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Oxidation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin

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ABSTRACT: *1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin (**3**), synthesized from 1,2-bis(phenylmethyl) benzene (**1**), was subjected to oxidation to give 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4**) as a mixture of diastereomers separable by column chromatography. (1R*,2R*,4S*)-1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4-meso-1**) was obtained preferentially from (1R*,4S*)-1,4-dihydro-1,4-diphenyl-2,3-benzodithiin (**3-meso**) with m-chloroperbenzoic acid (m-CPBA). The **4-meso-1** stereoisomer afforded an unexpected product 1,3-diphenylbenzo[c]thiophene (**5**) upon further oxidation with mCPBA. On the other hand, oxidation of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxides (4-dl and 4-meso), with Oxone gave 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxide (**7**).* © 2001 John Wiley & Sons, Inc. Heteroatom Chem12:209–216, 2001

INTRODUCTION

In our continued investigation of the chemical behavior of benzopolysulfides [1–5], for example, benzopentathiepins [6–11], benzotrithioles [12–19], and the related compounds [20–22], we have found an important cycloaddition of 1,4-dihydro-2,3-benzodithiin to alkenes in the presence of a Lewis acid to give interesting macrocyclic tetrathiaethers via an episulfonium intermediate [23]. On the other hand, recent interest of several chemists has focused on the biological behavior of the benzodithiins showing anti-viral activity [24,25]. Here, our further interest is directed to the reactivity of 1,4-dihydro-2,3-benzodithiin having bulky substituents at the 1 and 4 positions. To our knowledge, there has been no report of the synthesis and reactions of 1,4-dihydro-1,4-diphenyl-2,3-dithiin (**3**). In this article, we report the synthesis and chemical behavior of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin (**3**) with respect to oxidation.

RESULTS AND DISCUSSION

*Synthesis and Structure of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin (**3**)*

A new compound, 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin (**3**), was synthesized in 58% yield from 1,2-bis(phenylmethyl)benzene (**1**) as the starting compound (Scheme 1). Thus, treatment of **1** with *n*-butyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), followed by treatment with elemental sulfur, gave the dithiol, 1,2-bis(mercaptophenylmethyl)benzene (**2**). Oxidative cyclization of the dithiol **2** with iodine in the presence of triethylamine, in situ, gave the desired benzodithiin **3** consisting of two diastereomers (Scheme

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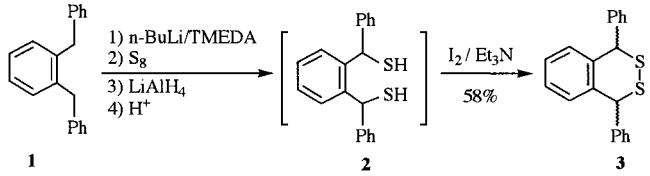


SCHEME 1

1). One of the two isomers was determined by X-ray crystallography to be the meso isomer, **3-meso** (1*R**,4*S**), as shown in Figure 1. Accordingly, the other one was the **3-dl** (1*R**,1*S**) isomer. Here, the ratio of **3-dl** and **3-meso** isomers obtained was estimated to be 1:4 by ^{1}H NMR spectroscopy; thus, this synthetic method gave the **3-meso** isomer preferentially. These two isomers were separated by column chromatography, and the structures of the products were confirmed spectroscopically. By X-ray crystallography, the structure of the dithiin **3-meso** was shown to have a twist-boat form, with 2.026 Å for the S–S bond length and −66.4° for the torsional angle of C1–S1–S2–C2. Other selected data for the bond lengths and angles are listed in Table 1.

