Complete Regioselective Formation of 2-(Arylsulfinyl)diphenyl Sulfides from 5-Arylthianthreniumyl Perchlorates

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Treatment of 5-arylthianthreniumyl perchlorates with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature gave 2-(arylsulfinyl)diphenyl sulfides (29-79% yields), which are the first examples for complete regioselective formation of *S*-monoxides from unsymmetrical arylthiodiphenyl sulfides.

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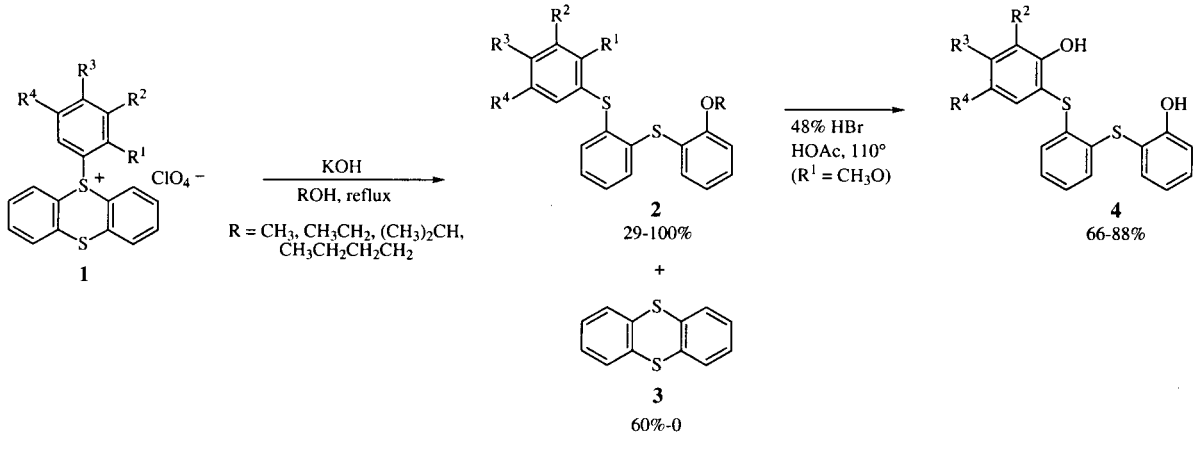
The oxidation of sulfides to sulfoxides is an extensively studied reaction in organic synthesis, and a variety of methods and reagents appear in the literature [1]. The synthesis of *S*-monoxides of symmetrical alkyl alkylthiomethyl sulfides [2], bis(phenylthio)methane [3], and phenylthiodiphenyl sulfide [4] has been achieved by the oxidation of the sulfides with stoichiometric amounts of appropriate oxidants. However, synthesis of the unsymmetrical counterparts, *i.e.*, α-alkylthiosulfoxides, has mostly relied on either displacement of α-halo sulfoxides with alkylthiolates [5] or addition of thiols to vinyl sulfoxides in the presence of a base [6]. Surprisingly, there have been no reports of the regioselective synthesis of *S*-monoxides of unsymmetrical arylthiodiphenyl sulfides. 2-Hydroxy-2'-(2-hydroxyarylthio)diphenyl sulfides (**4**) may be utilized as a building block for the synthesis of dithiaoxa and dithiaoxaaza macrocyles. In order to synthesize **4**, 2-alkoxy-2'-arylthiodiphenyl sulfides **2**, which are readily obtained by treatment of 5-arylthianthreniumyl perchlorates **1** with alcoholic potassium hydroxide at reflux [7], were dealkylated by employing 48% hydrobromic acid in acetic acid at 110°(Scheme 1). In contrast, *tert*-butoxy incorporated **2** (R = $(CH_3)_3C$) was not formed with *tert*-butanolic potassium hydroxide under similar conditions. After some trial, compound **2** (R = $(CH_3)_3C$) was obtained in 65% yield by treatment of **1** (R^1 = R^2 = R^4 = H, R^3 = OCH_2CH_3) with potassium *tert*-butoxide in tetrahydrofuran at reflux [8]. The formation of **2** (R = $(CH_3)_3C$) by changing the reaction conditions prompted us to investigate the reactions of **1** with potassium *tert*-butoxide in other solvents. The results are described herein.

