Synthesis of 2,3,8,9-Dibenzo-5,6-(substituted)benzo-1,4-dithio-7-oxacyclonona-2,5,8-trienes and Some Electrophilic Substitution Reactions

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Treatment of 5-(2-hydroxyaryl)thianthreniumyl perchlorates **1** with sodium hydride in tetrahydrofuran at reflux gave the title compounds **5** in excellent yields. For the reactivities of the compounds **5**, the selected compounds **5** were subjected under the conditions of electrophilic substitution reactions. Bromination of 5,6-{3-(2-butyl)benzo}-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**5f**) in acetic acid at 60° afforded two bromo compounds **9** (22%) and **10** (69%), which were oxidized by *m*-chloroperbenzoic acid to give tetraoxides **11** (95%) and **12** (97%), respectively. Treatment of **5f** with acetyl chloride in the presence of aluminum chloride in carbon disulfide at 0° gave an acetylated compound **13** (58%). Nitration of **5f** with nitric acid in acetic acid at 50° gave a nitro compound **17** (15%) together with 1,4-dioxide **7e** (22%) and a *S*-oxide **18** (3%) whose regiochemistry has not been established. On the other hand, 5,6-(3-methylbenzo)-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**5a**) reacted with acetyl chloride under the same conditions to give two acetylated compounds **15** (33%) and **16** (18%). The mechanism for the formation of **5** and the structural elucidation of these compounds are discussed.

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It has been well-known that thianthrene cation radical perchlorate reacts with benzene derivatives having an electron-donating groups in acetonitrile at room temperature to give 5-arylthianthreniumyl perchiorates **1** [1]. We have shown that compounds **1** can be utilized for the preparation of sulfur-containing aromatic compounds otherwise unaccessible such as 2-arylthio-2'-arylthiodiphenyl sulfides **2** [2], bis 2-[2'-(arylmercapto)phenylmercapto]-phenyl sulfides **3a** [3], bis 2-[2'-(arylmercapto)phenylmercapto]phenyl selenides **3b** [4] and 2,3,8,9-dibenzo-5,6-(substituted)benzo-1,4-dithio-7-azacyclonona-2,5,8-trienes **4** [5].

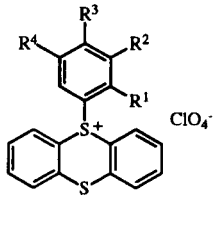
In a continuation of our efforts to explore the potential synthetic utility of compounds **1**, 5-(2-hydroxyaryl)thianthreniumyl perchorates **1** (R^1 = OH) were prepared and treated with sodium hydride in tetrahydrofuran at reflux to obtain 9-membered dithiaoxa cyclic compounds **5**. The results are described herein.

Results.

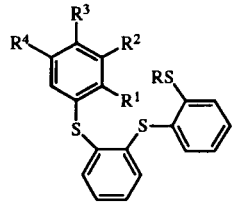
Various hydroxy compounds **1** (R^1 = OH) prepared which were including their physical and analytical data and reaction times are summarized in Table 1. Treatment of compounds **1** with sodium hydride in tetrahydrofuran at reflux gave the title compounds **5** as the major products along with a small amount of thianthrene (**6**).

The reaction conditions and yields of **5** and **6** are summarized in Table 2. The physical, analytical, ir and ^1H

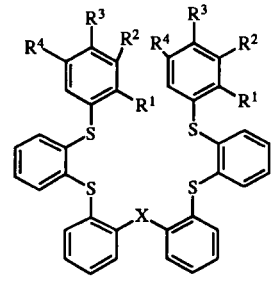
Compounds **1-6**



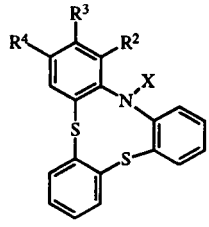
1



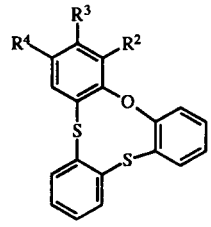
2, R = alkyl, aryl



3a, X = S
3b, X = Se



4, X = H, CH_3, CH_2CH_3, $COCH_3$



5

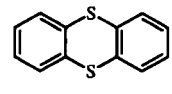


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Table 1
Physical and Analytical Data of Compounds 1 (R^1 = OH)

Compound	R^2	R^3	R^4	Time hours	Mp °C	Yield %	Molecular Formula	Analysis% Calcd./Found C	H	S
1a	H	H	CH_3	0.5	236-238 [b]	97	$C_{19}H_{15}ClO_5S_2$	53.96	3.58	15.16
								53.88	3.59	15.14
1b	H	H	$CH(CH_3)_2$	18	212-214 [c]	99	$C_{21}H_{19}ClO_5S_2$	55.93	4.25	14.22
								55.79	4.11	14.15
1c	H	H	$C(CH_3)_3$	0.5	220-222 [c]	95	$C_{22}H_{21}ClO_5S_2$	56.83	4.55	13.79
								56.80	4.54	13.77
1d	H	H	Br	20	258-260 [c]	95	$C_{18}H_{12}BrClO_5S_2$	44.32	2.48	13.15
								44.19	2.39	13.07
1e	H	H	C_6H_5	3	243-245 [c]	99	$C_{24}H_{17}ClO_5S_2$	59.44	3.53	13.22
								59.42	3.41	13.27
1f	H	H	$HC(CH_3)CH_2CH_3$	0.5	202-204 [d]	98	$C_{22}H_{21}ClO_5S_2$	56.83	4.55	13.79
								56.80	4.41	13.63
1g	H	H	$C(CH_3)_2CH_2CH_3$	0.5	189-191 [c]	93	$C_{23}H_{24}ClO_5S_2$	57.67	4.84	13.39
								57.63	4.75	13.37
1h	H	CH_3	CH_3	0.5	211-213 [d]	97	$C_{20}H_{17}ClO_5S_2$	54.98	3.92	14.68
								54.93	3.77	14.58
1i	H	CH_3	$CH(CH_3)_2$	7	216-218 [c]	95	$C_{22}H_{21}ClO_5S_2$	56.83	4.55	13.79
								56.74	4.39	13.77
1j	H	$C(CH_3)_3$	H	0.5	210-212 [c]	99	$C_{22}H_{21}ClO_5S_2$	56.83	4.55	13.79
								56.80	4.51	13.77
1k	H	H	$C(CH_3)_3$	0.5	209-210 [c]	99 [a]				

[a] $R^1 = CH_3O$. [b] From acetone. [c] From ethanol. [d] From aqueous ethanol.

nmr spectroscopic data of compounds **5** are summarized in Tables 3 and 4, respectively.

In order to obtain information concerning the reactivity of compounds **5**, which are 9-membered cyclic compounds having both ether and thioether bonds, selected substituted compounds **5** were subjected to oxidation, bromination, Friedel-Craft acylation, and nitration reactions.

Table 2
Reaction Conditions and Yields of Compounds **5** and **6**

Compound mmoles	NaH mmoles	THF ml	Times hours		Yield %		
1a							
1.580	3.124	60	22	**5a**	89	**6**	4
1b							
0.364	1.158	50	42	**5b**	96	**6**	0
1c							
0.821	2.726	50	24	**5c**	84	**6**	11
1d							
1.784	5.994	80	61	**5d**	18 [a]	**6**	43
1e							
0.350	1.109	50	22	**5e**	68	**6**	3
1f							
0.353	1.142	50	42	**5f**	92	**6**	7
1g							
0.418	1.379	50	45	**5g**	94	**6**	3
1h							
0.915	2.919	60	48	**5h**	86	**6**	8
1i							
0.860	2.761	60	48	**5i**	92	**6**	7
1j							
0.418	1.338	50	49	**5j**	87	**6**	7

[a] Compound **5k** ($R^2 = R^3 = R^4 = H$), liquid, was isolated in 21% yield along with compound **5d**.

Table 3
Physical and Analytical Data of Compounds **5**

Compound	Mp (°C)	Molecular Formula	Analysis % Calcd./Found C	H	S
5a	90-92 [a]	$C_{19}H_{14}OS_2$	70.78	4.38	19.89
			70.65	4.29	18.77
5b	liquid	$C_{21}H_{18}OS_2$	71.96	5.18	18.29
			71.87	5.21	18.32
5c	liquid	$C_{22}H_{20}OS_2$	72.49	5.53	17.59
			72.35	5.49	17.42
5d	120-122	$C_{18}H_{11}BrOS_2$	55.82	2.86	16.56
			55.79	2.91	16.48
5e	161-163 [b]	$C_{24}H_{16}OS_2$	74.97	4.19	16.68
			74.81	4.08	16.59
5f	liquid	$C_{22}H_{20}OS_2$	72.49	5.53	17.59
			72.39	5.47	17.44
5g	liquid	$C_{23}H_{22}OS_2$	72.98	5.86	16.94
			72.89	5.78	16.93
5h	177-178	$C_{20}H_{16}OS_2$	71.39	4.79	19.06
			71.28	4.77	19.15
5i	98-99 [c]	$C_{22}H_{21}OS_2$	72.29	5.79	17.54
			72.17	5.61	17.50
5j	liquid	$C_{22}H_{20}OS_2$	72.49	5.53	17.59
			72.38	5.46	17.42
5k	liquid	$C_{18}H_{12}OS_2$	70.10	3.92	20.79

[a] From a mixture of methylene chloride and *n*-hexane. [b] From a mixture of carbon tetrachloride and *n*-hexane. [c] From *n*-hexane.

