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Reactions of 5-(alkyl)thianthrenium and other sulfonium salts with nucleophiles

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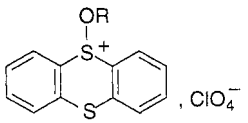
ABSTRACT: A series of 5-(alkyl)thianthrenium triflates (**3a–d, g–i**) with alkyl (R) groups Me (**a**), Et (**b**), isoPr (**c**), 2-Bu (**d**), cyclopentyl (**g**), cyclohexyl (**h**) and cycloheptyl (**i**) were prepared by alkylation of thianthrene (Th) with alkyl formate and trifluoromethanesulfonic (triflic) acid. Benzylation (**3f**) was achieved with benzyl bromide and silver triflate. 5-(Neopentyl)thianthrenium perchlorate (**3e**) was prepared by reaction of thianthrene cation radical perchlorate with dineopentyl mercury. Methyl- (**4a**) and cyclohexyldiphenylsulfonium triflate (**4b**) were made by alkylation of diphenyl sulfide. Benzyldimethyl- (**5a**), dibenzylmethyl- (**5b**) and benzylmethylphenylsulfonium perchlorate (**5c**) were prepared in standard ways. Reactions of these sulfonium salts with iodide ion and thiophenoxide ion were studied for comparison with our earlier reported reactions of comparable 5-(alkoxy)thianthrenium and methoxydiphenylsulfonium salts. It is deduced that reactions of **3**–**5** with nucleophiles (Nu^-) I^- and PhS^- follow traditional S_N2 and *E2C* paths. Thus, the salts **3a–c, e** and **f** gave virtually quantitative yields of RNu and Th, while small amounts of butene(s) were obtained from **3d**. The cycloalkyl salts **3g–i** gave amounts of cycloalkylNu and cycloalkene typical of competition of S_N2 and *E2C* routes in the classical reactions of cycloalkyl halides and tosylates with I^- and PhS^- ions. Whereas **4a** gave only S_N2 products, **4b** gave S_N2 and *E2C* products typical of S_N2/*E2C* competition. Among the salts **5a–c** displacement of the benzyl group was dominant (**5a**) or exclusive (**5b, c**), thus exhibiting the preferential displacement of a benzyl group that has been fully documented in earlier studies of S_N2 reactions. Qualitative comparison showed that **3a** (methyl) reacted much faster than **3e** (neopentyl) with PhS^-. Unlike alkoxysulfonium salts, the salts **3**–**5** do not appear to undergo reactions at the sulfonium sulfur atom. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: thianthrenium; sulfonium; nucleophilic reactions

INTRODUCTION

Recently, we reported the reactions of 5-(alkoxy)thianthrenium perchlorates (**1**) with iodide, bromide and thiophenoxide ions.[1,2] Compounds **1** were then relatively new members of the class of alkoxysulfonium salts, inviting study of their chemistry. We found that they engaged in three types of reaction with halide ions, namely, S_N2 substitution, *E2C* elimination and reaction at the sulfonium sulfur atom. The last type led to the formation of thianthrene (Th), the alcohol (ROH) corresponding with the 5-alkoxy group, and halogen (iodine or bromine). Similar reactions occurred with the more commonly known methoxydiphenylsulfonium tetrafluoroborate (**2**). Reactions of **1** and **2** with thiophenoxide (PhS^-) were different, however. Little or no S_N2 reaction occurred, in spite of thiophenoxide's being a better nucleophile than halide ions toward carbon, and no elimination was obtained, even with the cyclohexyloxy group, in spite of the propensity for cyclohexyl derivatives to undergo *E2C* elimination with PhS^-.[2] Instead, reaction at sulfonium sulfur was dominant, with the formation of Th, ROH and diphenyl disulfide (DPDS). We attributed this behavior to the remarkable thiophilicity of PhS^- and to the ease of displacement of an alkoxy group attached to sulfur in **1** and **2**.[2]



1

Ph_2S^+OMe, BF_4^-

2

Trialkyl-, triaryl- and alkylarylsufonium salts are well known tricordinate organosulfur compounds, and numbers of their reactions with nucleophiles have been reported. Among this class of compounds, 5-(alkyl)thianthrenium salts (**3**) are not so well known, and to our

