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Ring-opening reactions of 5-(aryl)thianthrenium bromides with aryl thiolates

Ding-Quan Qian,[1] Bo Liu,[1] Henry J. Shine,[1]* Ilse Y. Guzman-Jimenez[2] and Kenton H. Whitmire[2]

[1]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, USA
[2]Department of Chemistry, Rice University, Houston, Texas 77005, USA

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epoc ABSTRACT: A series of 5-(aryl)thianthrenium bromides (**6a–e**) with aryl (Ar) groups phenyl (**a**), *p*-tolyl (**b**), *p*-anisyl (**c**), *p*-chlorophenyl (**d**) and *p*-bromophenyl (**e**) was prepared by reaction of thianthrene 5-oxide with the appropriate Grignard reagent ArMgBr. Reactions of **6a–e** with aryl thiolates (Ar′SNa, Ar′ = phenyl, *p*-tolyl and *p*-chlorophenyl, **7a–c**) were carried out in MeCN at room temperature. Products from **6a–c** were a small amount of arene [benzene (**8a**) and toluene (**8b**)], and substantial amounts of ArSAr′ (**9**), thianthrene (Th) and a trisulfide, namely a 2-(ArS)-2′-(Ar′S)-diphenyl sulfide (**10**). Products from reactions of **6d,e** were smaller amounts of **9** and **10** but substantial amounts of 1,4-di(Ar′S)benzene (**11**) and a tetrasulfide (**12a–c**). The reactions that lead to products **9**–**12** are attributed to ligand coupling (LC) pathways in sulfuranes formed by attack of $Ar'S^-$ at the sulfonium S atom of **6**. In the formation of **11** and **12** the halogen atom (Cl, Br) is first displaced from **6d,e** by $Ar'S^-$, giving a new thianthrenium ion (**14**) from which sulfurane formation (**15**) follows. Products **10** and **12** result from opening of the thianthrenium ring of sulfuranes **13** and **15** through LC. Products were assayed with a combination of GC and isolation with TLC, and were identified with a combination of GC (authentic compounds), x-ray crystallography (**10a**), elemental analyses and high-resolution mass spectrometry. The reactions of **6** are compared with earlier reactions of 5-(alkoxy)-and 5-(alkyl)thianthrenium salts (**1** and **2**). Copyright © 2002 John Wiley & Sons, Ltd.
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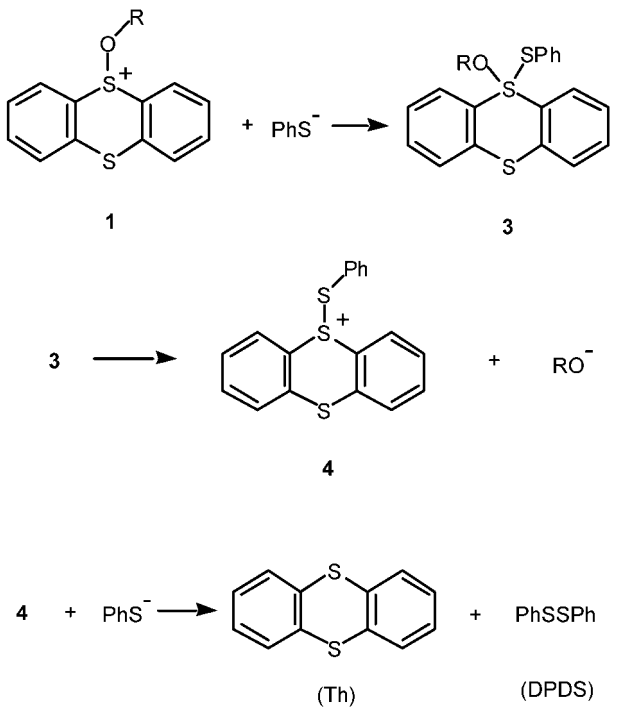
KEYWORDS: 5-(aryl)thianthrenium; nucleophilic reactions; aryl thiolates

INTRODUCTION

In earlier publications we reported on the reactions of nucleophiles such as iodide and thiophenoxide ions with 5-(alkoxy)- (**1**) and 5-(alkyl)thianthrenium ions (**2**). A clear distinction was found, particularly in the reactions of thiophenoxide ion. Reaction of this nucleophile with **1** occurred exclusively at the 5-thianthrenium sulfur atom. The alkoxy group was displaced (to become an alkanol), thianthrene (Th) was formed correspondingly, while thiophenoxide was converted into diphenyl disulfide (DPDS). A mechanism was proposed which invoked the participation of a sulfurane (**3**) and a 5-(thiophenoxy)thianthrenium ion (**4**) (Scheme 1).[1] In contrast, reactions of thiophenoxide with **2** were deduced to follow a mixture of S_N2 and elimination ($E2C^2$) pathways. The latter pathway was especially pronounced with 5-(cyclohexyl)thianthrenium ions.[3] It was deduced, furthermore, that if, in analogy



Scheme 1

Correspondence to: H. J. Shine, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, USA.
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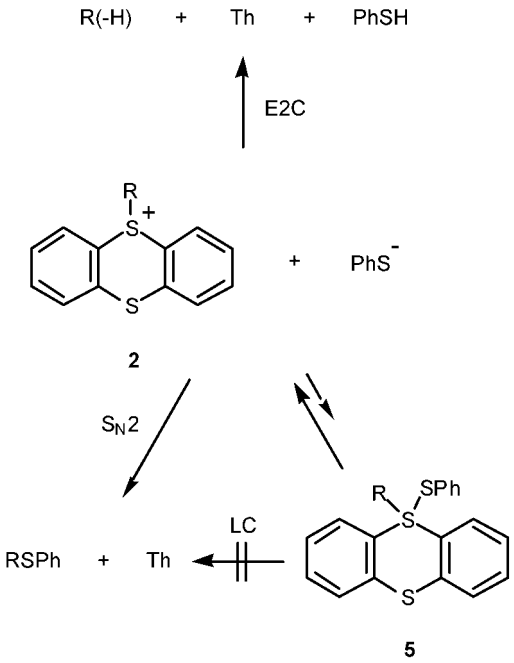


Scheme 2

with reactions of **1**, sulfurane (**5**) formation occurred in the reactions of **2**, it was reversible and was not responsible for product formation via ligand coupling (LC[4,5]) (Scheme 2).