Oxidations.

Table 4
Ir and ^1H nmr Spectral Data of Compounds **5**

Compound	ir (cm^{-1})	^1H nmr (deuteriochloroform) δ (ppm)
5a	3050, 2941, 1588, 1461, 1441, 1300, 1260, 1230, 1210, 1070, 850, 750 [a]	2.24 (s, 3H, CH_3), 6.85-7.52 (m, 11H, ArH)
5b	3055, 2975, 2935, 2880, 1575, 1460, 1400, 1327, 1300, 1259, 1235, 1070, 1040, 910, 876, 835, 780, 750 [a]	1.18 (d, 6H, $HC(CH_3)_2$), 2.80 (hept, 1H, $CH(CH_3)_2$), 6.80-7.55 (m, 11H, ArH)
5c	3050, 2950, 2890, 1571, 1455, 1382, 1358, 1295, 1251, 1221, 1150, 1125, 1067, 1036, 940, 885, 750, 710 [a]	1.29 (s, 9H, $C(CH_3)_3$), 6.86-7.58 (m, 11H, ArH)
5d	3010, 1590, 1451, 1291, 1243, 1214, 1117, 1076, 946, 872, 825, 750 [b]	6.65-7.59 (m, 11H, ArH)
5e	3035, 1455, 1420, 1296, 1247, 1218, 1114, 1057, 900, 880, 755, 697 [b]	7.00-7.88 (m, 16H, ArH)
5f	3050, 2960, 2935, 2875, 1576, 1460, 1400, 1379, 1304, 1258, 1230, 1128, 1070, 1040, 893, 864, 836, 755, 715 [a]	0.77 (t, 3H, CH_2CH_3), 1.18 (3H, $CHCH_3$), 1.49 (q, 2H, CH_2), 2.52 (sext, 1H, $CH(CH_3)CH_2$), 6.80-7.55 (m, 11H, ArH)
5g	3055, 2975, 2930, 1574, 1461, 1450, 1387, 1305, 1258, 1227, 1125, 1070, 1040, 888, 836, 755 [a]	0.65 (t, 3H, CH_2CH_3), 1.21 (s, 6H, $C(CH_3)_2$), 1.58 (q, 2H, CH_2CH_3), 6.82-7.76 (m, 11H, ArH)
5h	3050, 2975, 1610, 1588, 1578, 1490, 1466, 1440, 1386, 1363, 1300, 1257, 1240, 1216, 1186, 1070, 1040, 1025, 886, 860, 770, 745, 710, 652 [b]	2.18 (s, 6H, $2CH_3$), 6.65-7.51 (m, 10H, ArH)
5i	3055, 2960, 2930, 2875, 1555, 1489, 1450, 1385, 1362, 1258, 1241, 1210, 1160, 1069, 885, 787, 758, 745, 655 [b]	1.15 (d, 6H, $2CH_3$), 2.24 (s, 3H, CH_3), 3.00 (hept, 1H, $CH(CH_3)_2$), 6.51-7.55 (m, 10H, ArH)
5j	3100, 2950, 2900, 1600, 1585, 1550, 1461, 1390, 1360, 1304, 1254, 1230, 1151, 1125, 1060, 1051, 1035, 950, 910, 830, 750, 735, 655 [a]	1.28 (s, 9H, $C(CH_3)_3$), 7.02-7.45 (m, 11H, ArH)
5k	3060, 2960, 1575, 1471, 1426, 1370, 1291, 1256, 1238, 1205, 1091, 1040, 875, 760 [a]	6.64-7.60 (m, 12H, ArH)

[a] The ir recorded neat. [b] The ir was recorded in a potassium bromide pellet.

Treatment of compounds **5b-k** with sulfuryl chloride in methylene chloride for one hour at room temperature gave disulfoxides **7** in excellent yields. The reaction conditions and yields of compounds **7** are summarized in Table 5 and physical, analytical, ir, and ^1H nmr spectroscopic data of compounds **7** are summarized in Table 6.

The structure of compounds **7** were determined on the basis of the spectroscopic, mass spectral data and elemental analyses in addition to an X-ray crystallographic analysis of **7b**.

Crystal and refinement parameters for compound **7b** and atomic coordinates and equivalent isotropic thermal parameters of nonhydrogen atoms of **7b** are listed in Tables 7 and 8, respectively. Selected bond distances and angles of crystalline **7b** are tabulated in Tables 9 and 10, respectively.

On the other hand, oxidation of selected compounds **5f-i** with *m*-chloroperbenzoic acid in methylene chloride at room temperature gave tetraoxides **8a-d** in excellent yields. Reaction conditions and yields of compounds **8a-d** are summarized in Table 11 and while the physical, ana-

Table 5
Reaction Conditions and Yields of Compounds **7**

Compound	mmole	SO_2Cl_2 [a] mmole	CH_2Cl_2 [b] ml		Yield %
5b	0.140	0.296	30	**7a**	97
5c	0.251	0.674	20	**7b**	98
5d	0.088	0.185	20	**7c**	94
5e	0.049	0.014	10	**7d**	98
5f	0.198	0.415	30	**7e**	97
5g	0.116	0.244	20	**7f**	98
5h	0.306	0.674	30	**7g**	99
5i	0.214	0.452	30	**7h**	99
5j	0.255	0.533	20	**7i**	98
5k	0.062	0.133	10	**7j**	100

[a] Sulfuryl chloride. [b] Methylene chloride.

Table 6
Physical, Analytical, ir, and ^{1}H nmr Spectroscopic Data of Compounds **7**

Compound	Mp [a] (°C)	Molecular Formula	Analysis % Calcd./Found C	H	S	IR [b] (cm^{-1})	^{1}H nmr (deuteriochloroform) δ (ppm)
7a	253-255	$C_{21}H_{18}O_3S_2$	65.94 65.87	1.35 1.42	16.76 16.66	3060, 2960, 1489, 1465, 1448, 1255, 1232, 1162, 1097, 1075, 1043,1030, 885, 810, 789, 770, 660	1.27 (d, 6H, $2CH_3$), 3.00 (hept, 1H, $CH(CH_3)_2$), 7.09-7.61 (m, 7H, ArH), 7.71-8.19 (m, 4H, ArH)
7b	213-214	$C_{22}H_{20}O_3S_2$	66.65 66.63	1.39 1.41	16.17 16.03	3050, 2940, 1575, 1489, 1457, 1360, 1300, 1251, 1225, 1091, 1069, 1041, 1029, 910, 759, 739, 645	1.37 (s, 9H, $C(CH_3)_3$), 7.19-7.54 (m, 7H, ArH), 7.74-8.15 (m, 4H, ArH)
7c	302-304	$C_{18}H_{11}BrO_3S_2$	51.56 51.67	0.68 0.59	15.29 15.33	3050, 1583, 1569, 1455, 1240, 1224, 1158, 1098, 1067, 1042, 1038, 897, 808, 780, 759, 660	7.20-7.69 (m, 7H, ArH), 7.82-8.30 (m, 4H, ArH)
7d	263-265	$C_{24}H_{16}O_3S_2$	69.20 69.06	1.01 1.19	15.39 15.41	3050, 2960, 1465, 1254, 1230, 1096, 1074, 1048, 1030, 891, 810, 768, 750, 708	7.70-7.79 (m, 12H, ArH), 7.80-8.25 (m, 4H, ArH)
7e	236-238	$C_{22}H_{20}O_3S_2$	66.65 66.57	1.39 1.33	16.17 16.06	3050, 2905, 2930, 1578, 1450, 1250, 1225, 1160, 1095, 1040, 1022, 895, 827, 772, 755, 655	0.80 (t, 3H, CH_2CH_3), 1.23 (d, 3H, $CHCH_3$), 1.60 (quint, 2H, $CHCH_2CH_3$), 2.71 (sext, 1H, $CH(CH_3)CH_2$), 7.12-7.17 (m, 7H, ArH), 7.78-8.21 (m, 4H, ArH)
7f	201-202	$C_{23}H_{22}O_3S_2$	67.29 67.23	5.40 5.34	15.62 15.49	3050, 2955, 1577, 1482, 1460, 1295, 1255, 1238, 1160, 1097, 1070, 1044, 1029, 892, 833, 760, 655	0.63 (t, 3H, CH_2CH_3), 1.27 (s, 6H, $2CH_3$), 1.61 (q, 2H, CH_2CH_3), 7.21-7.60 (m, 7H, ArH), 7.75-8.19 (m, 4H, ArH)
7g	274-276	$C_{20}H_{16}O_3S_2$	65.19 65.02	4.38 4.19	17.40 17.38	3050, 2920, 1569, 1490, 1466, 1450, 1388, 1265, 1218, 1094, 1070, 1064, 1048, 1030, 1010, 767, 665	2.24 (s, 6H, $2CH_3$), 7.13-7.59 (m, 6H, ArH), 7.67-8.14 (m, 4H, ArH)
7h	265-268	$C_{22}H_{21}O_3S_2$	66.47 66.35	5.32 5.19	16.13 16.31	3060, 2960, 1576, 1485, 1463, 1389, 1277, 1255, 1215, 1160, 1094, 1064, 1043, 1030, 995, 763, 650	1.35 (d, 6H, $CH(CH_3)_2$), 2.35 (s, 3H, CH_3), 3.10 (hept, 1H, $CH(CH_3)_2$), 7.09-7.60 (m, 6H, ArH), 7.72-8.20 (m, 4H, ArH)
7i	260-262	$C_{22}H_{20}O_3S_2$	66.63 66.57	5.08 5.11	16.17 16.22	3025, 2960, 1588, 1570, 1455, 1391, 1259, 1215, 1089, 1064, 1037, 1022, 931, 756, 730, 650	1.31 (s, 9H, $C(CH_3)_3$), 7.15-7.57 (m, 7H, ArH), 7.76-8.21 (m, 4H, ArH)
7j	246-248	$C_{18}H_{12}O_3S_2$	63.51 63.49	3.55 3.52	18.84 18.83	3070, 1467, 1488, 1492, 1250, 1233, 1095, 1076, 1052, 1045, 804, 765, 660	7.05-7.55 (m, 8H, ArH), 7.81-8.17 (m, 4H, ArH)