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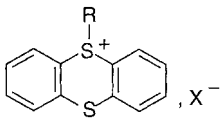
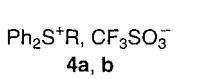
knowledge no studies have ever been reported of their reactions with nucleophiles such as the halide and thiolate ions. We are interested in these reactions particularly as to how they compare with the reactions of **1**. We report here, therefore, the reactions of I^- and PhS^- with the trifluoromethanesulfonate (triflate) and perchlorate salts **3a–i**, in which the alkyl group R is successively Me (**a**), Et (**b**), isoPr (**c**), 2-butyl (**d**), neopentyl (**e**), benzyl (**f**), cyclopentyl (**g**), cyclohexyl (**h**) and cycloheptyl (**i**). Furthermore, although numbers of reactions of sulfonium salts with nucleophiles are in the literature, not many are to be found with I^- and PhS^-. Consequently, for comparison with reactions of **3** we have studied and report the reactions of I^- and PhS^- with methyl- (**4a**) and cyclohexyldiphenylsulfonium triflate (**4b**), and of Br^- and PhS^- with a number of sulfonium perchlorates (**5**) containing the benzyl group, namely, benzyldimethyl- (**5a**), dibenzylmethyl- (**5b**) and benzylmethylphenylsulfonium perchlorate (**5c**). Our interest in these reactions, in comparison with reactions of **1** and **2**, was to find if halide and thiophenoxide ions would show their usual carbon nucleophilicities or if, particularly with PhS^-, reaction at sulfur would intervene.



3a - j

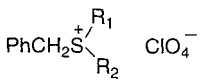
R = **a**, Me; **b**, Et; **c**, iPr; **d**, 2-butyl; **e**, neopentyl; **f**, benzyl; **g**, cyclopentyl; **h**, cyclohexyl; **i**, cycloheptyl; **j**, Pr

$X^- = CF_3SO_3^-$ (**a - d**, **f - j**); ClO_4^- (**e**)



4a, **b**

R = **a**, Me; **b**, cyclohexyl



5a-c

	R_1	R_2
a,	Me	Me
b,	Me	$PhCH_2$
c,	Me	Ph

RESULTS

5-(Alkyl)thianthrenium salts (3)

Little is to be found on the preparation and chemistry of these compounds in the literature. We reported from this laboratory some years ago the preparation of a number of 5-(alkyl)thianthrenium perchlorates, $Th^{+\cdot}RClO_4^-$, by reaction of thianthrene cation radical perchlorate, $Th^{+\cdot}ClO_4^-$, with dialkymercurials (R_2Hg) and tetraalkyltins (R_4Sn), with R being, for example, Me, Et, Bu, allyl and vinyl (Ref. 3 for Me_2Hg and Et_2Hg, Ref. 4 for R_4Sn, R = Me, Et, Bu, vinyl).

In these reactions, the radical $R^\cdot$ is formed initially in oxidation of the organometal by $Th^{+\cdot}$, and if trapped by another $Th^{+\cdot}$ gives the 5-(alkyl)thianthrenium ion.[5] If $R^\cdot$ is easily oxidized to R^+ by $Th^{+\cdot}$, the cation is trapped by solvent acetonitrile and **3** is not formed.[6] Hence this method has limitations. Thianthrene, like other diaryl sulfides, is not sufficiently nucleophilic to be alkylated by methods[7,8] that work well with dialkyl and alkyl aryl sulfides, although Saeva was able to alkylate it by reaction with *p*- cyanobenzyl bromide and silver triflate[9] (Ref. 7 has numerous references to earlier methods). Recently, Miyatake *et al.*[7] made **3a** in excellent yield by reaction of Th with methyl formate and triflic acid, and we used that method to prepare **3a–d**, **g–i** in the present work. This allowed us for the most part to avoid the use of organomercurails and organotins for alkylating Th. We were unable to prepare the 5-(neopentyl) triflate by this method because of difficulty in preparing neopentyl formate. Furthermore, we were unable to prepare that triflate by alkylating Th with neopentyl iodide and silver triflate. Therefore, we prepared 5-(neopentyl)thianthrenium perchlorate (**3e**) by our earlier method,[6] the reaction of $Th^{+\cdot}ClO_4^-$ with dineopentylmercury. Alkylation of Th with benzyl formate and triflic acid was unsuccessful. We found that benzyl formate itself reacted violently with triflic acid. Therefore, alkylation was carried out with benzyl bromide and silver triflate.[9] Attempts to prepare 5-propylthianthrenium triflate (**3j**) were thwarted by partial rearrangement that gave a mixture of **3j** and **3c** (shown by NMR); this experience differs from that of Miyatake *et al.*, who prepared butyldiphenylsulfonium triflate without rearrangement of the butyl group.[7] The same method was used for preparing **4a** and **b**, while customary alkylation techniques were used for preparing **5a–c**.

