans*-**2b**).

This compound was obtained as white needles in 64% yield, mp 231-232°, ^{1}H nmr: δ 2.20 (3H, s, Me), 4.70 (1H, s, H-2), 4.90 (1H, s, H-3'), 6.63 (2H, d, J=7.5 Hz, H-2",6"), 6.89 (2H, d, J=7.9 Hz, H-3$^+$,5$^+$), 6.95 (2H, t, J=7.3 Hz, H-3",5"), 6.98-7.10 (3 arom H, m), 7.49 (1H, d, J=7.4 Hz, H-8), 7.61 (1H, t, J=7.5 Hz, H-7), 7.72 (1H, t, J=7.7 Hz, H-6), 8.25 (1H, d, J=7.5 Hz, H-5); ^{13}C nmr: δ 59.1 (C-3), 61.0 (C-3'), 65.2 (C-2), 190.2 (C-4); ms (TSP): m/z 375 $(M+H)^+$.

Anal. Calcd. for $C_{23}H_{18}O_3S$: C, 73.78; H, 4.84. Found: C, 73.81; H, 4.81.

trans,cis-(±)-3'-(2-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,cis*-**2c**).

This substance was prepared as white plates in 58% yield, mp 208-209°; ^{1}H nmr: δ 4.68 (1H, s, H-2), 5.00 (1H, s, H-3'), 6.94-6.98 (2 arom H, m), 7.12 (1H, d, J=7.2 Hz, H-6$^+$), 7.17 (2H, d, J=7.6 Hz, H-2",6"), 7.20-7.26 (3 arom H, m), 7.38 (1H, t, J=7.5 Hz, H-4$^+$), 7.56 (1H, d, J=7.2 Hz, H-8), 7.63 (1H, t, J=7.1 Hz, H-7), 7.68 (1H, t, J=7.2 Hz, H-6), 8.36 (1H, d, J=7.6 Hz, H-5); ^{13}C nmr: δ 60.9 (C-3), 61.7 (C-2), 65.1 (C-3'), 189.7 (C-4); ms (TSP): m/z 391 $(M+H)^+$.

Anal. Calcd. for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.64. Found: C, 70.73; H, 4.6.

trans,trans-(±)-3'-(2-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,trans*-**2c**).

This compound was isolated as white plates in 39% yield, mp 207-208°; ^{1}H nmr: δ 3.43 (3H, s, Me), 4.64 (1H, s, H-2), 5.01 (1H, s, H-3'), 6.62 (2H, d, J=7.9 Hz, H-2",6"), 6.86 (1H, t, J=7.5 Hz, H-5$^+$), 6.90 (2H, t, J=8.0 Hz, H-3",5"), 6.99 (1H, t, J=7.4 Hz, H-4"), 7.08 (1H, t, J=7.9 Hz, H-4$^+$), 7.36 (1H, d, J=7.5, H-6$^+$), 7.48 (1H, d, J=7.6 Hz, H-8), 7.60 (1H, t, J=7.6 Hz, H-7), 7.73 (1H, t, J=7.6 Hz, H-6), 8.28 (1H, d, J=7.7 Hz, H-5); ^{13}C nmr: δ 58.9 (C-3'), 59.0 (C-3), 65.9 (C-2), 190.3 (C-4); ms (TSP): m/z 391 $(M+H)^+$.

Anal. Calcd. for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.64. Found: C, 70.79; H, 4.62.

trans,cis-(±)-3'-(4-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,cis*-**2d**).

This compound was prepared as white needles in 41% yield, mp 205-206°; ^{1}H nmr: δ 4.66 (1H, s, H-2), 4.72 (1H, s, H-3'), 6.96 (2H, d, J=8.6, H-3$^+$,5$^+$) 7.16 (2H, d, J=7.3 Hz, H-2",6"), 7.19-7.24 (3 arom H, m), 7.36 (2H, d, J=8.6 Hz, H-2$^+$,6$^+$), 7.55 (1H, d, J=7.6 Hz, H-8), 7.64 (1H, t, J=7.6 Hz, H-7), 7.68 (1H, t, J=7.6 Hz, H-6), 8.35 (1H, d, J=7.6 Hz, H-5); ^{13}C nmr: δ 61.2 (C-3), 61.5 (C-2), 67.9 (C-3'), 189.8 (C-4); ms (TSP): m/z 391 $(M+H)^+$.

Anal. Calcd. for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.64. Found: C, 70.73; H, 4.62.

trans,trans-(±)-3'-(4-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,trans*-**2d**).