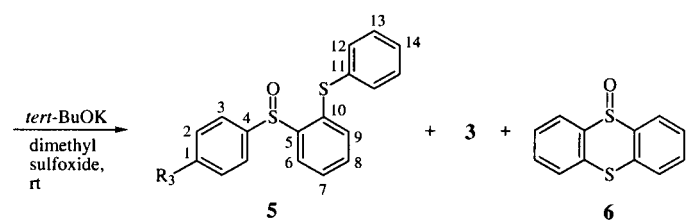
Scheme 1



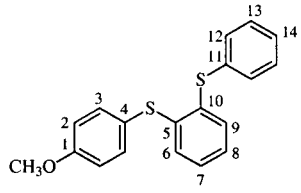
Results and Discussion.

Unexpectedly, treatment of **1** with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature gave 2-(arylsulfinyl)diphenyl sulfides **5** along with **3** and thianthrene 5-oxide (**6**) (Scheme 2). The quantities of the reactants, reaction times, and yields of compounds **3**, **5**, and **6** are described in Table 1 and their spectroscopic data are summarized in Table 2.

Scheme 2



Compound **7a**



7a

proton at C-3 of **5a** owing to the electron-withdrawing effects of sulfoxide functionality when the sulfur bonding to C-4 of **7a** is oxidized to sulfoxide. In fact, a doublet appeared at 7.62 ppm. In addition, the ^{13}C nmr spectra of **7a** and **5a** showed absorption at 136.5 ppm and 129.1 ppm, which are assignable to C-3 of **7a** and **5a**, respectively, by analyses of HOMO and HETERO COSY spectra. The upfield shift of ^{13}C nmr signals by the conversion from sulfide to sulfoxide functionality is in good agreement with the report in which the ^{13}C nmr bands of ortho carbons of aromatic sulfides exhibited upfield shift when the sulfides were converted to sulfoxides [9]. Furthermore, the ^{13}C nmr signal appeared at 123.8 ppm, attributable to a quaternary carbon C-4 of **7a**, shifted

Table 1

Reaction Conditions and Yields of 2-(Arylsulfinyl)diphenyl Sulfides **5**, Thianthrene (**3**), and Thianthrene 5-Oxide (**6**)

Compound	R^3 ($R^1 = R^2 = R^4 = H$)	mmole	$(CH_3)_3COK$ [a] (mmole)	DMSO [b] (ml)	Time (hours)		Yield (%) **5**	**3**	**6**
1a	CH_3O	0.367	0.533	60	2	**a**	79	13	
1b	CH_3CH_2O	0.343	0.515	50	1.5	**b**	76	12	
1c	$CH_3CH_2CH_2O$	0.665	1.66	30	1.5	**c**	75	11	
1d	$CH_3CH_2CH_2CH_2O$	0.323	0.588	25	2	**d**	59	15	
1e	CH_3	0.791	3.96	40	1.5	**e**	39	20	9
1f	$(CH_3)_2CH$	0.230	0.575	30	2	**f**	43	22	7
1g	CH_3CONH	0.384	0.960	30	2.5	**g**	29	12	47
1h	$CH_3CON(CH_3)$	0.647	1.21	15	2	**h**	75	16	
1i	$CH_3SO_2N(CH_3)$	0.600	0.900	40	2	**i**	66	9	13
1j	$C_6H_5SO_2N(CH_3)$	0.254	0.509	30	5	**j**	72	6	11
1k	p-$CH_3C_6H_4SO_2N(CH_3)$	0.521	1.04	30	2	**k**	74	7	11
1l	OH	0.489	1.22	30	6	**l**	66		
1m	NH_2	0.736	1.65	30	2	**m**	61, (79) [c]	10	
1n	$NHCH_3$					**n**	(78) [c]		

[a] $(CH_3)_3COK$: Potassium *tert*-butoxide. [b] DMSO: Dimethyl sulfoxide. [c] The number in parentheses represents yields of **5m** and **5n** prepared by the reactions of **5g** and **5h** with hydrazine monohydrate for 24 hours and 20 hours at 110°, respectively.

The regiochemistry of the monosulfoxides was determined based on the analyses of ^1H and ^{13}C nmr spectral data of **7a** [7] and **5a**. Since two doublets (7.41, 6.91 ppm) were observed from the ^1H nmr spectrum of **7a**, a doublet at 7.41 ppm was assigned to be a proton at C-3. One would expect a downfield shift of ^1H nmr signal of a