[a] From a mixture of methylene chloride and *n*-hexane. [b] The ir were recorded in a potassium bromide pellet.

lytical, ir, and ^{1}H nmr spectroscopic data of **8a-d** are summarized in Table 12.

Some Electrophilic Substitution Reactions (Bromination, Acetylation, and Nitration).

Treatment of compound **5f** (R^2 = R^3= H, R^4 = $C(CH_3)CH_2CH_3$) with bromine (1.239 mmoles) in acetic acid for 7 hours at 60° gave monobromo-compounds **9** and **10** in 22% and 69% yields, respectively (Scheme 1).

Acetylation of compound **5f** with acetyl chloride in the presence of aluminum chloride in carbon disulfide for 1.5 hours at 0° gave a single acetylated compound **13** in 58% yield along with a complex mixture, whereas the reaction of compound **5a** (R^2 = R^3 = H, R^4 = CH_3) under the same conditions gave two acetylated compounds **15** and **16** together with a complex mixture. Treatment of compounds **9**, **10**, and **13** with *m*-chloroperbenzoic acid (6 equivalents) in methylene chloride gave the corresponding disulfones **11**, **12**, and **14**. The structure of compounds **9**, **10**, and **13** were determined on the basis of the ir, ^{1}H nmr data and 2D spectra of compounds **11**, **12** and **14** as well as the spectroscopic data and elemental analyses of compounds **9**, **10** and **13**.

Table 7

Crystal and Refinement Parameters for Compound **7b**

Molecular Formula	$C_{22}H_{20}O_3S_2$
Molecular weight	396.5
Color	Colorless
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	8.152 (1)
b, Å	10.799 (2)
c, Å	11.234 (1)
α, deg	94.41 (1)
β, deg	93.86 (1)
γ, deg	96.28 (1)
V, Å^3	969.1 (3)
Z	2
ρ calc. g. cm^{-3}	1.36
Crystal size, mm	0.15 x 0.69 x 1.00
Scan type	w/2 θ
μ ($M_oK\alpha$)	2.7
N_b of measured reflections	3469
N_b of reflections used $F_o > 3\sigma$ (F_o)	2760
R	0.074
R_w	0.076
Diffractometer	Enraf-Nomius CAD 4

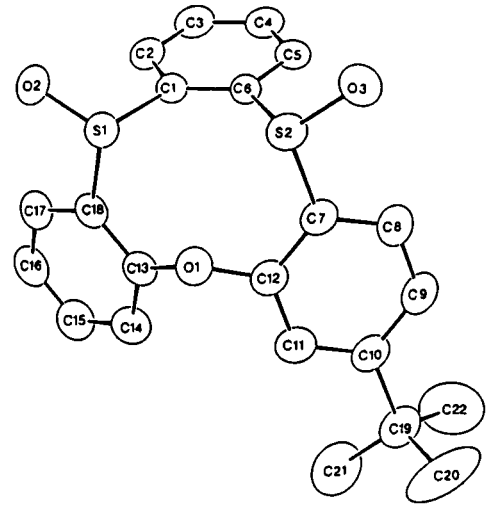


Figure 1. Molecular structure of compound **7b** with the atomic numbering scheme.

Nitration of **5f** with concentrated nitric acid in acetic acid for 3 hours at 50° gave a nitro compound **17**, a disulfoxide **7e**, and monosulfoxide **18** in 15, 22 and 16% yields, respectively. In the case of the compound **18**, it has not been established which sulfur atom of compound **5f** was oxidized to a sulfinyl group.

Table 8

Positional and Equivalent Isotropic Thermal Parameters of Nonhydrogen Atoms for **7b**

Atom	x	y	z	B_{eq} (Å^2)	Atom	x	y	z	B_{eq} (Å^2)
S1	0.3407	0.2526	0.7454	3.30	C10	0.7633	0.1523	0.2931	3.53
S2	0.6599	0.0998	0.6791	3.58	C11	0.6115	0.1725	0.3354	3.49
O1	0.4318	0.1786	0.5022	3.64	C12	0.5853	0.1666	0.4546	3.09
O2	0.2421	0.3116	0.8409	4.55	C13	0.3645	0.2924	0.5090	3.16
O3	0.8015	0.0403	0.7252	5.29	C14	0.3406	0.3546	0.4121	4.40
C1	0.5527	0.3240	0.7873	2.77	C15	0.2621	0.4687	0.4314	4.52
C2	0.5765	0.4433	0.8562	3.39	C16	0.2070	0.5099	0.5393	4.25
C3	0.7379	0.4989	0.8953	3.94	C17	0.2283	0.4435	0.6359	3.89
C4	0.8720	0.4345	0.8645	4.01	C18	0.3081	0.3384	0.6183	3.27
C5	0.8467	0.3142	0.7978	3.46	C19	0.7941	0.1537	0.1592	4.34
C6	0.6863	0.2597	0.7581	2.70	C20	0.7777	0.0170	0.0971	9.1
C7	0.7076	0.1352	0.5328	3.29	C21	0.6718	0.2315	0.1003	8.8
C8	0.8598	0.1146	0.4921	4.42	C22	0.9699	0.2171	0.1495	8.6
C9	0.8890	0.1254	0.3731	4.63					