*Oxidation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin (**3**)*

The oxidation of a disulfide bond is very important in the field of the chemistry of natural products containing this group and having biological activity [26]. Previously, the oxidation of 1,4-dihydro-2,3-benzodithiin with one equivalent of *m*-CPBA had been reported to give 1,4-dihydro-2,3-benzodithiin 2-oxide as the sole product, and 1,4-dihydro-2,3-benzodithiin 2,2-dioxide was obtained when two equimolar amounts of *m*-CPBA were used [27,28]. In order to characterize the behavior of each 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin **3-dl** and **3-meso**, we studied the oxidation with *m*-CPBA and related oxidants. Here, the formation of two sets of isomers (1*R**,2*R**,4*R**)- and (1*R**,2*S**,4*R**)-1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4-dl-1** and **4-dl-2**), and (1*R**,2*R**,4*S**) and (1*R**,2*S**,4*S**)-1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4-meso-1** and **4-meso-2**) are presumed to be formed by the oxidation of the two dithiin isomers **3-dl** and **3-meso**, respectively, as shown in Scheme 2. When an equimolar amount of *m*-CPBA was used for the oxidation of **3-dl**, a mixture of **4a** and **4b** containing two diastereomers, (1*R**,2*R**,4*R**)- and (1*R**,2*S**,4*R**)-1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4-dl-1** or **4-dl-2**) was obtained in a total 99% yield. The ratio of **4a** to **4b** was found to be 1:1.2 by the measurement of ^{1}H NMR. Unfortunately, we have so far failed to determine whether the structure of the products is **4-dl-1** or **4-dl-2**. On the other hand, oxidation of the **3-meso** isomer with an equimolar amount of *m*-CPBA gave only one orientation, (1*R**,2*R**,4*S**)-1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4-meso-1**), obtained in 93% yield as the sole product (Scheme 3). After purification of the product, the structure of **4-meso-1** was determined by X-ray crystallography (Figure 2). The crystal structure of **4-meso-1** corresponded to a boat form. The bond length for S1–S2 was 2.085 Å, and the torsional angles for C1–S1–S2–C2 and O1–S1–C1–C9 were −66.4° and −76.5°, respectively (Table 2). In order to examine the role of the oxidant in the

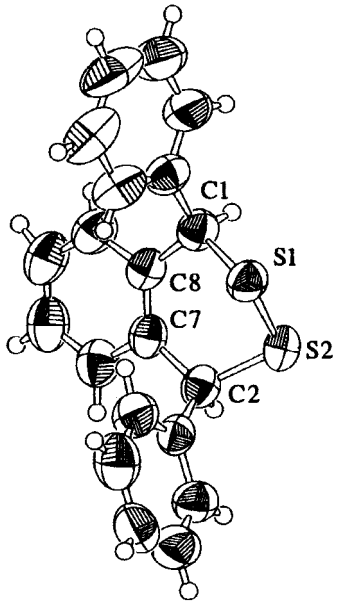
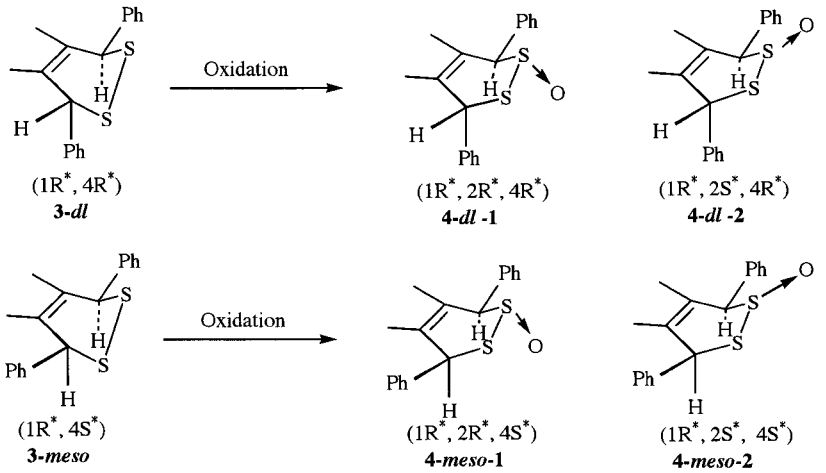


FIGURE 1 ORTEP view of dithiin **3-meso** (1*R**, 4*S**).

TABLE 1 Crystal Data of (1*R**, 4*S**)-1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin (**3-*meso***)

Crystal System	Monoclinic	V/Å$_3$	1640.6(6)
Space Group	$P2_1/c$	Z	4
a/Å	12.689(2)	Dc/g cm^{-3}	1.297
b/Å	8.080(3)	μ(CuKα)/cm^{-1}	28.63
c/Å	16.942(3)	R	0.049
β/°	109.18(2)	Rw	0.071

Bond Length (Å)		Bond Angles (°)	
S1–S2	2.026(1)	S2–S1–C1	97.8(1)
S1–C1	1.828(3)	S1–S2–C2	98.4(1)
S2–C2	1.817(4)	S1–C1–C8	113.6(2)
C1–C8	1.527(5)	S2–C2–C7	113.1(3)
C2–C7	1.523(5)		
C7–C8	1.390(5)	Torsional Angle (°)	
		C1–S1–S2–C2	−66.4(2)



SCHEME 2

reactivity, both an electrophilic oxidant, H_2O_2 in AcOH, and nucleophilic oxidant, $NaIO_4$ in EtOH-H_2O, were used and found to give only **4-meso-1** in high yields, 91 and 73%, respectively, as shown in Scheme 3. Based on these results, the preferential formation of the dithiin 2-oxide **4-meso-1** from the dithiin **3-meso** isomer is interpreted in accordance with the steric effect of the substituents. Thus, the oxidant approaches the sulfur atom of the disulfide bond so as to avoid the repulsion of three benzene rings, to give the oxidation product **4-meso-1**, as shown in Figure 3.