Scheme 3

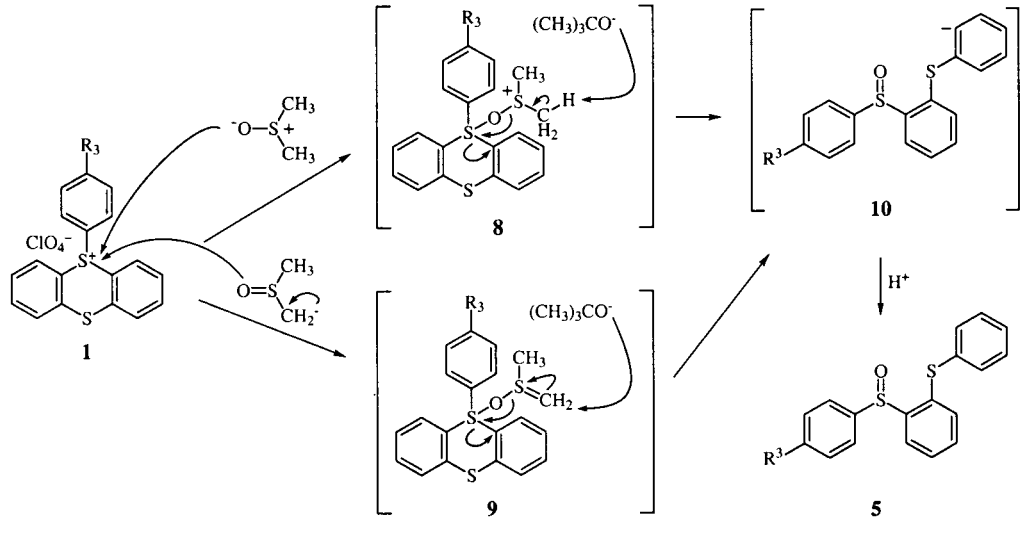


Table 2

Melting Points, Analytical, IR, and ^1H NMR Data of 2-(Arylsulfinyl)diphenyl Sulfides **5**