Reactions of 3–5 with nucleophiles

The data in Table 1 show that quantitative or close to quantitative yields of alkyl halide or alkyl phenyl sulfide and Th were formed when **3a–i** reacted with halide or thiophenoxide ion in acetonitrile solution. Exceptions were the reactions of **3h**, in which the major product of the cyclohexyl ring was cyclohexene, and **3g** and **i** from which smaller amounts of cycloalkene were obtained. A similar pattern in results was obtained with **4a** and **4b** (Table 2). Whereas the former gave quantitative yields of methyl iodide and thioanisole, the latter gave mostly cyclohexene. These results with **3h** and **4b** are typical of the $S_N2/E2C$ behavior reported years ago by Winstein, Eliel and co-workers,[10] That is, that in reactions of cyclohexyl halides and tosylates with halide and thiophenoxide ions, both S_N2 substitution and $E2C$

Table 1. Reactions of 5-(alkyl)thianthrenium salts (**3**)[a] with halide and thiophenoxide ions (X^-) in MeCN

			Products (%)[b]		
Compound	Alkyl group	X	RX	Th	Alkene
3a	Me	I	92	99	
3a	Me	PhS	101	101	
3a	Me	PhS[c]	102	99	
3b	Et	I	98	101	
3b	Et	PhS	97	98	
3c	iPr	I	100	99	
3c	iPr	PhS	103	102	
3d	2-Bu	PhS	94	100	4.5[d]
3e	neoPent	I	94	97	
3e	neoPent	PhS	98	99	
3f	$PhCH_2$	Br[e]	100	96	
3f	$PhCH_2$	PhS	98	99	
3f	$PhCH_2$	PhS[c]	100	99	
3g	C^f_5	I[g]	96	101	2.0
3g	C^f_5	PhS[h]	96	101	3.4
3h	C^i_6	I	20	103	79
3h	C^i_6	PhS	26	99	73
3i	C^j_7	I	88	100	7.0
3i	C^j_7	PhS	88	99	11

[a] All salts were trifluoromethanesulfonates, except **3e**, which was the percholorate.
[b] Measured with GC, except I_2.
[c] An equal amount of PhSH was included.
[d] Unidentified, based on response factor for 2-butene.
[e] Bu_4NBr was used.
[f] Cyclopentyl.
[g] An average of three experiments.
[h] An average of two experiments.
[i] Cyclohexyl.
[j] Cycloheptyl.

Table 2. Reactions of alkyldiphenylsulfonium TFS (**4**)[a] salts with iodide and thiophenoxide ions (X^-) in MeCN

			Products (%)[b]		
Compound	Alkyl group	X	RX	Ph_2S	Alkene
4a	Me	I	96	98	
4a	Me	PhS	98	101	
4b	C^c_6	I	15	95	77[d]
4b	C^c_6	PhS	26[e]	98[e]	71[d]

[a] Trifluoromethanesulfonate.
[b] Measured with GC.
[c] Cyclohexyl.
[d] Cyclohexene.
[e] Cyclohexyl phenyl sulfide and diphenyl sulfide appeared together as a single GC peak which was assayed as Ph_2S. The composition of the mixture was calculated on the basis that equal (mmol) amounts of ene and Ph_2S and of RX and Ph_2S has been formed.

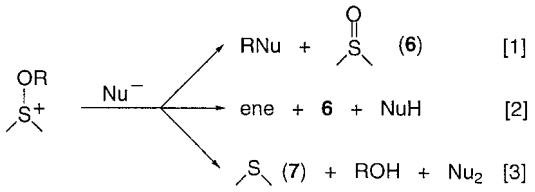
elimination occurred, often in almost equal amounts.[10,11] The concordance of the S_N2 and elimination reactions, in fact, led Winstein and co-workers to refer to the latter as the 'merged' mechanism, that is, an elimination merged with the pathway to substitution. This, then, appears to be the situation with reactions of **3h** and **4b** and to a lesser extent with **3g** and **i**. We use the terminology *E*2*C* here in a historical sense to emphasize the analogy of our weak-base initiated eliminations from cycloalkyl groups with those that were uncovered in earlier years.[10,11] Valence bond theory[12d] and temperature-dependent kinetic isotope effects[12g–i] have been used in later years to support an *E*2*C* transition state, but the concept itself remains controversial.[12c,e,f] Small amounts of iodine were indicated in some experiments by the color of the reaction solution and were measured in two cases, with **3e** (entry 9, Table 1, 7.3%) and **3i** (entry 18, 8.6%). In all reactions with NaSPh varying amounts of DPDS were also found.