Oxidation of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide **4-dl** *and* **4-meso**

When 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxides **4-dl** and **4-meso** were treated with an equimolar amount of *m*-CPBA in CH_2Cl_2, an interesting ring contraction was observed. Thus, 1,3-diphenylbenzo[*c*]thiophene (**5**) was obtained in yields of 41 and 48%, from **4-dl** and **4-meso**, respectively, as shown in Scheme 4. Since the similar yields were observed in the reactions of both **4-dl** and **4-meso**, it seems that the oxidation is not dependent on the stereochemistry. Interestingly, oxidation of **4-meso** with H_2O_2 in AcOH also afforded 1,3-dihydro-1,3-diphenylbenzo-[*c*]thiophene **6** but only in 22% yield (Scheme 4). However, we obtained a different result in oxidation of dithiin 2-oxides **4-dl** and **4-meso** with Oxone; thus, the corresponding 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxides (**7-dl** and **7-meso**) were obtained in 45 and 66% yields, respectively, as shown in Scheme 5. There are many reports in the literature of the formation of thiolsulfonates from thiolsulfinates by oxidation of the neighboring sulfur atom of the sulfinyl group via an α-disulfoxide

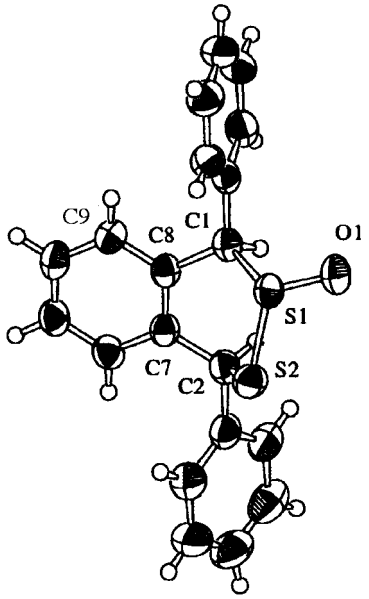


FIGURE 2 ORTEP view of benzodithiin oxide **4-meso-1** (1*R**, 2*R**, 4*S**).

[29–45]. Also, in our reaction, it seems that the oxidation proceeds to form the α-disulfoxide, benzodithiin 2,2-dioxide **7**.

Reaction Pathway

In order to clarify the formation of benzothiophene **5** from benzodithiin 2-oxide **4** by the action of *m*-CPBA, two fundamentally different reactions of dihydrobenzothiophene **6** were examined. Thus, the treatment of dihydrobenzothiophene **6** with two equimolar amounts of *t*-BuOK in tetrahydrofuran (THF) afforded 1,3-diphenylbenzo[*c*]thiophene **5** in

TABLE 2 Crystal Data of (1*R**, 2*R**, 4*S**)-1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4-*meso*-1**)

Crystal System	Monoclinic	V/Å$_3$	1656.0(4)
Space Group	$P2_1/a$	Z	4
a/Å	7.971(2)	Dc/g cm^{-3}	1.349
b/Å	19.276(2)	μ(CuKα)/cm^{-1}	29.10
c/Å	10.785(2)	R	0.038
β/°	92.18(2)	Rw	0.059

Bond Lengths (Å)		Bond Angles (°)	
S1–S2	2.085(1)	S2–S1–C1	98.48(8)
S1–O1	1.481(2)	S1–S2–C2	103.43(9)
S1–C1	1.873(3)	S1–C1–C8	115.9(2)
S2–C2	1.862(3)	S2–C2–C7	107.5(2)
C1–C8	1.509(3)		
C2–C7	1.505(4)	Torsional Angles (°)	
C7–C8	1.403(4)	C1–S1–S2–C2	−66.4(2)
		O1–S1–C1–C9	−76.5(2)