Compound	Mp (°C)	ir [a] (cm^{-1})	^1H nmr (deuteriochloroform) δ (ppm)	Molecular Formula	Analysis % Calcd./Found C	H	N	S
5a	115-117 [c]	1579, 1486, 1437, 1290, 1253, 1170, 1077, 1046, 1013,	3.76 (s, 3H, OCH_3), 6.84 (d, 2H, J = 6.84 Hz, ArH), 7.04 (m, 2H, ArH), 7.19 (m, 3H, ArH), 7.24 (d, 1H, J = 7.75 Hz, ArH), 7.36 (t, 1H, J = 7.54 Hz, ArH), 7.55 (t, 1H, J = 7.56 Hz, ArH), 7.62 (d, 2H, J = 6.83 Hz, ArH), 8.18 (d, 1H, J = 7.89 Hz, ArH). [b]	$C_{19}H_{16}O_2S_2$	67.03 67.17	4.74 4.69		18.83 18.56
5b	103-105 [c]	1582, 1486, 1435, 1294, 1250, 1168, 1077, 1045, 1021, 918	1.34 (t, 3H, J = 7.6 Hz, CH_3), 3.95 (q, 2H, J = 7.2 Hz, OCH_2), 6.56-7.77 (m, 12H, ArH), 8.17 (d, 1H, J = 8.2 Hz, ArH)	$C_{20}H_{18}O_2S_2$	67.77 67.82	5.12 5.10		18.09 18.15
5c	liquid	1584, 1488, 1437, 1299, 1248, 1166, 1075, 1046, 1018,	0.96 (t, 3H, J = 8.8 Hz, CH_3), 1.72 (sextet, 2H, J = 7.8 Hz, OCH_2CH_2), 3.88 (t, 2H, J = 6.8 Hz, OCH_2CH_2), 6.56-7.74 (m, 12H, ArH), 8.14 (d, 1H, J = 8.0 Hz, ArH)	$C_{21}H_{20}O_2S_2$	68.45 68.37	5.47 5.47		17.40 17.52
5d	51-53 [c]	1582, 1490, 1437, 1294, 1250, 1166, 1077, 1048, 1021,	0.89 (t, 3H, J = 6.4 Hz, CH_3), 1.13-1.87 (m, 4H, $OCH_2CH_2CH_2$), 3.92 (t, 2H, J = 6.8 Hz, OCH_2) 6.62-7.72 (m, 12H, ArH), 8.17 (d, 1H, J = 8.0 Hz, ArH)	$C_{22}H_{22}O_2S_2$	69.08 68.99	5.80 5.79		16.77 16.80
5e	68-70 [c]	1571, 1468, 1435, 1296, 1177, 1075, 1048, 1022,	2.27 (s, 3H, CH_3), 6.92-7.74 (m, 12H, ArH), 8.13 (d, 1H, J = 8.2 Hz, ArH)	$C_{19}H_{16}OS_2$	70.33 70.41	4.97 4.96		19.76 19.62
5f	liquid	1573, 1464, 1435, 1397, 1373, 1281, 1073, 1046, 1021,	1.18 (d, 6H, J = 16 Hz, $CH(CH_3)_2$), 2.84 (sept, 1H, J = 6.4 Hz, $CH(CH_3)_2$), 6.89-7.76 (m, 12H, ArH), 8.14 (d, 1H, J = 8.0 Hz, ArH)	$C_{21}H_{20}OS_2$	71.55 71.48	5.72 5.69		18.19 18.15
5g	156-158 [d]	3248, 1680, 1582, 1486, 1435, 1390, 1253, 1077, 1042, 1014,	2.04 (s, 3H, $COCH_3$), 6.88-7.94 (m, 12H, ArH), 8.07 (d, 1H, J = 8.2 Hz, ArH), 9.21 (s, 1H, NH)	$C_{20}H_{17}NO_2S_2$	65.37 65.34	4.66 4.63	3.81 3.75	17.45 17.50
5h	liquid	1661, 1578, 1483, 1435, 1338, 1294, 1070, 1048 1021,	1.84 (s, 3H, $COCH_3$), 3.19 (s, 3H, NCH_3), 6.93-7.66 (m, 10H, ArH), 7.76 (d, 2H, J = 8.6 Hz, ArH), 8.13 (d, 1H, J = 8.2 Hz, ArH)	$C_{21}H_{19}NO_2S_2$	66.12 66.15	5.02 5.00	3.67 3.70	16.81 16.90
5i	liquid	1576, 1475, 1437, 1344, 1259, 1163, 1142, 1078, 1051, 1024,	2.79 (s, 3H, SO_2CH_3), 3.26 (s, 3H, NCH_3), 6.89-7.73 (m, 10H, ArH), 7.73 (d, 2H, J = 8.4 Hz, ArH), 8.09 (d, 1H, J = 8.2 Hz, ArH)	$C_{20}H_{19}NO_3S_3$	57.53 57.48	4.59 4.56	3.35 3.37	23.04 23.07
5j	liquid	1576, 1474, 1437, 1348, 1170, 1081, 1050, 1022,	3.10 (s, 3H, NCH_3), 6.92-7.80 (m, 17H, ArH), 8.09 (d, 1H, J = 8.0 Hz, ArH)	$C_{25}H_{21}NO_3S_3$	62.61 62.58	4.41 4.40	2.92 2.90	20.06 20.09
5k	liquid	1581, 1477, 1437, 1348, 1164, 1080, 1051, 1019,	2.37 (s, 3H, $C_6H_4CH_3$), 3.11 (s, 3H, NCH_3), 6.87-7.79 (m, 16H, ArH), 8.09 (d, 1H, J = 8.0 Hz, ArH)	$C_{26}H_{23}NO_3S_3$	63.26 63.22	4.70 4.67	2.84 2.80	19.49 19.53
5l	liquid	3192, 1574, 1488, 1432, 1277, 1160, 1074, 1035	6.48-7.64 (m, 13H, ArH, OH), 8.13 (d, 1H, J = 8.2 Hz, ArH)	$C_{18}H_{14}O_2S_2$	66.23 66.15	4.32 4.30		19.65 19.47
5m	161-163 [d]	3408, 3336, 3224, 1629, 1585, 1493, 1435, 1307, 1074, 1037	4.05 (s, 2H, NH_2), 6.50 (d, 2H, J = 10 Hz, ArH), 6.86-7.64 (m, 10H, ArH), 8.14 (d, 1H, J = 8.2 Hz, ArH)	$C_{18}H_{15}NOS_2$	66.43 66.38	4.65 4.69	4.30 4.25	19.70 19.59
5n	164-165 [d]	3320, 1589, 1464, 1435, 1270, 1179, 1078, 1011	2.80 (s, 3H, NCH_3), 6.46 (d, 2H, J = 7.2 Hz, ArH), 6.96-7.22 (m, 11H, ArH), 8.18 (d, 1H, J = 8.0 Hz, ArH)	$C_{19}H_{17}NOS_2$	67.23 67.15	5.05 5.01	4.13 4.17	18.89 18.95