This substance was isolated as white plates in 40% yield, mp 215-216°; ^{1}H nmr: δ 3.70 (3H, s, Me), 4.68 (1H, s, H-2), 4.88 (1H, s, H-3'), 6.60-6.65 (4 arom H, m), 6.96 (2H, t, J=7.0 Hz, H-3",5"), 7.01 (1H, t, J=7.6 Hz, H-4"), 7.06 (2H, d, J=8.7 Hz, H-2$^+$, 6$^+$), 7.49 (1H, d, J=7.6 Hz, H-8), 7.61 (1H, t, J=7.6 Hz, H-7), 7.72 (1H, t, J=7.6 Hz, H-6), 8.25 (1H, d, J=7.7 Hz, H-5); ^{13}C nmr: δ 59.2 (C-3), 61.0 (C-3'), 65.3 (C-2), 190.2 (C-4); ms (TSP): m/z 391 $(M+H)^+$.

Anal. Calcd. for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.64. Found: C, 70.80; H, 4.63.

trans,cis-(±)-3'-(4-Fluorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,cis*-**2e**).

This compound was obtained as white needles in 46% yield, mp 246-247°; ^{1}H nmr: δ 4.60 (1H, s, H-2), 4.73 (1H, s, H-3'), 7.12 (2H, t, J=8.6 Hz, H-3$^+$,5$^+$), 7.16 (2H, d, J=7.3 Hz, H-2",6"), 7.19-7.27 (3 arom H, m), 7.43 (2H, dd, J=5.3, 8.6 Hz, H-2$^+$,6$^+$), 7.56 (1H, d, J=7.5 Hz, H-8), 7.64 (1H, t, J=7.5 Hz, H-7), 7.69 (1H, t, J=7.5 Hz, H-6), 8.35 (1H, d, J=7.6 Hz, H-5); ^{13}C nmr: δ 60.8 (C-3), 61.3 (C-2), 66.9 (C-3'), 189.3 (C-4); ms (TSP): m/z 379 $(M+H)^+$.

Anal. Calcd. for $C_{22}H_{15}FO_3S$: C, 69.84; H, 3.99. Found C, 69.87; H, 3.97.

trans,trans-(±)-3'-(4-Fluorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,trans*-**2e**).

This substance was prepared as white needles in 34% yield, mp 242-243°; ^{1}H nmr: δ 4.63 (1H, s, H-2), 4.90 (1H, s, H-3'), 6.62 (2H, d, J=7.6 Hz, H-2",6"), 6.89 (2H, t, J=8.5 Hz, H-3$^+$,5$^+$), 6.97 (2H, t, J=7.3 Hz, H-3",5"), 7.03 (1H, t, J=7.2 Hz, H-4$^+$), 7.12 (2H, dd, J=5.3, 8.5 Hz, H-2$^+$,6$^+$), 7.50 (1H, d, J=7.6 Hz, H-8), 7.63 (1H, t, J=7.6 Hz, H-7), 7.75 (1H, t, J=7.6 Hz, H-6), 8.26 (1H, d, J=7.6 Hz, H-5); ^{13}C nmr: δ 59.1 (C-3), 60.5 (C-3'), 65.4 (C-2), 189.9 (C-4); ms (TSP): m/z 379 $(M+H)^+$.

Anal. Calcd. for $C_{22}H_{15}FO_3S$: C, 69.84; H, 3.99. Found: C, 69.81; H, 4.01.

trans,cis-(±)-3'-(2-Chlorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,cis*-**2f**).

This substance was isolated as pale yellow needles in 45% yield, mp 205-206°; ^{1}H nmr: δ 4.64 (1H, s, H-2), 4.99 (1H, s, H-3'), 7.17 (2H, d, J=7.5 Hz, H-2",6"), 7.18-7.25 (4 arom H, m), 7.27 (1H, t, J=7.6 Hz, H-5$^+$), 7.35 (1H, t, J=7.8 Hz, H-4$^+$), 7.47 (1H, d, J=8.0 Hz, H-3$^+$), 7.60 (1H, d, J=7.4 Hz, H-8), 7.66 (1H, t, J=7.6 Hz, H-7), 7.70 (1H, t, J=7.6 Hz, H-6), 8.35 (1H, d, J=7.4 Hz, H-5); ^{13}C nmr: δ 61.1 (C-3), 61.9 (C-2), 65.6 (C-3'), 189.1 (C-4); ms (TSP): m/z 395 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{15}ClO_3S$: C, 66.93; H, 3.83. Found: C, 66.90; H, 3.85.

trans,trans-(±)-3'-(2-Chlorophenyl).-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1-Oxide (*trans,trans*-**2f**).