29% yield. This result suggests that it is possible to form benzothiophene **5** from dihydrobenzothiophene **6** by a reaction sequence that does not involve an oxidizing agent. However, the treatment of **6** with an equimolar amount of *m*-CPBA afforded 1,3-dihydro-1,3-diphenylbenzo[*c*]thiophene 2-oxide **8**, not benzothiophene **5**, in 58% yield (Scheme 6). This result implies that the dihydrobenzothiophene **6** is not an intermediate in the formation of benzothiophene **5**. On the other hand, in the case of the oxidation of **4-meso** with H_2O_2 in AcOH, it is conceivable that dihydrobenzothiophene **6** is formed directly by desulfonylation of benzodithiin 2,2-dioxide **7** with ring contraction. Accordingly, a plausible reaction pathway for the formation of benzothiophene **5** and dihydrobenzothiophene **6** is interpreted as follows (Scheme 7). The oxidation of benzodithiin 2-oxide **4** with *m*-CPBA affords initially the disulfenic acid **A**. The intermediate **A** is converted to dithiin 2-oxide **B**, and then **B** gives benzothiophene **5** by desulfinylation. The oxidation of benzodithiin 2-oxide **4** with H_2O_2 in AcOH affords sulfurane intermediate **C**, and following ligand coupling, gives dihydrobenzothiophene **6** [46–48]. In yet another type of oxidation reaction, the treatment of benzodithiin 2-oxide **4** with Oxone gave α-disulfoxide **D**, which rearranges to benzodithiin 2,2-dioxide **7** [29–45].

CONCLUSION

New 1,4-dihydro-1,4-diphenylbenzodithiin **3** having bulky substituents at the 1 and 4 position was synthesized and characterized by oxidation with various oxidants. The benzodithiin 2-oxide **4** obtained by oxidation of dithiin **3** gave interesting products, benzothiophene **5** and dihydrobenzothiophene **6**, on further oxidation. On the other hand, the oxidation with Oxone afforded benzodithiin 2,2-dioxide **7**.

EXPERIMENTAL

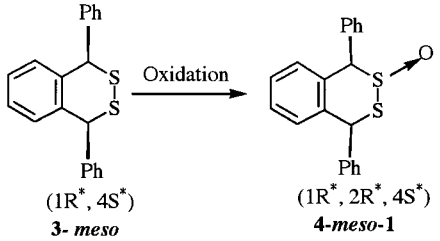
All melting points were determined on the Mel-Temp apparatus and were uncorrected. Elemental analyses were performed by use of the Yanagimoto MT-3 Analyzer. IR spectra were recorded as KBr pellets on a JASCO FT-7300 unit. The ^{1}H and ^{13}C NMR spectra were taken on Hitachi R-1500 and Bruker AC-400P instruments. Mass spectra (EI) were recorded on a Hitachi M-2000 instrument at 70 eV.

*Preparation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin (**3**)*

n-Buthyllithium in hexane (2.5 equiv.) and TMEDA (2.8 mL, 2.5 equiv.) were added to a solution of 1,2-bis(phenylmethyl)benzene (**1**) (1935 mg, 7.5 mmol) in hexane (80 mL) and then the reddish mixture obtained was stirred for 6 hours at room temperature. After addition of elemental sulfur (720 mg, 22.5 mg atom), the mixture obtained by evaporation of the solvent was treated with $LiAlH_4$ (724 mg) and stirred in THF (150 mL) for 2.5 hours at room temperature. The solution was treated with ice water (100 mL) and acidified (ca. pH 1) with conc. HCl aq.. To the solution obtained by extraction with $CHCl_3$ (150 mL), iodine (509 mg) and triethylamine (0.3 mL) in $CHCl_3$ (200 mL) were added slowly, and the mixture was stirred for 15 hours at room temperature. After the usual workup, the mixture was purified by chromatography on silica gel. The diastereomers, (1*R**,4*R**)- and (1*R**,4*S**)-1,4-dihydro-1,4-diphenyl-2,3-benzodithiin((**3-dl** and **3-meso**) were separated by preparative chromatography.

(1R,4R*)-1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin(**3-dl**).* Colorless crystals; m.p. 135.0–136.0°C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 2H, CH), 7.01 (dd, 2H, J = 3.5, 2.3 Hz, ArH), 7.14 (dd, 2H, J = 3.5, 2.3 Hz, ArH), 7.23–7.34 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.7, 127.0, 127.3, 128.2, 129.0, 131.3, 136.2, 143.0. IR (KBr) ν 3052, 3021, 2364, 1488, 752, 714 (cm^{-1}). MS *m/z* 320 (M^+). Anal. Calcd for $C_{20}H_{16}S_2$: C, 74.95; H, 5.03%. Found: C, 74.68; H, 5.01%.