We have now studied the reactions of 5-(aryl)thianthrenium bromides (**6a–e**) with sodium arylthiolates (**7a–c**) in acetonitrile (MeCN) at room temperature. The reactions are divided into two series, the first in which the 5-(aryl) group is phenyl, *p*-tolyl and *p*-anisyl (**6a–c**) and the second in which it is *p*-chlorophenyl and *p*-bromophenyl (**6d,e**).

RESULTS

As far as we are aware, the 5-(aryl)thianthrenium bromides **6** are not to be found in the literature. They were prepared by reaction of the appropriate arylmagnesium bromide with thianthrene 5-oxide (ThO), according to the method for preparing triarylsulfonium bromides from diaryl sulfoxides.[6] The identities of **6a–e**, of reactants **7a–c** and of products **8a,b, 9a–1, 10a–1, 11a–c** and **12a–c** are shown in Scheme 3. Products **8, 9** and **11** were assayed with gas chromatography (GC). Where necessary, authentic products were prepared (**9b–l, 11a**); others (**11b,c**) were identified by isolation and comparison with literature information. Products **10** and **12** were isolated with column and preparative thin-layer chromatography (TLC). They were identified with x-ray crystallography (**10a**), and either elemental analysis (**10f,h,i,l**) or high-resolution mass spectrometry (**10b–e,g,j,k** and **12a–c**). The ^{1}H NMR spectrum of each of the products **9–12** was consistent with its structure.

Reactions of 6a–c with 7a–c

The products of these reactions were Th, **8a,b, 9a–d,f,h,i**

Table 1. Products of reactions of **6a–c** with **7a–c**[a]

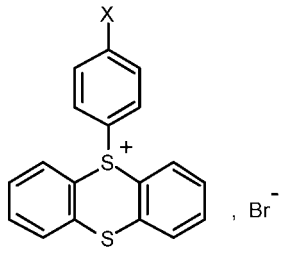
Run	Reactants		Products (%)				Sum (%) of (Th + **10**)/**6**
	6	**7**	**8**	**9**	Th	**10**	
1	**a**	**a**	**a**, 2.5	**a**, 7.9	17	**a**, 79	96
2	**a**	**b**	**a**, 1.2	**b**, 5.7	6.5	**b**, 91	98
3	**a**	**c**	**a**, 2.2	**d**, 9.5	21	**d**, 75	96
4	**b**	**a**	**b**, 4.2	**b**, 7.6	14	**b**, 82	96
5	**b**	**b**				**l**, 99	99
6	**b**	**c**	**b**, 4.2	**f**, 4.8	17	**f**, 79	96
7	**c**	**a**		**c**, 2.3	3.6	**c**, 84	88
8	**c**	**b**		**h**, 1.6	1.6	**h**, 94	96
9	**c**	**c**		**i**, 1.6	5.4	**i**, 89	94

[a] In MeCN at room temperature.

Table 2. Products of reactions of **6d,e** with **7a–c**[a]

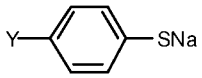
Run	Reactants		Products (%)					Sum (%) of (Th + **10** + **12**)/**6**
	6	**7**	**9**	**11**	Th	**10**	**12**	
10	**d**	**a**	**d**, 3.1	**a**, 43	47	**d**, 16	**a**, 33	96
11	**d**	**b**	**f**, 3.4	**b**, 33	37	**f**, 17	**b**, 41	98
12	**d**	**c**		**c**, 70	65	**k**, 6.7	**c**, 22	96
13	**e**	**a**	**e**, 2.2	**a**, 42	48	**e**, 17	**a**, 32	96
14	**e**	**b**	**g**, 2.6	**b**, 34	33	**g**, 18	**b**, 48	99
15	**e**	**c**	**j**, 1.1	**c**, 60	60	**j**, 11	**c**, 25	96

[a] In MeCN at room temperature.



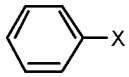
6a-e

X				
H	Me	MeO	Cl	Br
6a	**6b**	**6c**	**6d**	**6e**

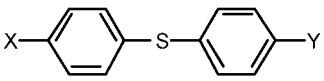


7a-c

Y		
H	Me	Cl
7a	**7b**	**7c**

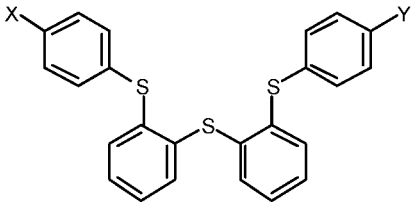


8a, X = H; **8b**, X = Me



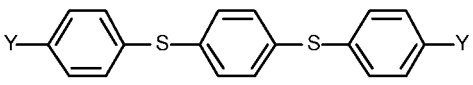
9

	X	Y
9a	H	H
9b	H	Me
9c	H	MeO
9d	H	Cl
9e	H	Br
9f	Me	Cl
9g	Me	Br
9h	Me	MeO
9i	MeO	Cl
9j	Br	Cl
9k	Cl	Cl
9l	Me	Me