This compound was prepared as pale yellow needles in 46% yield, mp 234-235°; ^{1}H nmr: δ 4.67 (1H, s, H-2), 5.08 (1H, s, H-3'), 6.62 (2H, d, J=7.6 Hz, H-2",6"), 6.86-6.95 (4 arom H, m), 7.02 (1H, t, J=7.4 Hz, H-4"), 7.08 (1H, t, J=7.7 Hz, H-4$^+$), 7.21 (1H, t, J=7.6 Hz, H-5$^+$), 7.46 (1H, d, J=7.7 Hz, H-6$^+$), 7.52 (1H, d, J=7.6 Hz, H-8), 7.64 (1H, t, J=7.5 Hz, H-7), 7.76 (1H, t, J=7.7 Hz, H-6), 8.29 (1H, d, J=7.7 Hz, H-5); ^{13}C nmr: δ 59.4 (C-3), 59.5 (C-3'), 65.9 (C-2), 189.5 (C-4); ms (TSP): m/z 395 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{15}ClO_3S$: C, 66.93; H, 3.83. Found: C, 66.96; H, 3.81.

General Procedure for the Synthesis of Sulfones **3a-f**.

Epoxide **1a-f** (0.20 g, 0.50-0.60 mmoles) was dissolved in anhydrous methylene chloride (10.0 ml) and dimethyldioxirane (*ca.* 0.05-0.1 *M* acetone solution, 3.0 mmoles) was added and the solution was allowed to stand at room temperature for 18 hours. The solvent was evaporated *in vacuo* and the residue was crystallized from methanol to afford sulfones **3a-f**.

trans,cis-(±)-2,3'-Diphenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,cis*-**3a**).

This compound was prepared as white needles in 82% yield, mp 169-170°; ^{1}H nmr: δ 4.46 (1H, s, H-2), 4.79 (1H, s, H-3'), 7.20 (2H, d, J= 7.1 Hz, H-2",6"), 7.22-7.34 (3 arom H, m), 7.41 (2H, dd, J=7.0; 3.5 Hz, H-2$^+$,6$^+$), 7.42-7.50 (3 arom H, m), 7.70-7.86 (3 arom H, m), 8.35 (1H, d, J=7.5 Hz, H-5); ^{13}C nmr: δ 64.2 (C-3), 66.2 (C-2), 68.3 (C-3'), 188.6 (C-4); ms (TSP): m/z 377 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{16}O_4S$: C, 70.21; H, 4.28. Found: C, 70.18; H, 4.29.

trans,trans-(±)-2,3'-Diphenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,trans*-**3a**).

This substance was obtained as white needles in 71% yield, mp 209-210°; ^{1}H nmr: δ 4.40 (1H, s, H-2), 5.05 (1H, s, H-3'), 6.62 (2H, d, J= 7.5 Hz, H-2",6"), 6.98 (2H, t, J= 7.5 Hz, H-3",5"), 7.01-7.12 (5 arom H, m), 7.15 (1H, t, J= 7.0 Hz, H-4$^+$), 7.75-7.86 (3 arom H, m), 8.27 (1H, d, J=7.3 Hz, H-5); ^{13}C nmr: δ 62.9 (C-3'), 63.7 (C-3), 68.5 (C-2), 188.0 (C-4); ms (TSP): m/z 377 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{16}O_4S$: C, 70.21; H, 4.28. Found: C, 70.24; H, 4.26.

trans,cis-(±)-3'-(4-Methylphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,cis*-**3b**).

This compound was prepared as white needles in 80% yield, mp 234-235°; ^{1}H nmr: δ 2.42 (3H, s, Me), 4.47 (1H, s, H-2), 4.75 (1H, s, H-3'), 7.19 (2H, d, J= 6.9 Hz, H-2",6"), 7.25-7.35 (7 arom H, m), 7.73-7.85 (3 arom H, m), 8.35 (1H, d, J=7.3 Hz, H-5); ^{13}C nmr: δ 64.4 (C-3), 66.2 (C-2), 68.5 (C-3'), 188.7 (C-4); ms (TSP): m/z 391 (M+H)$^+$.