(1R,4S*)-1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin (**3-meso**).* Colorless crystals; m.p. 113.0–113.5°C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (s, 2H, CH), 6.97 (dd, 2H, J = 3.5, 2.5 Hz, ArH), 7.10



Reagent	Yield (%)
m-CPBA (1 eq.)/ CH_2Cl_2, rt, 1 h,	93
H_2O_2(1eq.)/AcOH, rt, 27 h,	91
$NaIO_4$(1eq.)•EtOH-H_2O, 80 °C, 1 h,	73

SCHEME 3

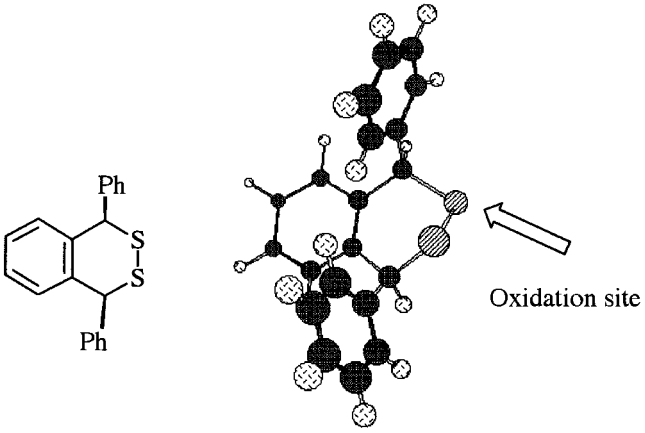
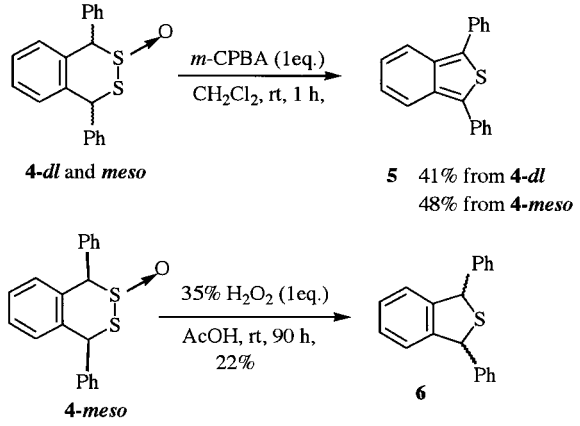
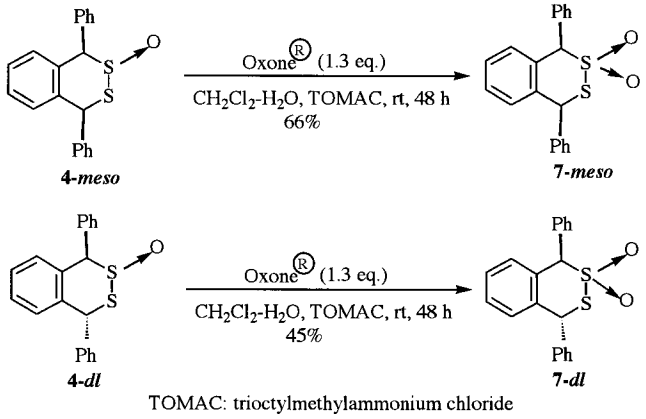


FIGURE 3 Oxidation Site of (1*R**, 4*S**)-1,4-dihydro-1,4-diphenyl-2,3-benzodithiin (**3-meso**).



SCHEME 4



SCHEME 5

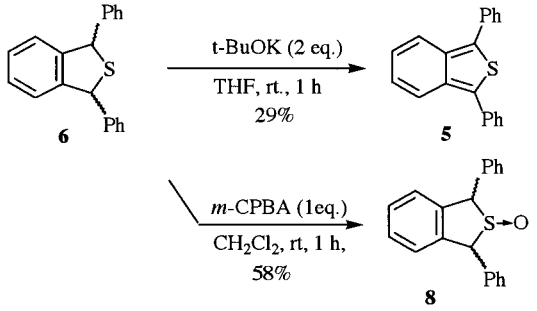
(dd, 2H, J = 3.5, 2.5 Hz, ArH), 7.27–7.28 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.0, 126.9, 127.6, 128.4, 129.3, 131.1, 136.6, 142.1. IR (KBr) ν 3056, 3023, 2363, 1486, 1451, 741, 697 (cm^{-1}). MS *m/z* 320 (M^+). Anal. Calcd for $C_{20}H_{16}S_2$: C, 74.95; H, 5.03%. Found: C, 75.17; H, 4.84%.