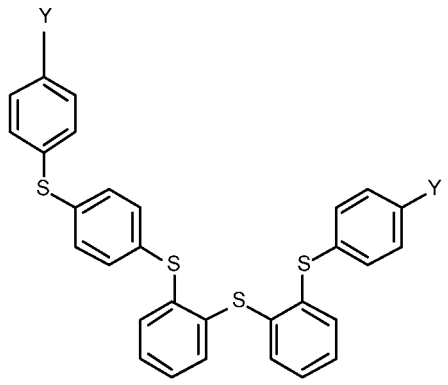
10

	X	Y
10a	H	H
10b	H	Me
10c	MeO	H
10d	H	Cl
10e	Br	H
10f	Cl	Me
10g	Br	Me
10h	MeO	Me
10i	MeO	Cl
10j	Br	Cl
10k	Cl	Cl
10l	Me	Me



11

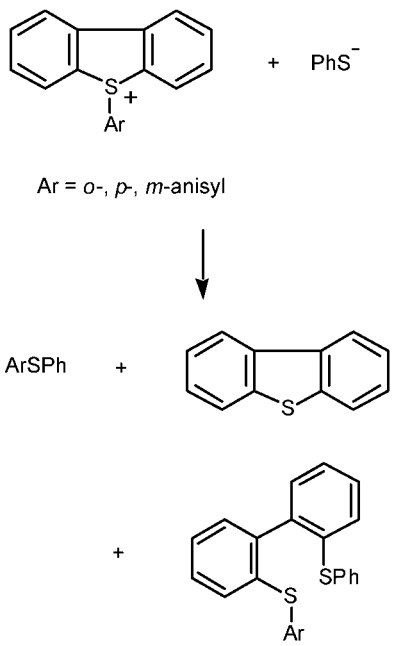
Y		
H	Me	Cl
11a	**11b**	**11c**



12

Y		
H	Me	Cl
12a	**12b**	**12c**

Scheme 3



Scheme 4

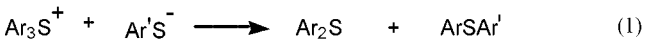
and **10a–d,f,h,i,l**. Their yields are listed in Table 1. A detailed example is given for reaction of **6a** with **7a** (Experimental). The major product by far in all reactions was a trisulfide (**10**), the certification of whose structure is given with the Ortep diagram of **10a**. Lesser amounts of a diaryl sulfide (**9**) and of Th were obtained. In the reaction of **6b** with **7b** the trisulfide (**10l**) was, in fact, the only product found. The arenes **8a,b** were obtained from **6a,b** in small amounts that varied, however, from one experiment to another. Products **10** arise from the opening of the thianthrenium ring by the thiolate nucleophile. Therefore, the sum of the yields of **10** and Th should equal the amount of reactant **6** that was used. That this is the case can be seen in Table 1, where the sum is expressed as a percentage of the amount of **6**. In principle, the sum of the yields of **8** and **9** should equal the yield of Th, but this is not borne out well in Table 1.

Reactions of 6d,e with 7a–c

Yields of products of these reactions are listed in Table 2. There are notable differences from the distribution of products in Table 1. A diaryl sulfide (**9d–g,j,k**) and a trisulfide (**10d–g,j,k**) were formed but not in as large amounts as in reactions of **6a–c**. Instead, the dominant products were a 1,4-di(arylthio)benzene (**11a–c**), in which the arylthio groups have been supplied by the nucleophile, and a tetrasulfide (**12a–c**), which again contains two arylthio groups from the nucleophile. Products **8** (X = Cl, Br) were not found. In these reactions, the sum of the yields of **9** and **11** should equal the yield of Th, and this is borne out reasonably well in all runs. Also, the sum of the yields of Th, **10** and **12** should equal the amount of **6** that was used. This is also borne out and is expressed as a pecentage of **6** in Table 2.

DISCUSSION

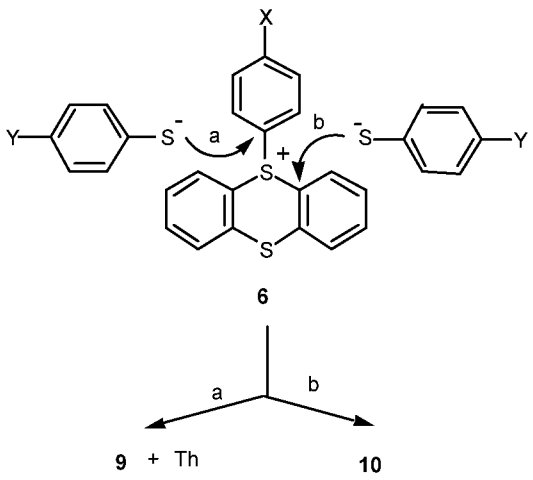
Few reactions of thiolate ions with sulfonium salts are to be found in the literature. Oae and Khim reported reactions of aryl thiolates with triarylsulfonium ions in boiling ethanol.[7] Displacement of an aryl group with the formation of diaryl sulfides occurred in high yield [Eqn. (1)] and was attributed to *ipso*-attack on the displaced aryl group. An alternative route to products is addition of thiolate to sulfonium sulfur, forming a sulfurane, which would collapse by LC[4,5] to the observed products. This route was ruled out because reaction at sulfonium sulfur was expected also to cause ejection of an aryl group by ligand exchange, with formation of an arene, either benzene or toluene, and none of these arenes was found.