Anal. Calcd. for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.64. found C, 70.73; H, 4.62.

trans,trans-(±)-3'-(4-Methylphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,trans*-**3b**).

This compound was isolated as white needles in 77% yield, mp 198-199°; ^{1}H nmr: δ 2.23 (3H, s, Me), 4.40 (1H, s, H-2), 5.01 (1H, s, H-3'), 6.64 (2H, d, J= 7.8 Hz, H-2",6"), 6.80-7.00 (6 arom H, m), 7.10 (1H, t, J= 7.6 Hz, H-4"), 7.75-7.86 (3 arom H, m), 8.25 (1H, d, J= 7.6 Hz, H-5); ^{13}C nmr: δ 63.0 (C-3'), 63.8 (C-3), 68.4 (C-2), 188.1 (C-4); ms (TSP): m/z 391 (M+H)$^+$.

Anal. Calcd. for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.64. Found: C, 70.79; H, 4.66.

trans,cis-(±)-3'-(2-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,cis*-**3c**).

This compound was obtained as white plates in 85% yield, mp 189-190°; ^{1}H nmr: δ 3.85 (3H, s, Me), 4.47 (1H, s, H-2), 4.98 (1H, s, H-3'), 6.91-7.02 (2 arom H, m), 7.08 (1H, d, J= 7.3 Hz, H-6$^+$), 7.19 (2H, d, J= 6.9 Hz, H-2",6"), 7.22-7.30 (3 arom H, m), 7.42 (1H, t, J= 7.9 Hz, H-4$^+$), 7.70-7.78 (2 arom H, m), 7.83 (1H, d, J= 7.4 Hz, H-8), 8.35 (1H, d, J=7.2 Hz, H-5); ^{13}C nmr: δ 64.2 (C-3), 66.0 (C-3'), 66.4 (C-2), 188.7 (C-4); ms (TSP): m/z 407 (M+H)$^+$.

Anal. Calcd. for $C_{23}H_{18}O_5S$: C, 67.97; H, 4.46. Found: C, 68.01; H, 4.45.

trans,trans-(±)-3'-(2-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,trans*-**3c**).

This substance was prepared as white plates in 90% yield, mp 226-227°; ^{1}H nmr: δ 3.32 (3H, s, Me), 4.34 (1H, s, H-2), 5.11 (1H, s, H-3'), 6.31 (1H, d, J= 8.3 Hz, H-3$^+$), 6.61 (2H, d, J= 7.6 Hz, H-2",6"), 6.84-6.98 (3 arom H, m), 7.02-7.16 (2 arom H, m), 7.35 (1H, d, J= 7.4 Hz, H-6$^+$), 7.76 (1H, t, J= 7.4 Hz, H-7), 7.78-7.85 (2 arom H, m), 8.27 (1H, d, J=7.5 Hz, H-5); ^{13}C nmr: δ 60.9 (C-3'), 63.6 (C-3), 69.0 (C-2), 188.2 (C-4); ms (TSP): m/z 407 (M+H)$^+$.

Anal. Calcd. for $C_{23}H_{18}O_5S$: C, 67.97; H, 4.46. Found: C, 67.94; H, 4.43.

trans,cis-(±)-3'-(4-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,cis*-**3d**).

This compound was isolated as white plates in 74% yield, mp 173-174°; ^{1}H nmr: δ 3.87 (3H, s, Me), 4.45 (1H, s, H-2), 4.73 (1H, s, H-3'), 6.99 (2H, d, J= 8.7 Hz, H-3$^+$,5$^+$), 7.19 (2H, d, J= 7.5 Hz, H-2",6"), 7.26-7.36 (5 arom H, m), 7.72-7.85 (3 arom H, m), 8.34 (1H, d, J=7.2 Hz, H-5); ^{13}C nmr: δ 64.7 (C-3), 66.5 (C-2), 68.7 (C-3'), 188.9 (C-4); ms (TSP): m/z 407 (M+H)$^+$.

Anal. Calcd. for $C_{23}H_{18}O_5S$: C, 67.97; H, 4.46. Found: C, 67.93; H, 4.48.

trans,trans-(±)-3'-(4-Methoxyphenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans,trans*-**3d**).