*Oxidation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin (**3**)*

To a solution of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin (**3**) (49 mg, 0.15 mmol) in CH_2Cl_2 (5 mL), *m*-CPBA (27 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added dropwise, and the mixture was stirred for 1 hour at 0°C. The mixture obtained by the usual workup was purified by silica gel chromatography to give a mixture containing two diastereomers of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxides (**4-dl** and **4-meso**). Each isomer was isolated in pure form by preparative chromatography. The oxidation of benzodithiin **3** with other oxidants, H_2O_2 and $NaIO_4$, was carried out in the same manner.

*1,4-Dihydo-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4a**).* Colorless crystals; m.p. 163°C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (s, 1H, CH), 6.04 (s, 1H, CH), 7.04–7.47 (m, 14H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.5, 75.1, 127.6, 128.2, 128.4, 128.5, 128.6, 128.9, 128.99, 129.04, 129.3, 130.3, 133.1, 134.1, 137.3, 137.8. IR (KBr) ν 3061, 1493, 1445, 1085 (SO), 702, 469, 446 (cm^{-1}). MS *m/z* 286 (M^+ – 50). Anal. Calcd for $C_{20}H_{16}S_2O$: C, 71.39; H, 4.79%. Found: C, 71.45; H, 5.01%.

1,4-Dihydo-1,4-diphenyl-2,3-benzodithiin 2-oxide



SCHEME 6

*(***4b***)*. Colorless crystals; m.p. 149.0°C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (s, 1H, CH), 6.17 (s, 1H, CH), 7.18–7.45 (m, 14H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.2, 70.9, 127.9, 128.1, 128.5, 128.8, 128.87, 128.92, 129.03, 129.4, 129.9, 130.7, 131.4, 134.8, 135.4, 139.7. IR (KBr) ν 3064, 1489, 1452, 1086 (SO), 702, 472, 439 (cm^{-1}). MS *m/z* 286 ($M^+ - 50$). Anal. Calcd for $C_{20}H_{16}S_2O$: C, 71.39; H, 4.79%. Found: C, 71.43; H, 4.93%.

(1R, 2R*, 4S*)-1,4-Dihydro-1, 4-diphenyl-2, 3-benzodithiin 2-oxide (***4-meso-1***)*. (73% yield); colorless plates; m.p. 145.0°C (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1H, CH), 5.85 (s, 1H, CH), 6.95–6.97 (m, 1H, ArH), 7.05 (m, 1H, ArH), 7.19–7.22 (m, 2H, ArH), 7.40–7.49 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.3, 75.1, 127.2, 127.6, 127.8, 128.75, 128.83, 129.0, 129.2, 129.8, 130.9, 131.0, 131.8, 134.6, 136.5, 139.5. IR (KBr) ν 3062, 3029, 1495, 1453, 1059 (SO), 776, 739, 700, 467 (cm^{-1}). MS *m/z* 320($M^+ - 16$). Anal. Calcd for $C_{20}H_{16}S_2O$: C, 71.39; H, 4.79%. Found: C, 71.40; H, 4.62%.

*Oxidation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (***4***) with m-CPBA*

To a solution of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4**) (34 mg, 0.1 mmol) in CH_2Cl_2 (3 mL), *m*-CPBA (19 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was added dropwise, and the solution was stirred for 1 hour at room temperature. After the usual workup, the mixture obtained was purified by silica gel chromatography, to give 1,3-diphenylbenzo[*c*]thiophene (**5**) (48% from **4-meso** and 41% from **4-dl**).

*1,3-Diphenylbenzo[c]thiophene (***5***)*. Yellow crystals, m.p. 119.0°C (hexane)(lit. 118°C) [49]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 and 7.84 (AA′BB′, J = 3.0, 6.9 Hz, 4H, ArH), 7.38 (t, J = 7.5 Hz, 2H, ArH), 7.50 (t, J = 7.5 Hz, 4H, ArH), 7.69 (t, J = 7.5 Hz, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.1, 124.2, 127.5, 129.0, 129.2, 134.2, 134.3, 135.2. IR (KBr) ν 3060, 1596, 1508, 1481, 1443, 1262, 1194, 1081, 1032, 760, 744, 693, 579, 421 (cm^{-1}). MS *m/z* 286 (M^+). Anal. Calcd for $C_{20}H_{14}S$: C, 83.87; H, 4.93%. Found: C, 83.93%; H, 4.88%.