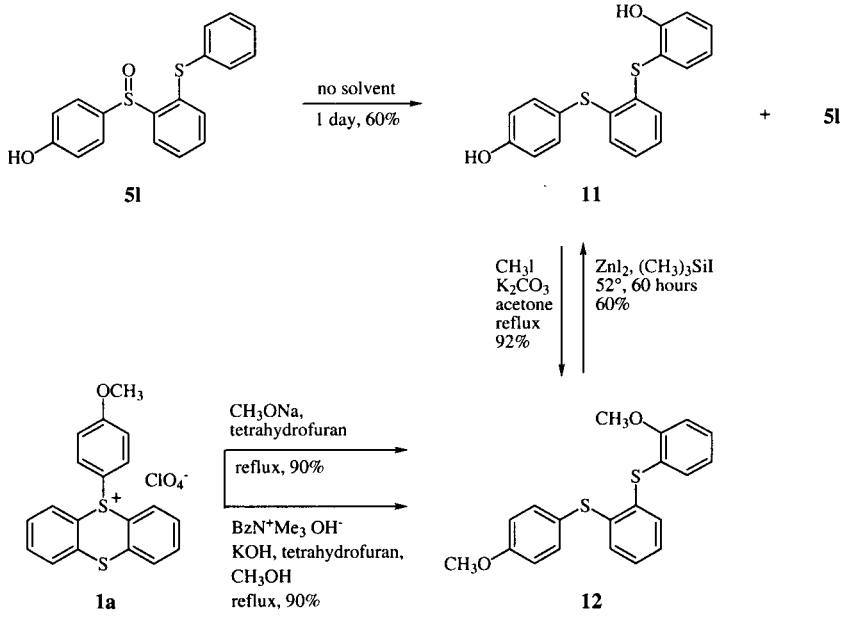
[a] From potassium bromide pellet, except for **5c, 5f, 5h, 5i, 5j, 5k**, and **5m**, which were taken on potassium bromide plates. [b] Taken from 300 MHz nmr spectrophotometer, otherwise from 80 MHz nmr spectrophotometer. [c] From a mixture of *n*-hexane and dichloromethane. [d] From a mixture of *n*-hexane and ethyl acetate.

downfield below 132 ppm, which clearly indicates the oxidation of the sulfur bonding to the *p*-anisyl group rather than the oxidation of the other sulfur atom.

The complete regioselective formation of the monosulfoxides **5** can be explained by nucleophilic attack of either dipolar oxygen on dimethyl sulfoxide or dimsyl anion on the trivalent sulfur cation of **1** to form sulfurane intermediates **8** and **9**, respectively (Scheme 3). The oxygen transfer between two sulfur atoms of the sulfurane intermediates **8** and **9**, concomitant with a C-S bond cleavage of the thianthrene moiety, generates a phenyl anion **10** which protonates to give a sulfinyl sulfide **5**. Compounds **3** and **6** would be formed through the bond-reorganization of the sulfurane intermediates **8** and/or **9** [10]. In order to obtain further evidence of the oxygen transfer from dimethyl sulfoxide, **1a** (0.10 g, 0.24 mmole) was treated with sodium hydride (0.17 g, 4.00 mmoles) in freshly dried dimethyl sulfoxide (10 ml) for 20 minutes at room temperature under nitrogen atmosphere. From the reaction mixture was isolated **5a** in 56% yield.

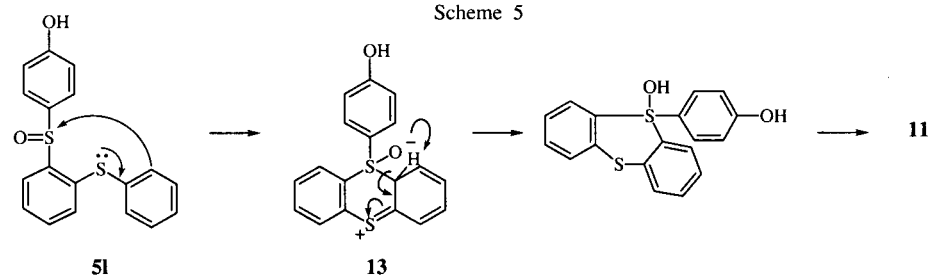
Interestingly, compound **5l** was slowly converted to 2-(4-hydroxyphenylthio)-2'-hydroxydiphenyl sulfide (**11**) at room temperature (Scheme 4). Methylation of compound **11** with iodomethane in the presence of potassium carbonate in acetone at reflux temperature gave 2-(4-methoxyphenylthiophenyl)-2'-methoxydiphenyl sulfide (**12**). The physical and spectroscopic data obtained for the latter were identical with those of the authentic sample, which was prepared either by the reaction of **1a** with sodium methoxide in tetrahydrofuran at reflux or by the reaction of **1a** with potassium hydroxide in the presence of benzyltrimethylammonium hydroxide ($BzN^+Me_3OH^-$) in methanol at reflux.