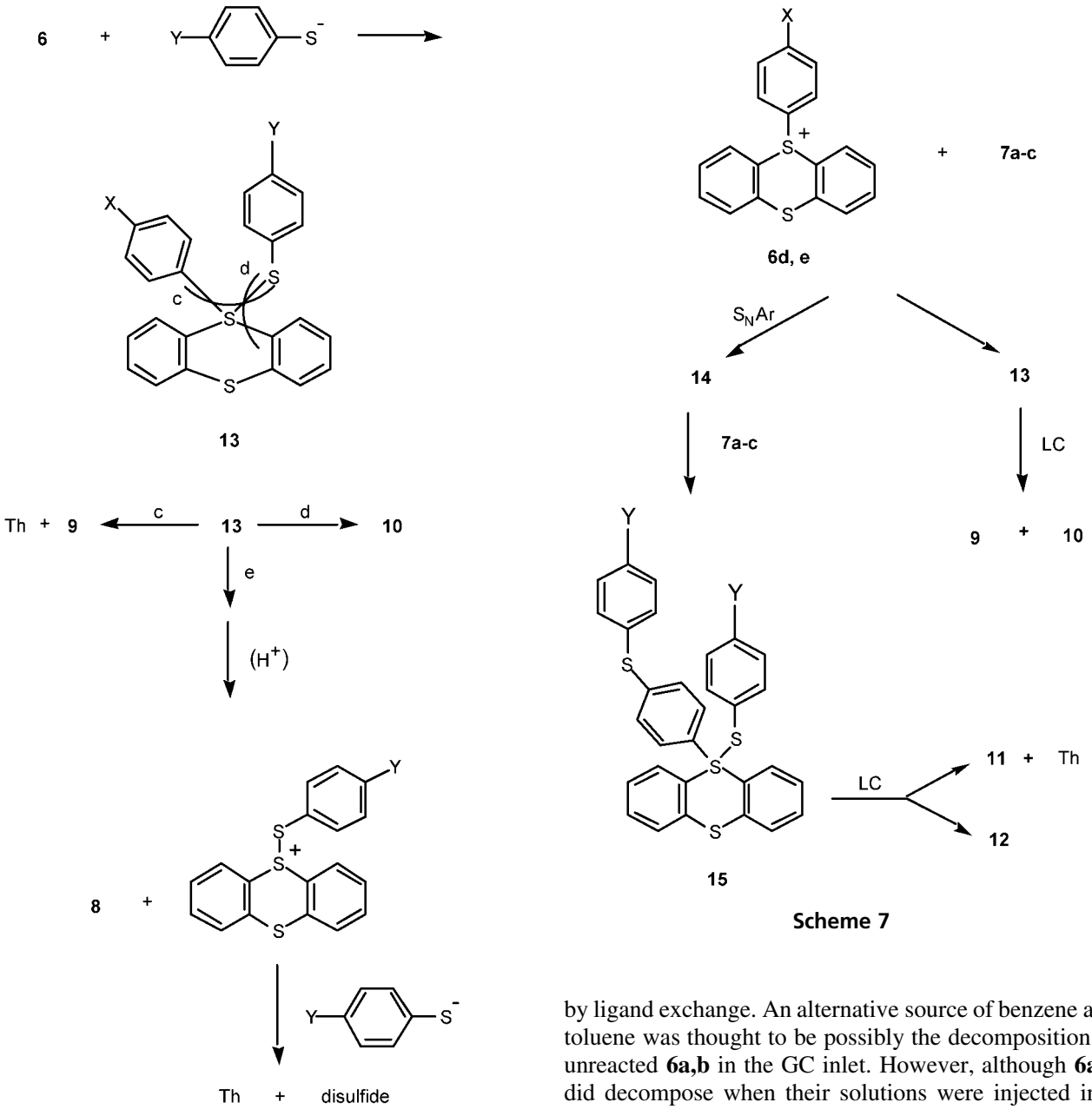
(1)

More closely related to our work is that of Mori *et al.* on reactions of thiophenoxide ion with 5-(aryl)dibenzothiophenium ions in boiling methanol.[8] In these reactions a diaryl sulfide (ArSPh) was formed and ring opening also occurred (Scheme 4). On the basis of the effect of the methoxy group's position on the relative yields of diaryl sulfide and ring opening among the three (anisyl)dibenzothiophenium ions, Mori *et al.* concluded that the products were formed by *ipso*-attack reactions. Oae, on the other hand, later quoted these reactions as typical examples how products could be formed by LC within a sulfurane.[4,5]

These examples are illustrative of the dilemma common to reactions involving sulfonium compounds with nucleophiles, that is, in distinguishing between direct reactions (such as S_N2 and *ipso*-attack) and LC