*Oxidation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (***4-meso***) with H_2O_2*

To a solution of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide (**4-meso**) (100 mg, 0.3 mmol) in AcOH (10 mL), 35% H_2O_2 (0.02 mL, 0.3 mmol) was added dropwise and the mixture was stirred for 90 hours at room temperature. After the usual workup, the mixture obtained was purified by silica gel chromatography to give a mixture of two diastereomers of 1,3-dihydro-1,3-diphenylbenzo[*c*]thiophene (**6a** and **6b**) (19 mg, 22%) as an oily matter. This product contains two isomers, **6a** and **6b**, and each isomer was not isolated in completely pure form by chromatography.

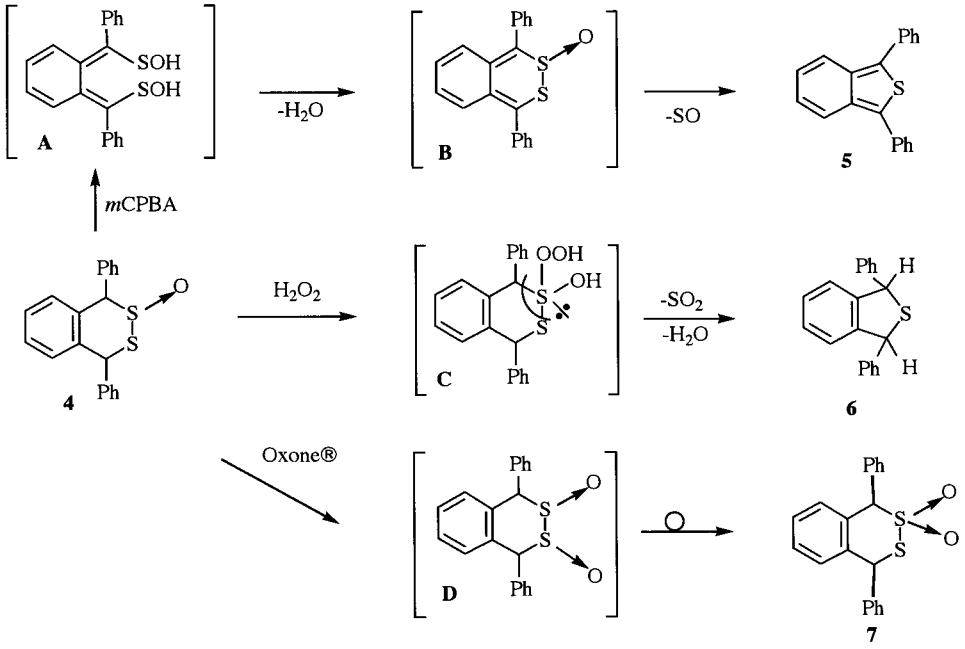
Diastereomer **6a**. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (s, 2H, CH), 6.94 and 7.19 (AA′BB′, J = 3.3, 5.7 Hz, 4H, ArH), 7.28–7.31 (m, 2H, ArH), 7.33–7.37 (m, 4H, ArH) 7.41–7.44 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.4, 125.5, 127.3, 127.6, 128.6, 129.0, 142.9, 144.5. IR (neat) ν 3062, 3027, 2884, 1596, 1483, 1452, 1073, 1030, 740, 697, 639, 592, 497, 436 (cm^{-1}). MS *m/z* 288 (M^+).

Diastereomer **6b**. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (s, 2H, CH), 7.03 and 7.20 (AA′BB′, J = 3.2, 5.7 Hz, 4H, ArH), 7.23–7.34 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.6, 125.5, 127.4, 127.5, 128.2, 128.7, 143.9, 144.2.

Oxidation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide **4-dl** *with Oxone*

To a solution of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide **4-dl** (108 mg, 0.32 mmol) and trioctylmethylammonium chloride (TOMAC) (catalytic amounts) in CH_2Cl_2 (12 mL), a solution of Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (518 mg, 0.417 mmol) in water (6 mL) was added dropwise. The solution was stirred for 48 hours at room temperature. After the usual workup, the mixture obtained was purified by silica gel chromatography to give 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxide **7-dl** (60 mg, 53%).