Scheme 4



Compound **11** is envisaged to be formed *via* a sulfurane intermediate **13** (Scheme 5). The result indicates that compound **11** is thermodynamically more stable than its structural isomer **5l**. In fact, the isomerization of **5l**, exhibiting a maximum absorption at 258 nm in dimethyl sulfoxide, to **11**, which exhibited a maximum absorption at 259 nm in the same solvent, was confirmed by the observation of an isosbetic point at 300 nm (Figure 1). However, no other 2-(arylsulfinyl)diphenyl sulfides **5** prepared gave isomerization products analogous to **11** at room temperature.

Scheme 5



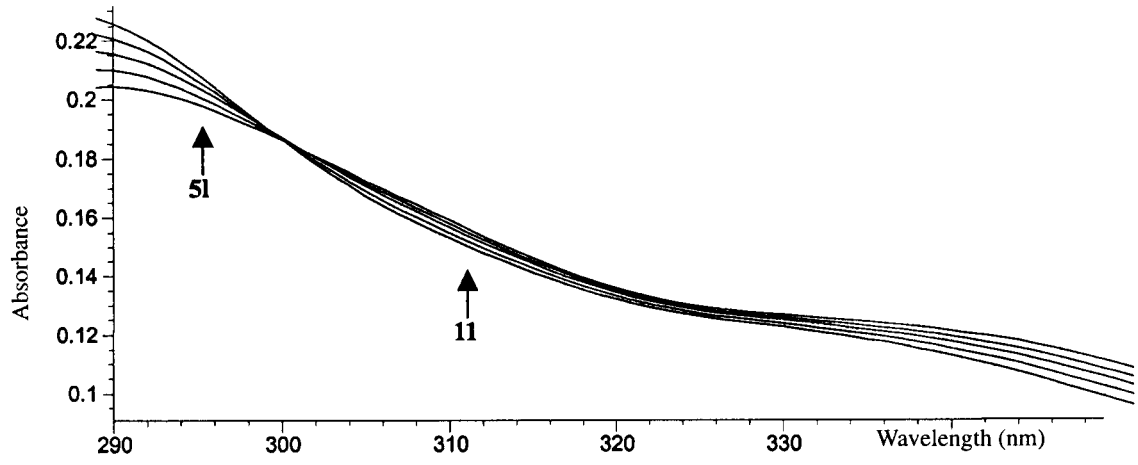


Figure 1. Spectra of 2-(4-hydroxyphenylsulfinyl)diphenyl sulfide (**5l**) and 2-(4-hydroxyphenylthio)-2'-hydroxydiphenyl sulfide (**11**) in dimethyl sulfoxide.

In conclusion, treatment of 5-arylthianthreniumyl perchlorates with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature gave 2-(arylsulfinyl)diphenyl sulfides which were the first examples of the regioselective formation of *S*-monoxides from unsymmetrical arylthiodiphenyl sulfides.

EXPERIMENTAL

5-Arylthianthreniumyl perchlorates **1** were prepared by the literature methods [11]. Potassium *tert*-butoxide was purchased from Aldrich. Chem. Inc. Dimethyl sulfoxide was dried over calcium hydride and distilled prior to use. Infrared spectra were obtained on a Shimadzu IR-470 spectrophotometer. The proton nuclear magnetic resonance spectra were recorded at 80 MHz and 300 MHz spectrometers in deuteriochloroform solution containing tetramethylsilane as an internal standard. Mass spectra were obtained by electron impact at 70 eV. Elemental analyses were determined by the Korea Basic Science Center. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Column chromatography was performed on a silica gel (Merck 230-400 mesh, ASTM). Thin layer chromatography was carried out on Merck chromatogram sheet (Kiesel gel 60 F_{254}). Chromatogram was visualized by a mineral UV lamp.

General Procedures for the Reactions of 5-Arylthianthreniumyl Perchlorates **1** with Potassium *tert*-Butoxide in Dimethyl Sulfoxide.