Scheme 5



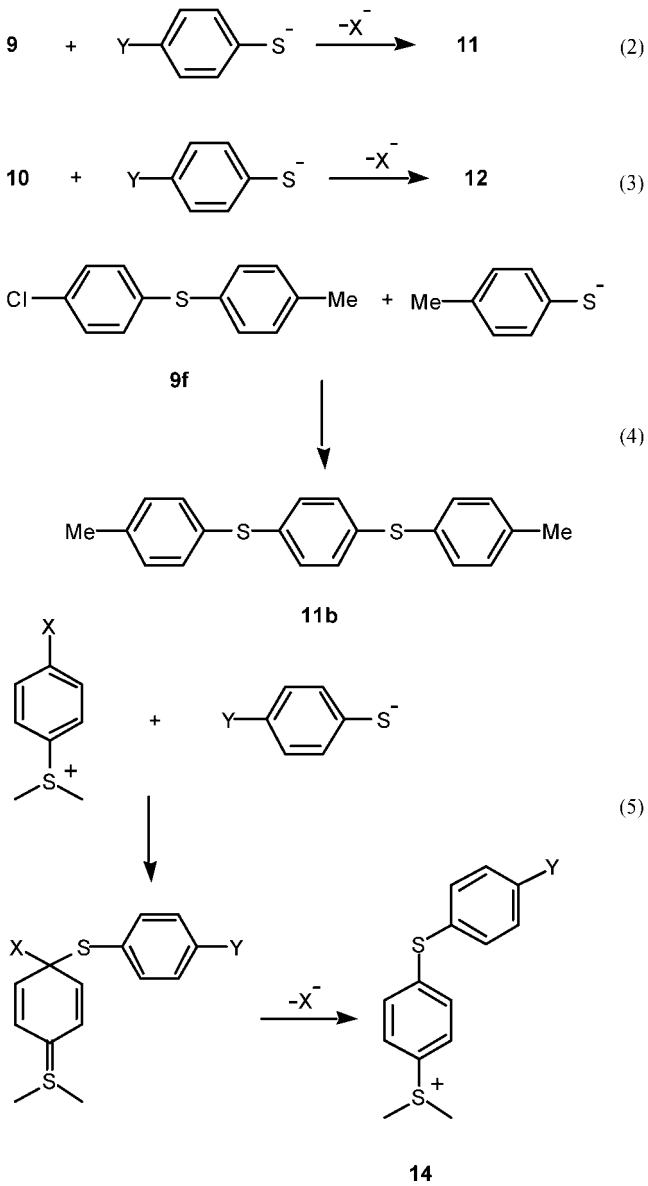
Scheme 6

Scheme 7

within sulfurane intermediates.[9–11] In our earlier work we argued against LC and for $S_N2/E2C$ reactions with **2**,[3] but for reaction at sulfonium sulfur with **1**.[1] In the reactions of **6a–c** with **7a–c**, the products **9** and **10** could arise from *ipso*-pathways as shown in Scheme 5 (paths a and b). These products could also arise from thiophilic addition to sulfonium sulfur and LC within the sulfurane (**13**), Scheme 6 (paths c and d). Thiophilic addition would also account for the formation of products **8a,b** (path e); products that, being diagnostic of sulfurane formation, were sought but not found by Oae and Khim.[7] At first sight, it seems improbable that an arylthiolate (whose conjugate acid has pK_a in the range 6–8) could displace, for example, phenyl anion (with pK_a analogously 43[12]) by ligand exchange. An alternative source of benzene and toluene was thought to be possibly the decomposition of unreacted **6a,b** in the GC inlet. However, although **6a,b** did decompose when their solutions were injected into the GC column, neither benzene nor toluene was found. Consequently, exchange of ligands appears to have occurred, albeit in small amounts. That exchange (path e) would lead subsequently to the formation of a diaryl disulfide, a product that was obtained and was assayed in a few runs. However, the diaryl disulfide is also formed by inadvertent oxidation of the thiolate nucleophile, and the two routes cannot be distinguished. This possible product of reaction, therefore, does not play a further role in our discussion.

In the reactions of **6d,e**, although **9** and **10** are formed, the dominant products are **11** and **12**. We thought, initially, that these may have been formed by aromatic nucleophilic substitution *after* **9** and **10** had been formed [Eqns (2) and (3)]. We tested this possibility with reaction between **9f** and **7b** [Eqn. (4)], under the conditions typical of reactions of **6** (room temperature,

24 h, MeCN). Had reaction occurred, **11b** would have been formed, but none was detected with GC. In support of this finding of unreactivity, we note that the nucleophilic aromatic substitution reactions that we *did* have to achieve in order to prepare authentic products **9b–l** had to be carried out at high temperature in ethylene glycol solution (Experimental). Our conclusion is that the aromatic substitution needed in the formation of **11** and **12** must occur in **6d,e** themselves. That reaction is promoted by the sulfonium group, as shown in abbreviated form in Eqn. (5), much in the way that nitro groups facilitate substitution in halobenzenes.[13] We summarize our interpretation of the reactions of **6d,e** in Scheme 7, wherein we propose that aromatic nucleophilic substitution (**14**) and LC reactions within sulfuranes (**13** and **15**) account for all products.



Our present and recent work[1,3] with reactions between 5-(substituted)thianthrenium salts and thiolates brings out notable differences. 5-(Alkoxy) groups in **1** are displaced entirely, 5-(alkyl) groups in **2** undergo S_N2/*E2C* reactions, while 5-(aryl) groups in **6** lead mainly to diaryl sulfides and ring opening. Ring opening was not observed at all in reactions of **1** and **2**, and appears, in reactions with thiolates, to be limited to 5-(aryl)thianthrenium ions. These differences reflect the relative ease of displacing an alkoxy group, as compared with alkyl and aryl anions, through ligand exchange. Although resistant to ligand exchange, the alkyl groups of **2** are subject to easy S_N2 and *E2C* reactions. In contrast, aryl groups, unactivated toward substitution and ligand exchange, appear to direct reactions into LC paths.

EXPERIMENTAL

The solvent MeCN was dried as described earlier.[1] Aryl thiols used in preparing **7a–c** and aryl halides used in preparing Grignard reagents for **6a–e** and in preparing diaryl sulfides **9b–l** were from commercial sources; **9a** is commonly available. GC was carried out with columns A and B described earlier.[1] Silica gel of 60–200 mesh was used for column chromatography. The plates used in preparative TLC were commercial pre-coated silica gel 60 F_{254}, 20 × 20 cm. Mass spectrometric data were provided by Dr Terry Marriott, Rice University. Elemental analyses were performed by Desert Analytics (Tucson, AZ, USA).