Table 9

Selected Bond Distances (Å) for **7b**

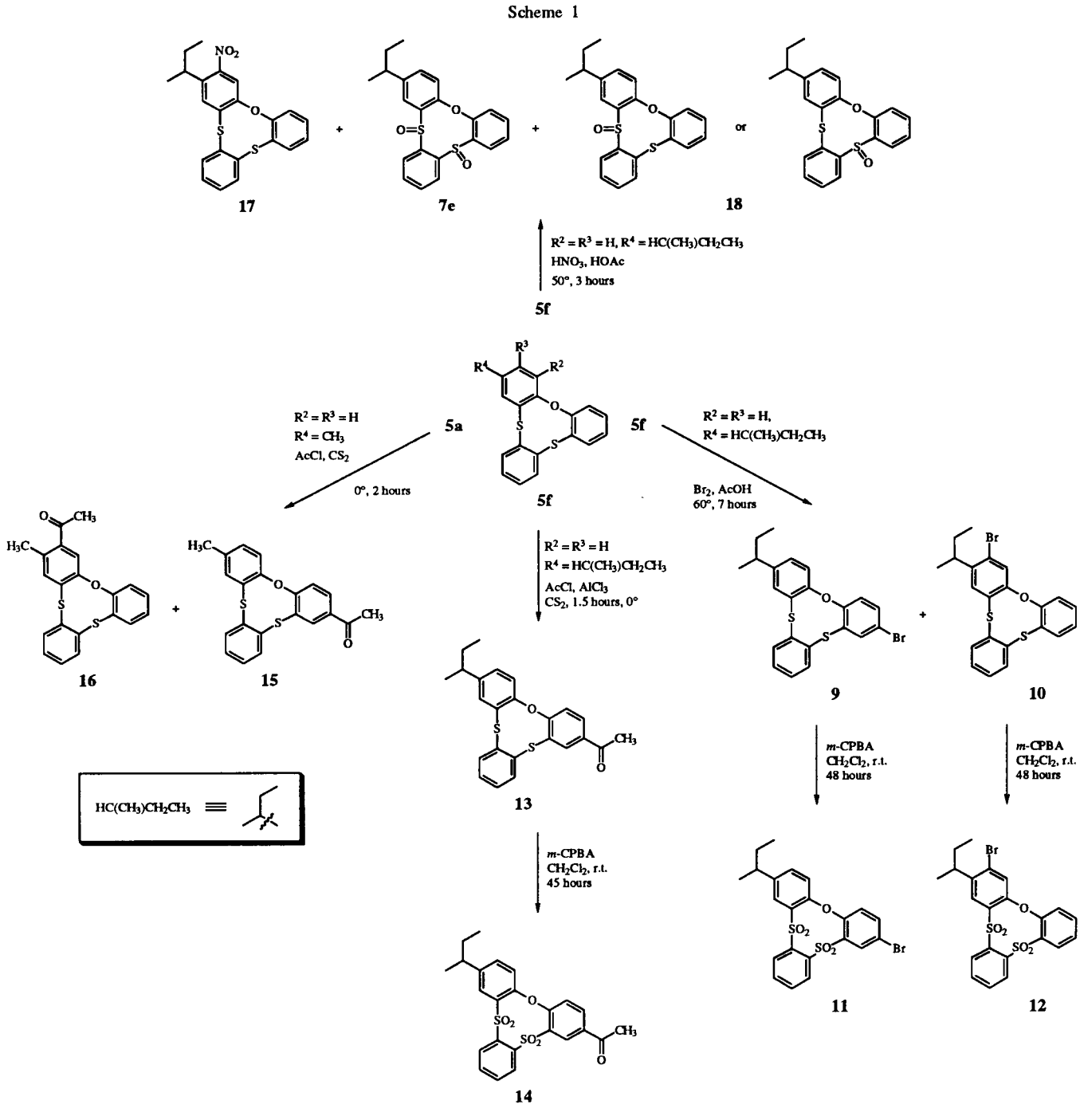
Atom 1	Atom 2	Distance
O2	S1	1.494
C1	S1	1.815
O3	S2	1.481
S2	C6	1.807
S1	C18	1.807
S2	C7	1.798
C12	O1	1.404
O1	C13	1.394
C1	C6	1.387
C7	C12	1.387
C10	C19	1.543
C13	C8	1.374

The structure of compound **17** was determined on the basis of spectroscopic data and elemental analyses.

Discussion.

Treatment of 5-(2-hydroxyaryl)thiantreniumyl perchlorates **1** (R^1 = OH) with sodium hydride in tetrahydrofuran at reflux afforded cyclic 9-membered dithiaoxa compounds in excellent yields. These results seem to be remarkable in view of the formation of 1,4,7-dithiaoxacyclononane in 6% yield [6] which is the only cyclic 9-membered dithiaoxa compound reported. The mechanism of formation of compounds **5** might be explained on the basis of an intramolecular nucleophilic attack of the phenoxide ion **22** at the ipso position of the thianthrene

Scheme 1



ring **22**, followed by a bond cleavage between the trivalent sulfur cation and the carbon atom of the ipso-position involving either a Meisenheimer complex intermediate **23a** [7] or a direct displacement of sulfide without involvement of the aromatic π electrons (**23b**) [8] as proposed for the Smiles rearrangement and 2,3,8,9-dibenzo-5,6-(substituted)benzo-1,4-dithio-7-azacyclonona-2,5,8-trienes [5] (Scheme 2). The formation of a sulfurane by interaction between the oxygen atom of the phenoxide ion and the trivalent sulfur cation of **22** is unlikely because of the unfavorable geometrical situation as described for the nitrogen analogs [5]. However one cannot rule out the involvement of a radical mechanism associated with an intramolecular electron transfer between the phenoxide ion and the trivalent sulfur cation, leading to diradical **24**. Compounds **5** might be formed by coupling of diradical **25** generated by the orbital reorganization of sulfuranyl radical **24**.

Table 10
Selected Bond Angles (degrees) for **7b**

Atom 1	Atom 2	Atom 3	Angle
O2	S1	C1	105.1
C1	S1	C18	95.6
O3	S2	C6	105.8
C6	S2	C7	97.7
C12	O1	C13	120.5
S1	C1	C2	117.4
S2	C6	C1	122.2
S2	C7	C8	119.7
O1	C12	C7	115.3
O1	C13	C14	124.3
S1	C18	C13	120.2
O2	S1	C18	105.5
O3	S2	C7	106.1
S1	C1	C6	121.6
S2	C6	C5	117.5
S2	C7	C12	120.3

Table 11
Reaction Conditions and Yields of Compounds **8**

Compound	mmole	*m*-CPBA [a] mmoles	CH_2Cl_2 [b] ml	Time hours	Yield	%
5f	0.121	0.724	20	48	**8a**	100
5g	0.198	1.19	25	48	**8b**	99
5h	0.178	1.08	20	20	**8c**	100
5i	0.176	1.06	20	43	**8d**	99

[a] *m*-Chloroperbenzoic acid. [b] Methylene chloride.

In order to ascertain the possible involvement of a radical mechanism, the reaction of **1c** ($R^2 = R^3 = H$, $R^4 = C(CH_3)_3$) with sodium hydride was carried out in the presence of tributyltin hydride at reflux under a nitrogen atmosphere. From the reaction were isolated compounds **5c**, **6**, and 2'-hydroxy-5'-*t*-butylphenylthiodiphenyl sulfide (**26**). The yields of the three compounds depends to some extent on the concentration of tributyltin hydride. The results are summarized in Table 13.

Noteworthy is the isolation of compound **26**, which has never been isolated in the absence of tributyltin hydride under the same conditions. The yield of compound **26** increased somewhat when the concentration of tributyltin hydride was increased two-fold (entry 2 and 3), whereas a large excess of tributyltin hydride did not increase the yield of compound **26** very much (entry 4). At the same time, the yield of compound **5c** decreased successively from 50% to 13% with the increase of the concentration of tributyltin hydride (entries 1-4). The decrease in the yields of **5c** along with the increase in the yields of compounds **26** with the increase in the concentration of trybutyltin hydride coupled with the non-formation of compounds **26** in the absence of tributyltin hydride reagent suggests the involvement of a radical mechanism.

Abstraction of a hydrogen atom by the phenoxy radical of diradical **24**, followed by an orbital reorganization of the sulfuranyl radical **27** would give arylthiophenyl radical **28**, which then abstracts a hydrogen atom to give compound **26**. When the same reaction was carried out in the presence of tributyltin deuteride under the same conditions, a mixture consisting of compounds **26**, **29**, **30**, and **31** was isolated and was subjected to mass spectral analysis. Abundances of molecular ion (M^+), ($M^+ +1$), and ($M^+ +2$) ions of compound **26** and those of the corresponding

Table 12
Physical, Analytical, ir, and ^1H nmr Spectroscopic Data of Compounds **8**

Compound	Mp °C	Molecular Formula	Analysis % Calcd./Found C	H	S	ir [c] (cm^{-1})	^1H nmr ($CDCl_3$) δ (ppm)
8a	208 - 209 [a]	$C_{22}H_{20}O_5S_2$	61.66 61.47	4.70 4.59	14.96 14.83	3100, 2955, 1588, 1477 1446, 1333, 1310, 1268 1235, 1168, 1150, 1072 710, 661	0.85 (t, 3H, CH_2CH_3), 1.26 (d, 3H, $CHCH_3$), 1.62 (quint, 2H, $CHCH_2CH_3$), 2.62 (sext, 1H, $CH(CH_3)CH_2$), 7.07-8.46 (m, 11H, ArH)
8b	209 - 210 [b]	$C_{23}H_{22}O_5S_2$	64.42 64.39	5.01 5.06	14.49 14.38	3100, 2990, 1588, 1477 1445, 1338, 1310, 1270 1235, 1172, 1147, 1108 1073, 770, 705, 660	0.68 (t, 3H, CH_2CH_3), 1.29 (s, 6H, $2CH_3$), 1.59 (q, 2H, CH_2CH_3), 7.02-8.45 (m, 11H, ArH)
8c	258-259	$C_{20}H_{16}O_5S_2$	59.98 59.84	4.03 4.21	16.01 16.22	3100, 2940, 1577, 1497 1469, 1448, 1385, 1369 1335, 1304, 1261, 1215 1140, 1135, 1107, 1021 775, 720, 695, 665	2.28 (s, 6H, $2CH_3$), 6.94-8.42 (m, 10H, ArH)
8d	245 - 247 [a]	$C_{22}H_{21}O_5S_2$	61.51 61.45	4.93 4.58	14.93 14.79	3100, 2975, 1588, 1472 1448, 1338, 1310, 1269 1218, 1174, 1150, 1108 1075, 770, 703, 659	1.24 (d, 6H, $CH(CH_3)_2$), 2.38 (s, 3H, CH_3), 3.09 (hept, 1H, $CH(CH_3)_2$), 6.96-8.48 (m, 10H, ArH)

[a] From a mixture of methylene chloride and *n*-hexane. [b] From methanol. [c] The ir were recorded in a potassium bromide pellet.