1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxide **7-dl**. Colorless crystals, m.p. 135°C (de-



SCHEME 7

comp.) ($CHCl_3$/hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 1H, CH), 6.25 (s, 1H, CH), 6.90–6.94 (m, 4H, ArH), 7.16–7.21 (m, 6H, ArH), 7.37–7.47 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.5, 77.5, 127.8, 128.0, 128.85, 128.94, 129.4, 129.5, 129.6, 129.7, 131.0, 131.4, 132.0, 134.8, 135.6, 138.3. IR (KBr) ν 3061, 2909, 1491, 1454, 1328 (SO_2), 1134 (SO_2), 732, 698, 625, 570 (cm^{-1}). MS *m/z* 288 ($M^+ - 64$). Anal. Calcd for $C_{20}H_{16}O_2S_2$: C, 68.15; H, 4.58%. Found: C, 68.46; H, 4.91%.

Oxidation of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide **4-meso** *with Oxone*

To a solution of 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2-oxide **4-meso** (50 mg, 0.15 mmol) and TOMAC (catalytic amount) in CH_2Cl_2 (6 ml), a solution of Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (242 mg, 0.195 mmol) in water (6 mL) was added dropwise. The solution was stirred for 48 hours at room temperature. After the usual workup, the mixture obtained was purified by silica gel chromatography to give 1,4-dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxide **7-meso** (35 mg, 66%).

1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxide **7-meso.** Colorless crystals, m.p. 135°C (decomp.)($CHCl_3$/hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (s, 1H, CH), 6.21 (s, 1H, CH), 6.95–6.96 (m, 1H, ArH), 7.02–7.04 (m, 1H, ArH), 7.18–7.26 (m, 2H, ArH), 7.39–7.46 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.4, 74.4, 128.27, 128.31, 128.4, 129.1, 129.2, 129.5, 129.7, 131.3, 132.8, 134.0, 134.3, 135.1, 137.4. IR (KBr) ν 3030, 1710, 1493, 1453, 1320 (SO_2), 1126 (SO_2), 746, 698, 559, 542 (cm^{-1}). MS *m/z* 288 (M^+-64). Anal. Calcd for $C_{20}H_{16}O_2S_2$: C, 68.15; H, 4.58%. Found: C, 68.20; H, 4.81%.

Thermolysis of 1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxide (7)

1,4-Dihydro-1,4-diphenyl-2,3-benzodithiin 2,2-dioxide, which contains two isomers **7-dl** and **7-meso,** was heated under reflux in xylene for 24 hours and the formation of 1,3-dihydro-1,3-diphenylbenzo [*c*]thiophene (**6**) was observed by ^{1}H NMR spectroscopy.

*Deprotonation of 1,3-Dihydro-1,3-diphenylbenzo[c]thiophene (***6***) with t-BuOK*

To a solution of 1,3-dihydro-1,3-diphenylbenzo [c]thiophene (**6**) (6 mg, 0.02 mmol) in THF (2 mL), *t*-BuOK (3 mg, 0.02 mmol) was added, and the solution was stirred for 1 hour at room temperature. After usual workup, the mixture was purified by chromatography on silica gel to give 1,3-diphenylbenzo[*c*]thiophene (**5**) (2 mg, 29%).

*Oxidation of 1,3-Dihydro-1,3-diphenylbenzo[c]thiophene (***6***) with m-CPBA*

To a solution of 1,3-dihydro-1,3-diphenylbenzo[*c*]thiophene (**6**) (46 mg, 0.16 mmol) in CH_2Cl_2

(10 mL), *m*-CPBA (29 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) was added, and the solution was stirred for 1 hour at room temperature. After the usual workup, the mixture obtained was purified by chromatography on silica gel to give 1,3-dihydro-1,3-diphenylbenzo[*c*]thiophene 2-oxide (**8**) (28 mg, 58%).

*1,3-Dihydro-1,3-diphenylbenzo[c]thiophene 2-oxide (**8**).* Colorless crystals, m.p. 180°C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (s, 2H, CH), 6.99, and 7.33 (AA′BB′, J = 3.3, 5.6 Hz, 4H, ArH), 7.40–7.45 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.6, 126.5, 128.8, 129.2, 129.3, 129.7, 134.4, 135.9. IR (KBr) ν 3030, 1599, 1497, 1455, 1073 (SO), 1029, 799, 776, 751, 700, 491, 438 (cm^{-1}). MS *m/z* 286 ($M^+ - 18$). Anal. Calcd for $C_{20}H_{16}OS$: C, 78.91; H, 5.30%. Found: C, 78.97, H, 5.34%.

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