*5-(Aryl)thianthrenium bromides (**6a–e**).* These were prepared by reaction of ThO with an arylmagnesium bromide. An example is given with **6a**. Phenylmagnesium bromide was prepared from 4.12 g (26.2 mmol) of bromobenzene and 600 mg (24.7 mmol) of Mg in 30 ml of diethyl ether. To the solution was added 30 ml of benzene and the ether was distilled off. A solution of 1.15 g (4.96 mmol) of ThO in 15 ml of benzene was added and the mixture was boiled under reflux in N_2 for 18 h. To the cooled solution was added 2 ml of 48% HBr in 2 ml of water. The benzene layer was washed with 2 × 20 ml of 5% HBr solution. All aqueous portions combined were extracted with 3 × 60 ml of $CHCl_3$. The combined benzene and $CHCl_3$ solution was evaporated to give 1.38 g (3.70 mmol, 74.7% based on ThO) of **6a**, m.p. 264–265 °C. This was purified by precipitation from solution in $CHCl_3$–acetone (1:5) with diethyl ether, m.p. 269–270.5 °C.

Anal. Calcd for $C_{18}H_{13}S_2Br$ (**6a**): C, 57.9; H, 3.51; S, 17.2; Br, 21.4. Found: C, 57.9; H, 3.41; S, 16.9; Br, 21.7%.

Preparation of 5-(*p*-tolyl)thianthrenium bromide (**6b**) from *p*-tolylmagnesium bromide gave 49%, m.p. 248–249 °C.

Anal. Calcd for $C_{19}H_{15}S_2Br$ (**6b**): C, 58.9; H, 3.90; S, 16.6; Br, 20.6. Found: C, 58.7; H, 3.83; S, 16.4; Br, 20.6%.

5-(*p*-Anisyl)thianthrenium bromide (**6c**), 69%, had m.p. 225–226.5 °C. 5-(*p*-Chlorophenyl)thianthrenium bromide (**6d**), 48%, had m.p. 258–259 °C. 5-(*p*-Bromophenyl)thianthrenium bromide (**6e**), 63%, had m.p. 268–269.5 °C. When first isolated, **6c–e** were yellow solids. Reprecipitation gave slightly yellow or white products.

Anal. Calcd for $C_{18}H_{12}S_2Br_2$ (**6e**): C, 47.8; H, 2.67; S, 14.2; Br, 35.3. Found: C, 47.9; H, 2.67; S, 13.8; Br, 35.1%.

*Sodium arylthiolates (**7a–c**).* An example is given with **7b**. Sodium (820 mg, 35.7 mmol) and 40 ml of dry diethyl ether were placed in a three-necked flask equipped with a dropping funnel, reflux condenser and stirrer bar. A solution of an excess of *p*-thiocresol (6.5 g, 54 mmol) in 40 ml of diethyl ether was added with stirring and heating to reflux until all of the sodium had disappeared. The white solid was filtered, washed several times with hexane and dried under vacuum to give 5.1 g (34.9 mmol, 97%) of **7b**.

*Diaryl sulfides (**9a–l**) and 1,4-bis(arylthio)benzenes (**11a–c**).* These compounds were prepared by heating the appropriate halobenzene with an aryl thiolate at a temperature in the range of 150–200 °C in ethylene glycol solution containing a small amount of the catalyst 1,2-ethylbis(diphenylphosphino)nickel(II) bromide for 15–24 h. ^{1}H NMR spectra (δ ppm, J in Hz) were obtained in $CDCl_3$ at 200 MHz. An example is given with **9f**.

In a Pyrex pressure tube were placed 200 mg (1.04 mmol) of *p*-bromochlorobenzene, 150 mg (1.03 mmol) of **7b**, 10 mg of catalyst and 3 ml of ethylene glycol. The sealed tube was heated at 175 °C in a silicone oil bath for 15 h. To the cooled solution was added 50 ml of water. The mixture was extracted with 3×30 ml of CH_2Cl_2. The combined CH_2Cl_2 solution was dried ($MgSO_4$) and concentrated under vacuum. The residue was placed on a 12 in column of silica gel and eluted with light petroleum (b.p. 35–60 °C) to give 140 mg (0.597 mmol, 58%) of **9f**, m.p. 67–69 °C. This was chromatographed again twice, m.p. 71.5–73 °C. Lit.[14] m.p. 73 °C.

Analogous reactions gave **9b** (from *p*-bromotoluene and **7a**, 200 °C, 24 h), 51%, as an oil with a single GC peak. ^{1}H NMR: 7.322–7.114, m, 9H; 2.342, s, 3H. Lit.[15] b.p. 145–147 °C (2 mmHg).

9c (from *p*-iodoanisole and **7a**, 160 °C, 22 h), 66%, b.p. 222–225 °C (75 mmHg), m.p. 30–30.5 °C. Lit.[16] b.p. 138–140 °C (2 mmHg). ^{1}H NMR: 7.417, d, 2H, 8.70; 7.3–7.1, m, 5H; 6.897, d, 2H, 8.81; 3.820, s, 3H.

9d (from *p*-bromochlorobenzene and **7a**, 200 °C, 24 h), 47%, as an oil with single GC peak. Lit.[17] b.p. 120 °C (2mmHg). ^{1}H NMR: 7.361–7.229, m, 5H; 7.216, m, 4H.

9e (from *p*-dibromobenzene and **7a**, 180 °C, 17 h), 41%, as an oil. Lit.[15] b.p. 153–155 °C (3 mmHg). ^{1}H NMR: 7.395, d, 2H, 8.63; 7.361–7.253, m, 5H; 7.159, d, 2H, 8.54.