Scheme 2

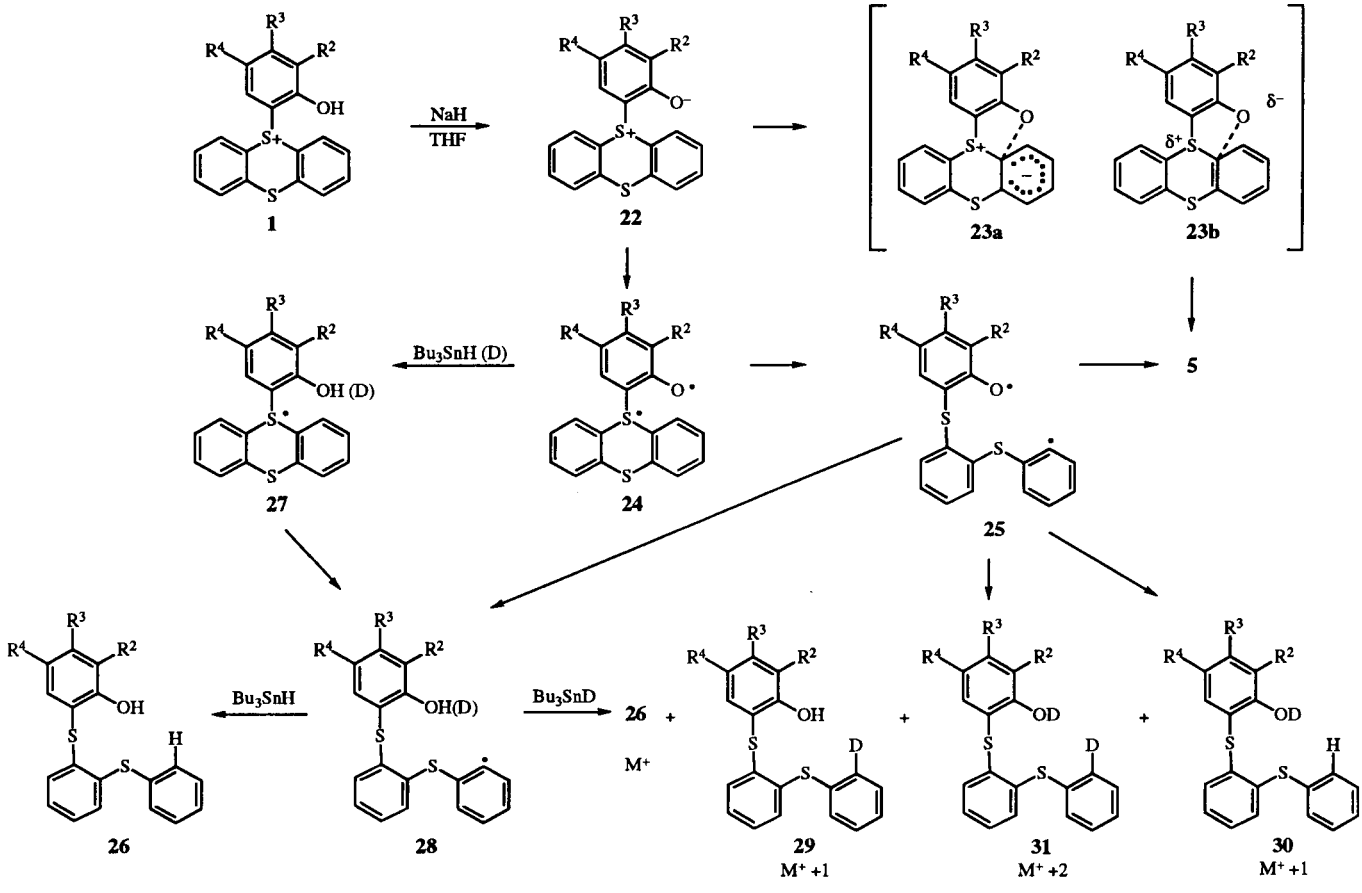


Table 13

Reaction Conditions and Yields of Compounds **5c**, **26**, and **6**

Entry	Compound **1c** mmole	NaH [a] equiv	Bu_3SnH [b] equiv	THF [c] ml	Time hours	Yield % **5c**	**26**	**6**
1	0.645	3	1.5	50	23	50	25	10
2	0.645	3	3	50	23	34	25	11
3	0.645	3	6	50	23	28	40	10
4	0.645	3	12	50	23	13	42	21
5	0.645	1	1	50	23	48	8	8

[a] Sodium hydride. [b] Tributyltin hydride. [c] Tetrahydrofuran.

ions obtained from the mixture are summarized in Table 14. Table 14 shows that the mixture obtained from the reaction with tributyltin deuteride exhibited higher abundances in both of M^+ +1, and M^+ +2 ions, compared with those of the corresponding ions from compound **26**. The result is indicative of deuterium atom incorporation by radical species **24**, **25**, and/or **27**. At this moment, it is uncertain whether M^+ +1 ion originated from compound **29** or from compound **30**.

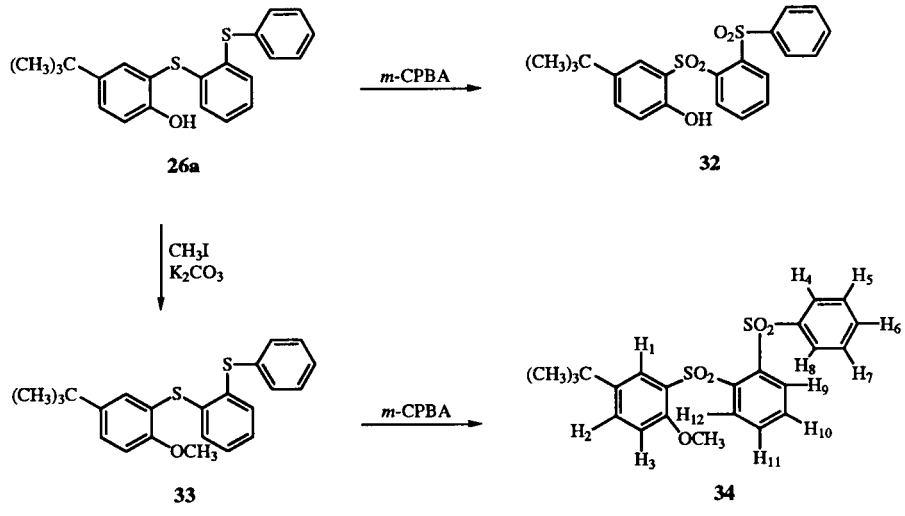
Table 14

Abundances of molecular ion M^+, $M^+ + 1$, and $M^+ + 2$ ions

	M^+	M^++1	M^++2
From compound **26**	100	23.65	11.83
From the mixture	100	35.17	15.69

The structure of compound **26** was determined on the basis of the spectroscopic, mass spectral data and elemental analyses. The structure was further confirmed by 2D ^1H nmr spectroscopy. Compound **26a** ($R^2 = R^3 = H$, $R^4 = C(CH_3)_3$) was oxidized by *m*-chloroperoxybenzoic acid to give disulfone **32** whose ^1H nmr (300 MHz, deuteriochloroform) spectrum did not allow sufficient resolution to assign the aromatic protons. However, the assignments were possible by transformation of **26a** to disulfone **34**. Figure 3 shows the 2D ^1H nmr spectrum of disulfone **34**. The ^1H nmr spectral data are tabulated in Table 15.

Compounds **26a**, **32-34**



26a **32** **33** **34**

Table 15

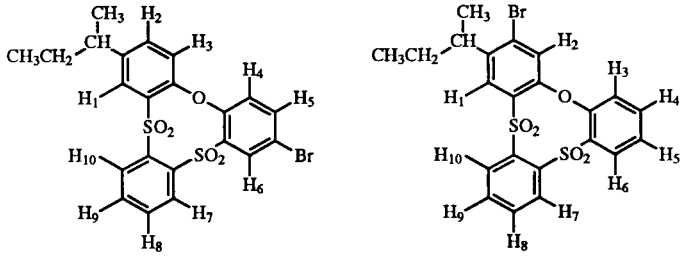
^{1}H nmr (300 MHz, deuteriochloroform) Spectral Data of Compound **34**

δ (ppm)	Assignment
1.39 (s, 9H)	$C(CH_3)_3$
3.59 (s, 3H)	CH_3O
6.80 (d, 1H, J = 8.5 Hz)	H_3 coupled with H_2
7.47-7.58 (m, 4H)	H_2, H_5, H_6, H_7
7.79-7.81 (m, 2H)	H_{10} or H_{11} coupled with H_9 or H_{11}
7.91 (d, 2H, J = 7.9 Hz)	H_4, H_8 coupled with H_5 and H_7, respectively
8.31(d, 1H, J = 2.1 Hz)	H_1 coupled with H_2
8.44 (m, 1H)	H_9 or H_{12} coupled with H_{10} or H_{11}, respectively
8.59 (m, 1H)	H_9 or H_{12} coupled with H_{10} or H_{11}, respectively

Bromination.