This substance was prepared as white plates in 84% yield, mp 170-171°; ^{1}H nmr: δ 3.71 (3H, s, Me), 4.38 (1H, s, H-2), 4.99 (1H, s, H-3'), 6.58-6.70 (4 arom H, m), 6.91-7.03 (4 arom H, m), 7.10 (1H, t, J= 7.4 Hz, H-4") 7.72-7.86 (3 arom H, m), 8.25 (1H, d, J= 7.5 Hz, H-5); ^{13}C nmr: δ 63.1 (C-3'), 64.0 (C-3), 68.6 (C-2), 188.2 (C-4); ms (TSP): m/z 407 (M+H)$^+$.

Anal. Calcd. for $C_{23}H_{18}O_5S$: C, 67.97; H, 4.46. Found: C, 68.02; H, 4.44.

trans,*cis*-(±)-3'-(4-Fluorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans*,*cis*-**3e**).

This compound was prepared as white plates in 86% yield, mp 244-245°; ^{1}H nmr: δ 4.37 (1H, s, H-2), 4.74 (1H, s, H-3'), 7.10-7.21 (4 arom H, m), 7.22-7.30 (3 arom H, m), 7.40 (2H, dd, J= 8.5, 5.2 Hz, H-2$^+$,6$^+$), 7.73-7.89 (3 arom H, m), 8.34 (1H, d, J= 6.9 Hz, H-5); ^{13}C nmr: δ 64.3 (C-3), 66.3 (C-2), 67.7 (C-3'), 188.4 (C-4); ms (TSP): m/z 395 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{15}FO_4S$: C, 67.01; H, 3.83. Found: C, 67.04; H, 3.81.

trans,*trans*-(±)-3'-(4-Fluorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans*,*trans*-**3e**).

This substance was obtained as white plates in 84% yield, mp 242-243°; ^{1}H nmr: δ 4.34 (1H, s, H-2), 5.01 (1H, s, H-3'), 6.64 (2H, d, J= 7.8 Hz, H-2",6"), 6.80 (2H, t, J= 8.5 Hz, H-3$^+$,5$^+$), 6.91-7.05 (4 arom H, m), 7.12 (1H, t, J= 7.6 Hz, H-4"), 7.71-7.86 (3 arom H, m), 8.26 (1H, d, J=7.5 Hz, H-5); ^{13}C nmr: δ 62.4 (C-3'), 63.7 (C-3), 68.5 (C-2), 187.8 (C-4); ms (TSP): m/z 395 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{15}FO_4S$: C, 67.01; H, 3.83. Found: 66.98; H, 3.85.

trans,*cis*-(±)-3'-(2-Chlorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans*,*cis*-**3f**).

This compound was isolated as white needles in 72% yield, mp 172-173°; ^{1}H nmr: δ 4.46 (1H, s, H-2), 4.99 (1H, s, H-3'), 7.16 (1H, d, J= 7.9 Hz, H-6$^+$), 7.19 (2H, d, J= 7.3 Hz, H-2",6") 7.26-7.32 (5 arom H, m), 7.40 (1H, t, 7.9 Hz, H-4$^+$), 7.51 (1H, d, J= 7.6 Hz, H-3$^+$), 7.76-7.80 (2 arom H, m), 7. 85 (1H, d, J= 7.1 Hz, H-8), 8.35 (1H, d, J=7.2 Hz, H-5); ^{13}C nmr: δ 64.2 (C-3), 66.3 (C-2), 66.5 (C-3'), 188.1 (C-4); ms (TSP): m/z 411 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{15}ClO_4S$: C, 64.32; H, 3.68. Found: C, 64.29; H, 3.70.

trans,*trans*-(±)-3'-(2-Chlorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2'-oxiran]-4-one 1,1-Dioxide (*trans*,*trans*-**3f**).

This substance was prepared as white plates in 77% yield, mp 251-252°; ^{1}H nmr: δ 4.36 (1H, s, H-2), 5.12 (1H, s, H-3'), 6.60 (2H, d, J= 7.4 Hz, H-2",6"), 6.92 (1H, d, J= 7.7 Hz, H-3$^+$) 6.98 (2H, d, J= 7.3, H-3",5"), 7.03-7.19 (2 arom H, m), 7.28 (1H, t, J= 7.4 Hz, H-5$^+$), 7.48 (1H, d, J= 7.5 Hz, H-6$^+$), 7.72-7.89 (3 arom H, m), 8.29 (1H, d, J=7.5 Hz, H-5); ^{13}C nmr: δ 61.4 (C-3'), 63.7 (C-3), 69.0 (C-2), 187.3 (C-4); ms (TSP): m/z 411 (M+H)$^+$.

Anal. Calcd. for $C_{22}H_{15}ClO_4S$: C, 64.32; H, 3.68. Found: C, 64.35; H, 3.66.