In reactions of the benzyl derivatives **5a**–**c** (Table 3) with bromide and thiophenoxide ions, the benzyl group was displaced either exclusively (**5b** and **c**) or dominantly (**5a**). That is, in reaction of **5a** with PhS^-, some (6.4%) thioanisole was formed in addition to benzyl methyl sulfide, (94%). In reaction with Br^-, **5a** gave not only 94–95% of benzyl bromide and dimethyl sulfide, but also 7% of benzyl methyl sulfide. The last product requires the displacement of methyl from **5a** as methyl bromide, but we were unable to assay that compound with our GC columns.

Table 3. Reactions of benzyl(R_1)(R_2)sulfonium perchlorates (**5**) with bromide[a] and thiophenoxide ions (X^-) in MeCN

				Products (%)[b]					
Compound	R_1	R_2	X	$PhCH_2X$	$PhCH_2SR_1$	$PhCH_2SR_2$	R_1SR_2	R_1X	R_2X
5a	Me	Me	Br	95	3.6	3.6	94	[c]	[c]
5a	Me	Me	PhS	94	4.0	4.0	95	3.2	3.2
5b	Me	$PhCH_2$	Br	102	101				
5b	Me	$PhCH_2$	PhS	99	99				
5b	Me	$PhCH_2$	PhS[d]	103	100				
5c	Me	Ph	Br	97			94		
5c	Me	Ph	PhS	98			100		

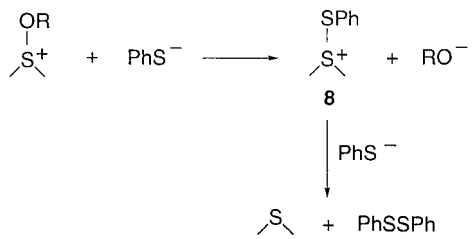
[a] The source of Br^- was KBr/18C6 except in the first entry, when Bu_4NBr was used.
[b] Measured with GC.
[c] MeBr was not measurable with our columns.
[d] 0.50 mmol each of NaSPh and PhSH.



Scheme 1

DISCUSSION

In the reactions of alkoxysulfonium salts **1** and **2**, akin to **3** and **4**, reaction at sulfonium sulfur played a significant role (halide ion) or dominant role (thiophenoxide ion).[1,2] For example, reactions of iodide ion with **1** led to the formation of RI and thianthrene 5-oxide [**6**, Eqn. (1)], to alkene and **6** [Eqn. (2)] and to thianthrene (Th, **7**), ROH and iodine [Nu_2, Eqn. (3)] in relative amounts depending on the nature of R in the alkoxy group. These reactions are shown in abbreviation in Scheme 1, with $Nu^- = I^-$, When the nucleophile was PhS^-, however, only **7**, ROH and diphenyl disulfide (Nu_2 = PhSSPh, DPDS) were formed, regardless of the nature of R. Similar behavior was noted with **2**. The reactions shown in Eqns (1) and (2) ($Nu^- = I^-$) were diagnosed as being S_N2 and *E2C* reactions, occurring in competition that became more pronounced as R in RO was changed from primary to secondary to cycloalkyl. As that change progressed, furthermore, formation of **7**, ROH and I_2 became more significant, and that was attributed to reaction of I^- at sulfonium sulfur, increasing in scale as the nature of R made S_N2/*E2C* reactions more difficult. In contrast, reactions of PhS^- with **1** and **2** were almost exclusively according to Eqn. (3). The difference in behavior of PhS^- and I^-, in spite of the well-known greater carbon nucleophilicity of PhS^-, was attributed to the thiophilicity of PhS^-, which not only directed its initial reaction to sulfonium sulfur, but also its even more facile follow-up reaction at the sulfenyl sulfur of the resulting phenylthiosulfonium ion (**8**), Scheme 2. The formation of **8** was further attributed not only to the thiophilicity of PhS^-, but also to the easy displacement of alkoxide. Whether, in the formation of **8**, an intermediate sulfurane, should be included, or whether direct displacement of alkoxide occurred, could not be decided.