The mixture of bromo compounds **9** and **10** was separated by a seven-fold preparative thin layer chromatography using a mixture of *n*-hexane and ethyl acetate (10:1) as an eluent. The structures of compounds **9** and **10** were determined on the basis of mass spectral data and elemental analyses together with 2D ^{1}H nmr spectra of disulfones **11** and **12**. The ^{1}H nmr spectral data for disulfones **11** and **12** are tabulated in Tables 16 and 17, respectively.

Compounds **11**, **12**



11 **12**

It is of interest that disulfone **12** bearing a bromine atom *ortho* to a secondary butyl group as well as *meta* to a phenoxy group is the major product (69%) and disulfone **11** bearing a bromine atom *para* to a phenoxy group is the minor product (22%). These results may indicate that an electron-donating effect of the secondary butyl group is stronger than that of the phenoxy group in these 9-membered cyclic dithiaoxa compounds because of an unfavor-

Table 16

^{1}H nmr (300 MHz, deuteriochloroform) Spectral Data of Compound **11**

δ (ppm)	Assignment
0.85 (t, 3H, J = 7.4 Hz)	CH_3CH_2
1.27 (d, 3H, J = 6.8 Hz)	CH_3CH
1.63 (quint, 2H, J = 7.4 Hz)	CH_3CH_2CH
2.74 (sext, 1H, J = 6.8 Hz)	CH_3CHCH_2
7.01 (d, 1H, J = 8.8 Hz)	H_4 coupled with H_5
7.16 (d, 1H, J = 8.3 Hz)	H_3 coupled with H_2
7.42 (dd, 1H, J = 8.5, 1.7 Hz)	H_2 coupled with H_1 and H_3
7.60 (dd, 1H, J = 8.5, 1.6 Hz)	H_5 coupled with H_4 and H_6
7.76-7.86 (m, 2H)	H_8, H_9
7.94 (d, 1H, J = 1.8 Hz)	H_1 coupled with H_2
8.24 (m, 2H)	H_7 or H_{10} coupled with H_8 and H_9, respectively H_6 signal is included.
8.48 (d, 1H, J = 7.63 Hz)	H_7 or H_{10} coupled with H_8 and H_9, respectively

able overlap between nonbonding orbitals on the oxygen atom and the pi orbitals of the phenyl ring, which results from severe ring strain of the rigid molecules. These results are in contrast with the predominant formation of *p*-bromodiphenyl ether compared with *o*-bromo analogues in the bromination of diphenyl ether under similar conditions [9].

Table 17

^{1}H nmr (300 MHz, deuteriochloroform) Spectral Data of Compound **12**

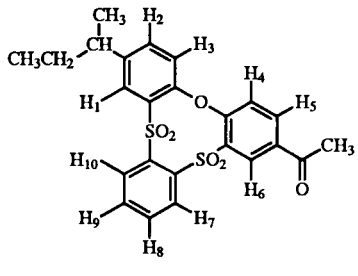
δ (ppm)	Assignment
0.92 (t, 3H, J = 7.4 Hz)	CH_3CH_2
1.26 (d, 3H, J = 6.8 Hz)	CH_3CH
1.60 (quint, 2H, J = 7.2 Hz)	CH_3CH_2CH
3.14 (sext, 1H, J = 6.7 Hz)	CH_3CHCH_2
7.22 (d, 1H, J = 8.1 Hz)	H_3
7.38 (s, 1H)	H_2
7.45 (dt, 1H, J = 7.7, 1.5 Hz)	H_5 coupled with H_6 and H_4, which is coupled with H_3
7.60 (dt, 1H, J = 7.7, 1.4 Hz)	H_4 coupled with H_3 and H_5, which is coupled with H_6
7.76-7.93 (m, 2H)	H_8 and H_9 coupled with H_7 and H_{10}
7.94 (s, 1H)	H_1
8.15 (dd, 1H, J = 8.1, 1.5 Hz)	H_6 coupled with H_4 and H_5
8.33-8.38 (m, 2H)	H_7 and H_{10} coupled with H_8 and H_9

Acetylation.

In contrast, acetylation of compound **5f** with acetyl chloride in the presence of aluminum chloride in carbon disulfide gave a single acetylated compound **13** (58%) which has an acetyl group in the *para* position of the phenoxy group. This might be explained by steric hindrance preventing the bulky acetyl-aluminum complex from approaching the *ortho* position of the secondary butyl group. In fact the reaction of compound **5a** having a less bulky methyl group than the secondary butyl group of **5f** under the same conditions gave two acetylated compounds **15** (33%) and **16** (18%) with some analogy to compounds **11** and **12**, respectively. Presumably even the methyl group exerts some steric hindrance effect upon the *ortho* position, leading to *para* product **16** as a minor product.

The orientation of the acetyl group in compound **13** was determined on the basis of 2D ^{1}H nmr spectral data of the disulfone **14**. The ^{1}H nmr spectral data of disulfone **14** are tabulated in Table 18.

Compound **14**



14

Table 18

^{1}H nmr (300 MHz, deuteriochloroform) Spectral Data of Compound **14**

δ (ppm)	Assignment
0.81 (t, 3H, J = 7.4 Hz)	CH_3CH_2
1.27 (d, 3H, J = 6.8 Hz)	CH_3CH
1.61 (quint, 2H, J = 7.4 Hz)	CH_3CH_2CH
2.61 (*s*, 3H)	CH_3CO
2.62 (sext, 1H, J = 6.8 Hz)	CH_3CHCH_2
7.17 (d, 1H, J = 8.7 Hz)	H_4 coupled with H_5
7.26 (d, 1H, J = 8.1 Hz)	H_3 coupled with H_2
7.48 (dd, 1H, J = 8.1, 2.1 Hz)	H_2 coupled with H_3 and H_1
7.75 (t, 1H, J = 7.5, 2.1 Hz)	H_9 coupled with H_8 and H_{10}
7.86 (t, 1H, J = 8.1, 2.1 Hz)	H_8 coupled with H_9 and H_7
7.95 (d, 1H, J = 2.1 Hz)	H_1 coupled with H_2
8.10 (dd, 1H, J = 8.7, 2.1 Hz)	H_5 coupled with H_4 and H_6
8.17 (d, 1H, J = 8.1 Hz)	H_{10} coupled with H_9
8.59 (d, 1H, J = 8.1 Hz)	H_7 coupled with H_8
8.68 (d, 1H, J = 2.1 Hz)	H_6 coupled with H_5

Nitration.

Treatment of **5f** with concentrated nitric acid in acetic acid at 50° gave a single nitro compound **17** (15%), disulfoxide **7e** (22%), and a monosulfoxide **18** (16%). The structure of compound **17** was determined on the basis of spectroscopic data and elemental analyses. In addition, the orientation of the nitro group was established by comparing the ^{1}H nmr spectrum of **17** with those of analogous type compounds **10** and **16**. The results in which a single nitro compound **17** having a nitro group *ortho* to the secondary butyl group are consistent with those in which compounds **10** and **16** having a bromine atom and a methyl group *ortho* to the secondary butyl and methyl groups, respectively are predominantly formed.

Monosulfoxide **18** shows a peak at 1070 cm^{-1}, indicative of the presence of S=O group. However, it is uncertain which sulfur atom of **5f** is oxidized. Further study is needed to delineate the regiochemistry for the formation of monosulfoxide **18**. The formation of monosulfoxide **18** and disulfoxide **7e** might be explained on the basis of the same mechanism as proposed by Olah, *et al.* [10] on the oxidation of sulfides by nitronium tetrafluoroborate in the presence of 18-crown-6. This was confirmed by treatment of **5f** with nitronium tetrafluoroborate under the same conditions; tlc (*n*-hexane:benzene = 2:1) shows the spots corresponding to compounds **18** (R_f = 0.50) and **7e** (R_f = 0.44).

EXPERIMENTAL

General Procedure for the Preparation of 5-(2-Hydroxyaryl)thianthreniumyl Perchlorates **1a-k** [11].

To a solution of thianthrene cation radical perchlorate (3 mmoles) in dried acetonitrile (50 ml) was added the phenol derivative (1.5 mmoles). The mixture was stirred for an appropriate time and worked up as described in the literature [11]. Consult

Table 1 for the reaction times, yields, and analytical data and Table 2 for ir and ^{1}H nmr spectroscopic data of compounds **1**.