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REFERENCES AND NOTES

[1] R. Doherty, D. D. Keane, K. G. Marathe, W. I. O'Sullivan, E. M. Philbin, R. M. Simons and P. C. Teague, *Tetrahedron Lett.*, 441 (1968).

[2] D. D. Keane, K. G. Marathe, W. I. O'Sullivan, E. M. Philbin, R. M. Simons and P.C. Teague, *J. Org. Chem.*, **35**, 2286 (1970).

[3] D. D. Keane, W. I. O'Sullivan, E. M. Philbin, R. M. Simons and P. C. Teague, *Tetrahedron*, **26**, 2533 (1970).

[4] D. D. Keane, W. I. O'Sullivan, E. M. Philbin, R. M. Simons and P. C. Teague, *Tetrahedron*, **27**, 3535 (1971).

[5] A. Lévai and E. H. Hetey, *Pharmazie*, **33**, 378 (1978).

[6] D. D. Dhavale, P. Joshi and K. G. Marathe, *J. Chem. Soc., Perkin Trans. 2*, 449 (1987).

[7] A. Lévai and Z. Szabó, *Pharmazie*, **47**, 56 (1992).

[8] G. Tóth, A. Lévai and Á. Szöllősy, *Liebigs Ann. Chem.*, 803 (1992).

[9] A. Lévai and Z. Szabó, *J. Chem. Research (S)*, 380 (1992).

[10]G. Tóth, A. Lévai, Á. Szöllősy and H. Duddeck, *Tetrahedron*, **49**, 863 (1993).

[11] C. Nemes, A. Lévai, T. Patonay, G. Tóth, S. Boros, J. Halász, W. Adam and D. Golsch, *J. Org. Chem.*, **59**, 900 (1994).

[12] A. Lévai and G. Tóth, *Trends Heterocyclic Chem.*, **4**, 89 (1995).

[13] A. Lévai, *Heterocyclic Commun.*, **3**, 211 (1997).

[14] A. Lévai, *Heterocyclic Commun.*, **5**, 151 (1999).

[15] K. Auwers and F. Arndt, *Ber. Dtsch. Chem. Ges.*, **42**, 2706 (1909).

[16] F. Arndt, W. Fleming, E. Scholz and V. Löwesohn, *Ber. Dtsch. Chem. Ges.*, **56**, 1269 (1923).

[17] J. J. Biernes and W. I. O'Sullivan, *Proc. Roy. Irish Acad.*, **77B**, 331 (1977).

[18] A. Lévai, Á. Szöllősy and G. Tóth, *Acta Chim. Hung.*, **128**, 359 (1991).

[19] G. Tóth, Á. Szöllősy, A. Lévai, G. Oszbach, W. Dietrich and H. Kühne, *Magn. Reson Chem.*, **29**, 801 (1991).

[20] G. Tóth, J. Halász, A. Lévai, C. Nemes and T. Patonay, *J. Chem. Soc., Perkin Trans. 2*, 547 (1996).

[21] A. Lévai and Z. Szabó, *Bull. Soc. Chim. Fr.*, **128**, 976 (1991).

[22] A. Lévai, A. M. S. Silva, T. Patonay and J. A. S. Cavaleiro, *J. Heterocyclic Chem.*, **36**, 1215 (1999).

[23] A. Lévai, *Org. Prep. Proced. Int.*, **34**, 415 (2002).

[24] W. Adam, D. Golsch, L. Hadjiarapoglou, A. Lévai, C. Nemes and T. Patonay, *Tetrahedron*, **50**, 13113 (1994).

[25] A. Lévai, G. Tóth, J. Kovács, T. Patonay and E. B. Vass, *Monatsh. Chem.*, **132**, 707 (2001).

[26] G. Tóth, J. Kovács, A. Lévai, E. Kleinpeter and A. Koch, *Magn. Reson. Chem.*, **39**, 251 (2001).

[27] T. Patonay, W. Adam, A. Lévai, P. Kövér, M. Németh, E. M. Peters and K. Peters, *J. Org. Chem.*, **66**, 2275 (2001).

[28] T. Patonay, W. Adam, J. Jekő, K. E. Kövér, A. Lévai, M. Németh and K. Peters, *Heterocycles*, **51**, 85 (1999).

[29] W. Adam, J. Bialas and L. Hadjiarapoglou, *Chem. Ber.*, **124**, 2377 (1991).