To a solution of **1** (0.23-0.79 mmole) in dimethyl sulfoxide (15-60 ml) was added potassium *tert*-butoxide (0.53-4.0 mmoles). The mixture was stirred at room temperature for an appropriate time, until no spot corresponding to **1** was observed on thin layer chromatogram (R_f = 0.3-0.4, chloroform:methanol = 9:1). The mixture was extracted with ethyl acetate (3 x 50 ml). The extracts were washed with water (9 x 30 ml), and then dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue, which was chromatographed on a silica gel (1.5 x 10 cm). Elution with *n*-hexane gave thianthrene (**3**). Subsequent elution with a mixture of *n*-hexane and ethyl acetate (2:1) gave 2-(arylsulfinyl)diphenyl sulfides **5**. In each case consult Table 1 for quantities of reactants, reaction times, and yields of compounds **3**, **5**, and **6** and Table 2 for melting points, analytical, and spectroscopic data of **5**.

Preparation of 2-(4-Anisylsulfinyl)diphenyl Sulfide (**5a**).

To a stirred suspension of sodium hydride (0.16 g, 4.00 mmoles, 60% dispersion in mineral oil) in freshly dried dimethyl sulfoxide (10 ml) for 10 minutes under nitrogen atmosphere was added **1a** (0.10 g, 0.24 mmole). The mixture was stirred for 20 minutes at room temperature, followed by addition of water (40 ml), which was extracted with dichloromethane (3 x 30 ml). The extracts were worked up as described in the general procedures foregoing. Chromatography of the residue gave **5a** (0.045 g, 56%); ^{13}C nmr (deuteriochloroform, 75 MHz): δ 55.8, 115.0, 125.2, 127.5, 129.1, 129.4, 129.7, 130.4, 131.7, 132.8, 134.5, 135.3, 136.5, 147.8, 162.3.

Deacetylation of 2-(4-Acetamidophenylsulfinyl)diphenyl Sulfide (**5g**).

Compound **5g** (41 mg, 0.112 mmole) was added to 98% hydrazine monohydrate (10 ml), and the mixture was heated at 110° for 24 hours. The reaction mixture was cooled to room temperature, followed by neutralization with 10% hydrochloric acid, which was extracted with dichloromethane (3 x 30 ml). The extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue, which was chromatographed on a silica gel (1.5 x 10 cm). Elution with a mixture of *n*-hexane and ethyl acetate (2:1) gave unreacted **5g** (12 mg, 29%) and 2-(4-aminophenylsulfinyl)diphenyl sulfide (**5m**) (21 mg, 79%). Consult Table 2 for melting point, analytical, and spectroscopic data of **5m**.

Deacetylation of 2-[4-(*N*-Methylacetamido)phenylsulfinyl]-diphenyl Sulfide (**5h**).

Compound **5h** (28 mg, 0.073 mmole) was treated with 98% hydrazine monohydrate (10 ml) for 20 hours at 110° as described for the reaction of **5g**. Work-up of the reaction mixture gave unreacted **5h** (6 mg, 21%) and 2-(4-*N*-methylaminophenylsulfinyl)diphenyl sulfide (**5n**) (15 mg, 78%). Consult Table 2 for melting point, analytical, and spectroscopic data of **5h**.

Rearrangement of 2-(4-Hydroxyphenylsulfinyl)diphenyl Sulfide (**5l**) to 2-(4-Hydroxyphenylthio)-2'-hydroxydiphenyl Sulfide (**11**).

Compound **5l** (104 mg, 0.321 mmole) showing only one spot on thin layer chromatogram (R_f = 0.2, *n*-hexane:ethyl acetate = 2:1) exhibited a new spot on thin layer chromatogram (R_f = 0.5, the same eluent) in addition to the spot corresponding to **5l** in 24 hours. Chromatography (1.5 x 10 cm) of the mixture using a mixture of *n*-hexane and ethyl acetate gave compound **11** (62 mg) and unrearranged **5l** (14 mg) in 60 and 14% yields, respectively. Compound **11** was recrystallized from a mixture of *n*-hexane and dichloromethane, mp 90-92°; ir (neat): 3432, 1600, 1569, 1486, 1438, 1246, 1176, 1028, 750 cm^{-1}; ^1H nmr (deuteriochloroform, 80 MHz): δ 5.54 (br s, 1H, OH), 6.56 (br s, 1H, OH), 6.74-7.58 (m, 12H, ArH).

Anal. Calcd. for $C_{18}H_{14}O_2S_2$: C, 66.23; H, 4.32; S, 19.64. Found: C, 66.37; H, 4.50; S, 19.46.

2-(4-Hydroxyphenylthio)-2'-hydroxydiphenyl Sulfide (**11**).