General Procedure for the Synthesis of 2,3,8,9-Dibenzo-5,6-(substituted)-benzo-1,4-dithio-7-oxacyclonona-2,5,8-trienes **5**.

To a solution of compounds **1** (1.78-0.35 mmole) in dried tetrahydrofuran (50-80 ml) was added sodium hydride (5.4-1.2 mmoles). The mixture was heated at reflux and then quenched with water (1 ml), which was extracted with methylene chloride (3 x 30 ml). The extracts were dried over magnesium sulfate. Evaporation of the solvent *in vacuo* gave a residue, which was chromatographed on silica gel (1.5 x 10 cm). Elution with *n*-hexane gave thianthrene (**6**). Subsequcnt elution with carbon tetrachloride gave **5**. Consult Table 3 for reaction conditions and yields of compounds **5** and **6**, and Table 4 for physical, analytical, ir, and ^{1}H nmr spectroscopic data of compounds **5**.

General Procedure for the Synthesis of 2,3,8,9-Dibenzo-5,6-(substituted)benzo-1,4-dithio-7-oxacyclonona-2,5,8-triene 1,4-Dioxides **7**.

To a solution of compounds **5** (0.062-0.306 mmole) in dried methylene chloride (20 ml) was added dropwise sulfuryl chloride (0.140-0.674 mmole) at room temperature. The mixture was stirred for two hours, followed by addition of ethanol (3 ml). After additional stirring was continued, the mixture was neutralized with sodium bicarbonate, followed by extraction with methylene chloride (3 x 30 cm). The combined extracts were washed with water (2 x 20 cm) and dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel column (1.5 x 10 cm). Consult Table 7 for reaction condition and yields of compounds **7** and Table 8 for physical, analytical, ir, and ^{1}H nmr spectroscopic data of compound **7**.

General Procedure for the Synthesis of 2,3,8,9-Dibenzo-5,6-(substituted)benzo-1,4-dithio-7-oxacyclonona-2,5,8-triene 1,1,4,4-Tetraoxides **8**.

To a solution of compounds **5** (0.121-0.198 mmole) in methylene chloride (20-25 ml) was added *m*-chloroperbenzoic acid (0.72-1.19 mmoles) at room temperature. The mixture was stirred for an appropriate time, followed by washing with saturated aqueous sodum bicarbonate (3 x 30 ml) and water (2 x 20 ml) in a sequence. The organic layer was dried over magnesium sulfate. Evaporation of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (3 x 10 cm).

Consult Table 13 for reaction condition and yields of compounds **8** and Table 14 for physical, analytical, ir, and ^{1}H nmr spectroscopic data of compounds **8**.

General Procedure for the Reaction of **1c** with Sodium Hydride in the Presence of Tri-*n*-butyltin Hydride.

To a solution of tri-*n*-butyltin hydride in dry tetrahydrofuran (50 ml) was added sodium hydride under a nitrogen atmosphere, which was heated for 20 minutes at reflux, followed by addition of compound **1c**. The mixture was refluxed for 23 hours and then cooled to room temperature. The solvent was removed *in vacuo* and the residue was extracted with methylene chloride (3 x 30 ml). The combined extracts were washed with water, followed by drying over magnesium sulfate. Removal of the solvent, followed by chromatography on a silica gel column (3 x 5 cm) using *n*-hexane (50 ml) as an eluent gave a mixture of tributyltin hydride and hexabutylditin. Elution next with the same solvent (70 ml) gave thianthrene (**6**). Subsequent elution with carbon tetrachloride (90 ml) gave **5c**. Elution with methylene chloride (50 ml) gave 5'-*t*-butyl-2'-hydroxyphenylthiodiphenyl sulfide (**26c**) as a liquid; ^{1}H nmr (deuteriochloroform): δ 1.25 (s, 9H, $C(CH_3)_3$), 6.13 (s, 1H, OH), 6.65-7.56 (m, 12H, ArH): ir (neat) 3430, 1579, 1570, 1501, 1482, 1458, 1439, 1362, 1284, 1265, 1249, 1209, 1179, 1035, 1023, 825, 745, 688 cm^{-1}; ms: m/z 366 (M^+, 100%).

Anal. Calcd. for $C_{22}H_{22}OS_2$: C, 72.09; H, 6.05; S, 17.49. Found: C, 72.17; H, 6.09; S, 17.51.

Consult Table 15 for reaction conditions and yields of compounds **5c**, **26c**, and **6**.

Reaction of **1c** with Sodium Hydride in the Presence of Tri-*n*-butyltin Deuteride.

From the reaction of **1c** (200 mg, 0.430 mmole) with sodium hydride (31 mg, 1.29 mmoles) in the presence of tri-*n*-butyltin deuteride (1.13 g, 3.88 mmoles) in dry tetrahydrofuran (40 ml) was obtained **6** (15 mg, 16%), **5c** (22 mg, 14%), and a mixture of **26c, 29,** and **31** (61 mg).

Reaction of 5,6-{3-(2-Butyl)benzo}-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**5f**) with Bromine.

To a solution of **5f** (452 mg, 1.24 mmoles) in acetic acid (50 ml) bromine (1.239 mmoles) was added dropwise at room temperature. The mixture was heated for 7 hours at 60°, followed by cooling to room temperature. After being treated with saturated sodium thiosulfate solution, the mixture was extracted with methylene chloride (3 x 30 ml), which was washed with water (2 x 20 ml), followed by drying over magnesium sulfate. Evaporation of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (1.0 x 10 cm). Elution with carbon tetrachloride (50 ml) gave a mixture showing many spots on the thin layer chromatogram. Subsequent elution with the same solvent (50 ml) gave a mixture (270 mg), which was separated by a repeated preparative thin layer chromatography (seven times) to give 60 mg (0.135 mmoles, 22%) of 5,6-{3-(2-butyl)benzo}-8,9-(4-bromobenzo)-2,3-benzo-1,4-dithio-7-oxacyclononan-2,5,8-triene (**9**); R_f = 0.23 (*n*-hexane), liquid; ^{1}H nmr (deteriochloroform): δ 0.80 (t, 3H, CH_3CH_2), 1.19 (d, 3H, CH_3CH), 1.52 (quint, 2H, CH_3CH_2CH), 2.53 (sext, 1H, CH_3CHCH_2), 6.79-7.62 (m, 10H, ArH); ir (neat): 1464, 1374, 1256, 1230, 1075, 759 cm^{-1}; ms: m/z 443 (M^+, 10%).

Anal. Calcd. for $C_{22}H_{19}BrOS_2$: C, 59.59; H, 4.32; S, 14.46. Found: C, 59.53; H, 4.51; S, 14.33.

5,6-{3-(2-Butyl-4-bromo)benzo}-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**10**).

This compound was obtained in 69% yield (185 mg) which was recrystallized from a mixture of *n*-hexane and methylene chloride, R_f = 0.28 (*n*-hexane), mp 114-116°; ^{1}H nmr (deuteriochloroform): δ 0.80 (t, 3H, CH_3CH_2), 1.19 (d, 3H, CH_3CH), 1.52 (quint, 2H, CH_3CH_2CH), 2.53 (sext, 1H, CH_3CHCH_2), 6.79-7.62 (m, 10H, ArH); ir (neat): 1573, 1460, 1380, 1364, 1258, 1236, 1205, 1083, 1070, 1039, 925 889, 820, 781, 760, 710 cm^{-1}; ms: m/z 443 (M^+, 13.4%).

Anal. Calcd. for $C_{22}H_{19}BrOS_2$: C, 59.59; H, 4.32; S, 14.46. Found: C, 59.64; H, 4.40; S, 14.51.

Preparation of 5,6-{3-(2-Butyl)benzo}-8,9-(4-bromobenzo)-2,3-benzo-1,4-dithio-7-oxacyclonona-2,5,8-triene 1,1,4,4-Tetraoxide (**11**).

From the reaction of **9** (34 mg, 0.077 mmole) with *m*-chloroperbenzoic acid (80 mg, 0.464 mmole) in dried methyl-

ene chloride (15 ml) for 48 hours compound **11** (37 mg, 95%) was obtained which was recrystallized from a mixture of methylene chloride and *n*-hexane, mp 223-224°; Consult Table 16 for ^{1}H nmr spectroscopic data; ir (potassium bromide): 3070, 2975, 2950, 2890, 1464, 1374, 1256, 1230, 1075, 759 cm^{-1}; ms: m/z 506 (M+, 13%), 508 (M$^+$+1, 7%).

Anal. Calcd. for $C_{22}H_{19}BrO_5S_2$: C, 52.08; H, 3.77; S, 12.64. Found: C, 52.14; 3.81; S, 12.73.

Preparation of 5,6-{3-(2-Butyl)benzo}-(4-bromo)-2,3,8,9-dibenzo-2,3-benzo-1,4-dithio-7-oxacyclonona-2,5,8-triene 1,1,4,4-Tetraoxide (**12**).