9g (from *p*-dibromobenzene and **7b**, 170 °C, 16 h), 37%, m.p. 83–84 °C. Lit.[18] m.p. 82.5 °C. ^{1}H NMR: 7.365, d, 2H, 8.41; 7.303, d, 2H, 8.08; 7.153, d, 2H, 8.29; 7.091, d, 2H, 8.25; 2.354, s, 3H.

9h (from *p*-iodoanisole and **7b**, 140 °C, 20 h), 89%, m.p. 45–46 °C. Lit.[19] m.p. 43–45 °C. ^{1}H NMR: 7.361, d, 2H, 8.84; 7.133, d, 2H, 8.48; 7.059, d, 2H, 8.32; 6.866, d, 2H, 8.84; 3.806, s, 3H; 2.299, s, 3H.

9i (from *p*-iodoanisole and **7c**, 150 °C, 2 d), 87%, m.p. 60.5–61.5 °C. Lit.[20] m.p. 60–61 °C. ^{1}H NMR: 7.405, d, 2H, 8.95; 7.194, d, 2H, 8.52; 7.068, d, 2H, 8.87; 6.904, d, 2H, 8.87; 3.828, s, 3H.

9j (from *p*-bromoiodobenzene and **7c**, 175 °C, 22 h), 56%, m.p. 102–103 °C. Lit.[21] m.p. 106–107 °C.

9k (from *p*-bromochlorobenzene and **7c**, 170 °C, 24 h), 61%, m.p. 94.5–95.5 °C. Lit.[22] m.p. 93–94 °C.

9l was prepared and reported earlier, m.p. 58–58.5 °C.[23]

11a was isolated in the preparation of **9e**, 43%, m.p. 81–82 °C. Lit.[14] m.p. 80 °C.

11b was isolated in the preparation of **9g**, 17%, m.p. 101–101.5 °C. Lit.[14] m.p. 95 °C.

11c was not prepared directly, but was isolated from the reaction of **6e** with **7c** and had m.p. 139.5–140.5 °C. Lit.[24] m.p. 140–141 °C.

*Reactions of 5-(aryl)thianthrenium bromides (**6a–e**) with sodium thiolates (**7a–c**).* Reactions in general were carried out in MeCN containing a GC standard or standards and at room temperature. That is, biphenyl was used as a standard in all reactions, but was accompanied by 2-butanone when product benzene or toluene was to be assayed on column B. At the beginning of all reactions the solution became orange or reddish–orange in color and the color faded to pale yellow within about 2 h. An attempt to characterize the orange color spectroscopically was made with the reaction of **6a** with **7b** but was not informative; a broad shoulder in the region of 380–425 nm was obtained which disappeared within 60 min. The assay of products depended on whether a trisulfide (**10**) was formed (from **6a–c**) or both **10** and a tetrasulfide (**12**) were formed (from **6d,e**). In all reactions, the products **8, 9, 11** and Th were assayed with GC. Also assayed with GC were the diaryl disulfides $YC_6H_4SSC_6H_4Y$, but those assays are not tabulated because we could not distinguish between disulfide formed as a reaction product and by inadvertent oxidation of **7**. Products **10** were assayed by weight after column chromatography in reactions of **6a–c** and by a combination of column chromatography and TLC in reactions of **6d,e**. Products **12** were assayed after column chromatography and TLC in these reactions, too. Examples of each type procedure are given.

*Reaction of 5-(phenyl)thianthrenium bromide (**6a**) with sodium thiophenoxide (**7a**).* A solution of 52.6 mg (0.729 mmol) of 2-butanone and 82.9 mg

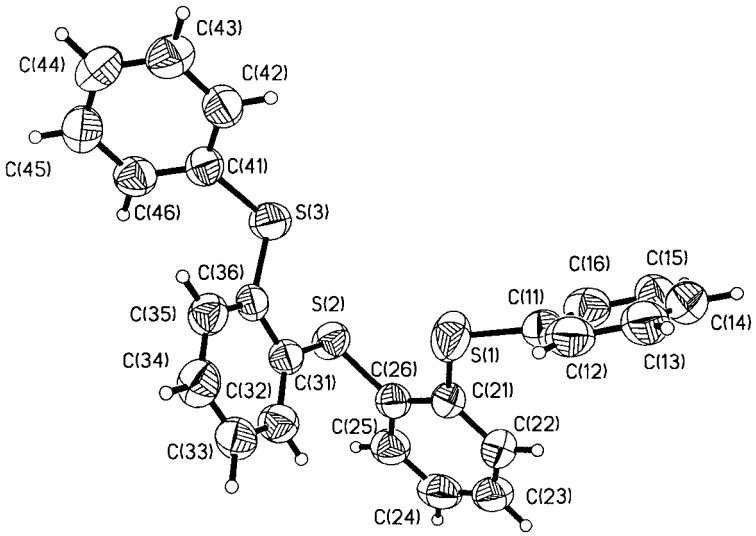


Figure 1. Ortep diagram of 2, 2′-bis(phenylthio)diphenyl sulfide (**10a**)

(0.537 mmol) of biphenyl in 20 ml of MeCN was placed in a flask containing a stirrer bar. To this were added 294 mg (0.788 mmol) of **6a** and 273 mg (2.07 mmol) of **7a**. The flask was capped with a rubber septum. When the reactants were mixed, the solution became orange in color, which faded to yellow in 1.5 h. The mixture was stirred for 2 d. Three GC assays were made on columns A and B, to give 0.0195 ± 0.0003 mmol (2.5%) of benzene (**8a**), 0.0626 ± 0.0008 mmol (7.9%) of diphenyl sulfide (**9a**), 0.1306 ± 0.004 mmol (16.6%) of Th and 0.127 ± 0.001 mmol of diphenyl disulfide (DPDS). Following the GC assays, the mixture was poured into 100 ml of water. The aqueous mixture was extracted with 3×30 ml of diethyl ether and the dried ($MgSO_4$) ether solution was concentrated in a rotary evaporator. The residue was transferred to a column of silica gel. Elutions with light petroleum, which were monitored with TLC, removed the earlier components of the mixture (**9a**, Th, DPDS). Elution with petroleum ether/ether (40:1 by volume) then removed 250 mg (0.621 mmol, 79%) of **10a**, m.p. 90–91 °C. A single crystal was grown successfully for X-ray crystallography (Figure 1).