To a solution of 2-methoxyphenyl-2'-(4-methoxyphenylthio)-diphenyl sulfide **12** (207 mg, 0.584 mmole) and zinc iodide (767 mg, 2.40 mmoles) in dried chloroform (30 ml) was added iodotrimethylsilane (925 mg, 4.62 mmoles). The mixture was stirred for 60 hours at 52°. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel (1.5 x 10 cm). Elution with a mixture of *n*-hexane and ethyl acetate (5:1) gave unreacted **12** (65 mg, 32%). Subsequent elution with the same solvent mixture (2:1) gave **11** (115 mg, 60%).

2-Methoxyphenyl-2'-(4-methoxyphenylthio)diphenyl Sulfide (**12**).

(i) To a solution of 5-(4-methoxyphenyl)thianthreniumyl perchlorate (**1a**) (260 mg, 0.614 mmole) in tetrahydrofuran (50 ml) was added a solution of benzyltrimethylammonium hydroxide (133 mg, 0.795 mmole) in methanol (10 ml), followed by addition of potassium hydroxide (44 mg, 0.786 mmole). The mixture was heated for 21 hours at reflux. After the solvent was removed *in vacuo*, the residue was extracted with dichloromethane (3 x 50 ml). The extracts were dried over magnesium sulfate. After the solvent was removed *in vacuo*, the residue was chromatographed on a silica gel (1 x 10 cm). Elution with a mixture of *n*-hexane and ethyl acetate (10:1) gave **12** (195 mg, 90%) which was recrystallized from *n*-hexane, mp 85-87°; ir (neat): 1588, 1492, 1245, 1079, 828 cm^{-1}; ^1H nmr (deuteriochloroform, 80 MHz): δ 3.80 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.82-7.65 (m, 12H, ArH); ms: m/z 354 (M^+, 100%), 323 (6), 200 (21), 171 (15).

Anal. Calcd. for $C_{20}H_{18}O_2S_2$: C, 67.77; H, 5.12; S, 18.09. Found: C, 67.85; H, 5.07; S, 18.22.

(ii) To a solution of **11** (109 mg, 0.334 mmole) in acetone (50 ml) containing potassium carbonate (185 mg, 1.34 mmoles) was added iodomethane (99 mg, 0.698 mmole). The mixture was heated for 6 hours at reflux. After the solvent was removed *in vacuo*, the residue was chromatographed on a silica gel (1 x 10 cm). Elution with a mixture of *n*-hexane and ethyl acetate (10:1) gave **12** (109 mg, 92%).

Acknowledgement.

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[7] K. Kim and M. N. Kim, *J. Heterocyclic Chem.*, **34**, 1 (1997). Compound **7a** had mp 68-70°; ^1H nmr (deuteriochloroform, 300 MHz): δ 3.81 (s, 3H, OCH_3), 6.87 (d, 1H, J = 7.51 Hz, ArH), 6.91 (dd, 2H, J = 6.70, 2.15 Hz, ArH), 7.03 (td, 1H, J = 7.35, 1.73 Hz, ArH), 7.08 (td, 1H, J = 7.23, 1.84 Hz, ArH), 7.20-7.34 (m, 6H, ArH), 7.41 (dd, 2H, J = 6.73, 2.18 Hz, ArH); ^{13}C nmr (deuteriochloroform, 75 MHz): δ 55.8, 115.6, 123.8, 126.5, 127.4, 128.5, 128.7, 129.7, 131.0, 133.2, 133.6, 135.7, 136.5, 142.3, 160.6); ir (potassium bromide): 3051, 2975 cm^{-1}; ms: m/z 324 (M^+, 100%).

Anal. Calcd. for $C_{19}H_{16}OS_2$: C, 70.33; H, 4.97; S, 19.77. Found: C, 70.25; H, 4.95; S, 19.80.

[8] 2-*tert*-Butoxy-2'-(4-ethoxyphenylthio)diphenyl sulfide was recrystallized from a mixture of *n*-hexane and dichloromethane, mp 73-74°; ^1H nmr (deuteriochloroform, 80 MHz): δ 1.36 (t, 3H, J = 7.8 Hz, OCH_2CH_3), 1.45 (s, 9H, $OC(CH_3)_3$), 3.98 (q, 2H, J = 7.8 Hz, OCH_2CH_3), 6.66-7.53 (m, 12H, ArH); ir (potassium bromide): 1586, 1566, 1485, 1461, 1435, 1385 cm^{-1}; ms: m/z 410 (M^+).

Anal. Calcd. for $C_{24}H_{26}O_2S_2$: C, 70.21; H, 6.38; S, 15.61. Found: C, 70.16; H, 6.33; S, 15.59.

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