From the reaction of **10** (68 mg, 0.153 mmole) with *m*-chloroperbenzoic acid (158 mg, 0.916 mmole) in dried methylene chloride (20 ml) for 48 hours compound **12** (75 mg, 97%) was obtained which was recrystallized from a mixture of methylene chloride and *n*-hexane, mp 219-221°; consult Table 17 for ^{1}H nmr spectroscopic data; ir (potassium bromide) 3065, 2975, 2940, 1573, 1460, 1380, 1364, 1258, 1236, 1205, 1083, 1070, 1039, 925, 889, 820, 781, 760, 710 cm^{-1}; ms: m/z 506 (M$^+$, 3%), 508 (M$^+$+1, 7%).

Anal. Calcd. for $C_{22}H_{19}BrO_5S_2$: C, 52.08; H, 3.77; S, 12.64. Found: C, 52.17; H, 3.69; S, 12.58.

Reaction of **5f** with Acetyl Chloride.

To a solution of **5f** (273 mg, 0.749 mmole) in the presence of aluminum chloride (200 mg, 1.50 mmoles) in carbon disulfide (15 ml) at ice-water temperature was added dropwise acetyl chloride (118 mg, 1.503 mmoles). The mixture was stirred for 1.5 hours, followed by removal of the solvent. The residue was poured into 10% aqueous hydrochloric acid (25 ml) cooled at ice-water temperature, which was extracted with methylene chloride (3 x 30 ml). The extracts were washed with water (2 x 20 ml), followed by drying over magnesium sulfate. The solvent was evaporated *in vacuo* and the residue was chromatographed on a silica gel column (1.5 x 12 cm). Elution with a mixture of *n*-hexane and ethyl acetate (5:1, 50 ml) gave a mixture of compounds showing many spots on the thin layer chromatogram. Subsequent elution with the same solvent mixture (70 ml) gave 5,6-{3-(2-butyl)benzo}-8,9-(4-acetylbenzo)-2,3-benzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**13**) (177 mg, 58%), liquid; ^{1}H nmr (deuteriochloroform): δ 0.73 (t, 3H, C*H*$_3$CH$_2$), 1.15 (d, 3H, C*H*$_3$CH), 1.50 (quint, 2H, CH$_3$C*H*$_2$CH), 2.50 (s, 3H, C*H*$_3$CO), 2.49 (sext, 1H, CH$_3$C*H*CH$_2$), 6.79-7.29 (m, 6H, ArH), 7.29-7.59 (m, 2H, ArH), 7.71-8.03 (m, 2H, ArH); ir (neat): 1686, 1587, 1473, 1455, 1380, 1275, 1250, 1070, 760, 739 cm^{-1}; ms: m/z 406 (M$^+$, 86%), 377 (100%).

Anal. Calcd. for $C_{24}H_{22}O_2S_2$: C, 70.96; H, 5.45; S, 15.77. Found: C, 70.84; H, 5.41; S, 15.69.

Preparation of 5,6-(3-*sec*-Butylbenzo)-8,9-(4-acetylbenzo)-2,3-benzo-1,4-dithio-7-oxacyclonona-2,5,8-triene 1,1,4,4-Tetraoxide (**14**).

From the reaction of **13** (59 mg, 0.123 mmole) with *m*-chloroperbenzoic acid (127 mg, 0.736 mmole) in methylene chloride (20 ml) for 45 hours compound **14** (57 mg, 98%) was obtained which was recrystallized from a mixture of methylene chloride and *n*-hexane, mp 191-192°; consult Table 18 for ^{1}H nmr spectroscopic data; ir (neat): 1696, 1590, 1481, 1340, 1317, 1254, 1171, 1150, 1100, 1070, 744, 729, 713 cm^{-1}; ms: m/z 470 (M$^+$, 17%).

Anal. Calcd. for $C_{24}H_{22}O_6S_2$: C, 61.26; H, 4.71; S, 13.63. Found: C, 61.33; H, 4.82; S, 13.59.

Reaction of 5,6-(3-Methylbenzo)-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**5a**) with Acetyl Chloride.

To a solution of **5a** (201 mg, 0.623 mmole) in the presence of aluminum chloride (124 mg, 0.932 mmole) in carbon disulfide (50 ml) was added dropwise acetyl chloride (64 mg, 0.815 mmoles) at ice-water temperature. The reaction mixture was stirred for 2 hours and worked up as described in the reaction of **5f**. Chromatography on a silica gel column (1.5 x 12 cm) using a mixture of *n*-hexane and ethyl acetate (4:1, 30 ml) as an eluent gave a mixture of compounds (10 mg). Subsequent elution with the same solvent mixture (80 ml) gave a mixture, which was separated by the repeated preparative thin layer chromatography (seven times) using a mixture of *n*-hexane and ethyl acetate (10:1), affording 5,6-(3-methylbenzo)-8,9-(4-acetylbenzo)-2,3-benzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**15**), which was recrystallized from a mixture of methylene chloride and *n*-hexane, R_f = 0.45 (*n*-hexane:ethyl acetate = 5:1), mp 147-149°; ^{1}H nmr (deuteriochloroform): δ 2.27 (s, 3H, CH$_3$), 2.49 (s, 3H, CH$_3$CO), 6.90-8.00 (m, 10H, ArH): ir (neat): 1690, 1586, 1475, 1451, 1425, 1380, 1355, 1304, 1275, 1249, 1204, 1140, 1070, 970, 915, 900, 840, 760, 745 cm^{-1}; ms; m/z 364 (M$^+$, 100%).

Anal. Calcd. for $C_{21}H_{16}O_2S_2$: C, 69.20; H, 4.42; S, 17.59. Found: C, 69.15; H, 4.53; S, 17.49.

Continuous elution with the same solvent afforded 5,6-(3-methyl-4-acetylbenzo)-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**16**), which was recrystallized from a mixture of methylene chloride and *n*-hexane: R_f = 0.50 (*n*-hexane:ethyl acetate = 5:1), mp 102-103°; ^{1}H nmr (deuteriochloroform): δ 2.42 (s, 6H, CH$_3$, CH$_3$CO), 6.90-7.56 (m, 10H, ArH): ir (neat): 1588, 1465, 1450, 1358, 1255, 1221, 1200, 1184, 1100, 1071, 1043, 990, 950, 891, 804, 756, 741 cm^{-1}; ms: m/z 364 (M$^+$, 100%).

Anal. Calcd. for $C_{21}H_{16}O_2S_2$: C, 69.20; H, 4.42; S, 17.59. Found: C, 69.15; H, 4.53; S, 17.54.

Reaction of **5f** with Nitric Acid in Acetic Acid.

To a solution of **5f** (234 mg, 0.642 mmole) in acetic acid (20 ml) was added dropwise nitric acid (0.16 ml) at room temperature. The mixture was heated at 50° for 3 hours, followed by addition of water (100 ml), which was extracted with methylene chloride (3 x 30 ml). The combined extracts were washed with water (2 x 20 ml) and dried over magnesium sulfate. Chromatography on a silica gel column (1.5 x 12 cm) using a mixture of *n*-hexane and ethyl acetate (5:1) as an eluent gave a mixture, which was separated by the repeated preparative thin layer chromatography (seven times) using a mixture of *n*-hexane and ethyl acetate (2:1). 5,6-{3-(2-butyl)-4-nitro}benzo-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene (**17**) (40 mg, 15%), liquid; ^{1}H nmr (deuteriochloroform): δ 0.84 (t, 3H, C*H*$_3$CH$_2$), 1.22 (d, 3H, C*H*$_3$CH), 1.62 (quint, 2H, CH$_3$C*H*$_2$CH), 3.15 (sext, 1H, CH$_3$C*H*CH$_2$), 7.08-7.61 (m, 10H, ArH); ir (neat) 1520, 1464, 1344, 1260, 1234, 1208, 1070, 898, 760 cm^{-1}; ms: m/z 409 (M$^+$, 100%).

Anal. Calcd. for $C_{22}H_{19}NO_3S_2$: C, 64.52; H, 4.68; N, 3.42; S, 15.66. Found: C, 64.48; H, 4.57; N, 3.34; S, 15.59.

Continuous elution with the same solvent mixture gave 5,6-{3-(2-butyl)benzo}-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene 1,4-dioxide (**7e**) (55 mg, 22%) and 5,6-{3-(2-butyl)benzo}-2,3,8,9-dibenzo-1,4-dithio-7-oxacyclonona-2,5,8-triene *S*-oxide (**18**) (7 mg, 3%).

Single Crystal X-ray Analysis of **7b**.

Crystallographic and refinement parameters are summarized in Table 7.

The data were collected on an Enraf-Nomius CAD 4 diffractometer using graphite-monochromated M_o-Kα radiation. The structure was solved by direct methods and subsequent Fourier maps. Refinements were carried out by full least-squares techniques. Non-hydrogen atoms were anisotropically refined. Atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol **IV**, 1974. All calculations and drawings were performed using a Micro VAX II computer with the SDP system.

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