*Reaction of 5-(p-chlorophenyl)thianthrenium bromide (**6d**) with sodium thiophenoxide (**7a**).* The reactants were 305 mg (0.748 mmol) of **6d** and 396 mg (3.00 mmol) of **7a**. The GC standard was biphenyl (95.8 mg, 0.622 mmol). After stirring overnight the orange color had become yellow. GC assays gave 0.0233 ± 0.0005 mmol (3.1%) of **9d**, 0.350 mmol $\pm$ 0.0034 mmol (47%) of Th and 0.0323 ± 0.0038 mmol (43%) of **11a**. The residue from pouring into water and extracting with ether was chromatographed with petroleum ether to remove biphenyl, Th, **9d** and DPDS. Then, elution with petroleum ether/ether (40:1) gave 31.4 mg of **10d**, 91.2 mg of **12a** and a mixture of **10d, 11a** and **12a**. This mixture was streaked on TLC plates and developed with petroleum ether/ether (40:1). Separated bands were scraped from the plates and extracted with acetone in a filter funnel. Work up gave 20.7 mg of **10d** and 36.3 mg of **12a**. Thus, the total of **10d**, obtained as an oil, was 52.1 mg (0.119 mmol, 15.9%) and of **12a**, obtained as an oil, was 127.5 mg (0.246 mmol, 32.9%). Crystallization of **10d**, obtained in reaction of **6a** with **7c**, from isopropyl alcohol gave m.p. 69–70 °C.

*Identification of trisulfides (**10a–l**) and tetrasulfides (**12a–c**).* Each of **10a–l** had a ^{1}H NMR spectrum consistent with its structure. Trisulfides were crystalline solids except **10e,g,j,k**, which were oils. A single crystal of **10a** was grown and an Ortep diagram was obtained. We were unsuccessful in attempts to do the same with other solid trisulfides. Elemental analyses were obtained of **10f,h,i,l**. The remaining trisulfides were characterized with high-resolution mass spectrometry masses. The tetrasulfides had acceptable ^{1}H NMR spectra. Each was characterized with its high-resolution mass spectrum mass.

Elemental analyses. **10f**, calcd for $C_{25}H_{19}S_3Cl$: C, 66.6; H, 4.25: S, 21.3; Cl, 7.86. Found: C, 66.4; H, 4.11; S, 21.2; Cl, 7.60%.

10h, calcd for $C_{26}H_{22}S_3O$: C, 69.9; H, 4.96; S, 21.5. Found: C, 70.1; H, 5.02; S, 21.3%.

10i, calcd for $C_{25}H_{19}S_3ClO$: C, 64.3; H, 4.10; S, 20.6; Cl, 7.59. Found: C, 64.3, H, 4.06; S, 20.4; Cl, 7.42%.

10l, calcd for $C_{26}H_{22}S_3$: C, 72.5; H, 5.15; S, 22.3. Found: C, 72.3; H, 5.14; S, 22.4%.

Mass spectrometry: molecular masses. The error in ppm is given in parentheses.

10b, calcd for $C_{25}H_{20}S_3$: 416.072719. Found: 416. 071504 (2.99).

10c, calcd for $C_{26}H_{20}S_3O$: 432.067633. Found: 432.067237 (0.92).
10d, calcd for $C_{24}H_{17}S_3Cl$: 436.018097. Found: 436.017406 (1.7).
10e, calcd for $C_{24}H_{17}S_3Br$: 479.967592. Found: 479.967775 (0.38).
10g, calcd for $C_{25}H_{19}S_3Br$: 495.981313. Found: 495.981357 (0.89).
10j, calcd for $C_{24}H_{16}S_3BrCl$: 513.928620. Found: 513.928112 (0.99).
10k, calcd for $C_{24}H_{16}S_3Cl_2$: 469.979125. Found: 469.980243 (2.2).
12a, calcd for $C_{30}H_{22}S_4$: 510.060442. Found: 510.060196 (0.48).
12b, calcd for $C_{32}H_{26}S_4$: 538.091742. Found: 538.091241 (0.93).
12c, calcd for $C_{30}H_{20}S_4Cl_2$: 577.982498. Found: 577.983218 (1.2).

X-ray crystallographic data. A suitable crystal was encapsulated in a capillary tube and mounted on the tip of a glass-fibre with epoxy cement. Data were collected with a Bruker AXS automated CCD diffractometer using the Bruker AXS package and using Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were calculated in ideal positions (riding model). Refinement of F^2 was performed using all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on all data will be even larger. All software used is contained in the SHELXTL 5.10 program library.[25]

Supplementary material

Five tables giving crystal data and structural refinements, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and equivalent isotropic displacement parameters for $C_{24}H_{18}S_3$ are available at the epoc website at http://www.wiley.com/epoc. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre under the deposition number CCDC 172558.

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