Scheme 2

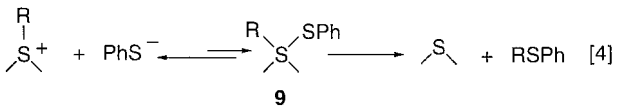
The data in Tables 1 and 2 show that reactions of **3** and **4** with I^- and PhS^- do not have the variability of reactions of **1** and **2**. Regardless of the structure of R in **3** and **4** reactions followed either S_N2 or *E2C* pathways. The latter pathway was particularly marked with cyclohexylsulfonium salts **3h** and **4b**, well in accordance with earlier classical studies of cyclohexyl halides and tosylate.[10,11] Furthermore, our comparative results with cyclopentyl- (**3g**) and cyclohexylthianthrenium (**3h**) salts almost parallel those obtained in Winstein's laboratory with cyclopentyl and cyclohexyl tosylates.[10b] That is, reactions of these tosylates (with Cl^- in acetone at 75 °C) gave 3.3 and 72.3% elimination, respectively, close to our results with I^- and PhS^- (Table 1). The difference in reactivities of the tosylates was attributed to the faster S_N2 reaction of cyclopentyl tosylate.[10b] Because reactions of simple cyclopentyl and cycloheptyl derivatives with thiolate ions could not be found in the literature, we carried out those reactions ourselves by stirring the cycloalkyl derivative overnight in MeCN solution containing an excess of NaSPh. Cyclopentyl bromide and tosylate each gave 97% of cyclopentyl phenyl sulfide and small amounts of cyclopentene. Cycloheptyl bromide gave 91% of cycloheptyl phenyl sulfide and 4.7% of cycloheptene. Cycloheptyl tosylate gave 91 and 6% of these products. Previously, McLennan[11] reported the reaction of cyclohexyl bromide with NaSPh, obtaining 55% of cyclohexene. Under our conditions, cyclohexyl bromide gave 56% of cyclohexene and 44% of cyclohexyl phenyl sulfide.

Our diagnosis of S_N2/*E2C* reactions with **3** and **4** is supported by the results of reactions of **5a**–**c**, Table 3. There it is seen that the benzyl rather than methyl group is displaced either exclusively (**5b, c**) or dominantly (**5a**). The preferred displacement of benzyl over methyl is diagnostic of S_N2 reactions and is in accordance with observations in a variety of earlier studies.[13] With respect to sulfonium salts, reaction of azide ion with dimethyl(1-phenylethyl)sulfonium chloride occurred exclusively at the l-phenylethyl group[14,15] and with inversion of configuration.[14] Thiourea reacted similarly with this sulfonium ion, but methoxide reacted preferentially at the methyl groups.[15] Dorman and Love used preferential attack at benzylic carbon in an adaptation of the Merrifield peptide process. That is, a dialkyl sulfide (e.g. Me_2S, Et_2S) leaving group was attached to the benzylic CH_2 group of the polymer, forming a polymer-linked dialkylbenzylsulfonium ion. Reaction with carboxylate occurred mainly (90%) at the benzylic carbon atom.[16] King *et al.* found that dibenzylethylsulfonium salts reacted with thiocyanate ion and thiourea exclusively at a benzyl group, with no sign of ethyl-group displacement.[17]

Our conclusion about the results in Tables 1–3, then, is that they are from S_N2 and *E2C* reactions and do not involve reaction at sulfonium sulfur. The reaction at sulfonium sulfur that we have reported for 5-alkox-

ythianthrenium ions (**1**), particularly with PhS^-, does not occur with the sulfonium salts **3**–**5**. The difference between reaction of **1, 2** and **3**–**5** is in the displacement of the group attached to sulfonium sulfur. The alkoxy group is easily displaced from **1** and **2** when a nucleophile attacks sulfonium sulfur. Analogous reaction with **3**–**5** would require displacement of a carbanion and that does not occur. The iodine measured in two reactions (**3e, i**), is suggestive of reaction at sulfonium sulfur, but the corresponding alkane was not found; the formation of iodine may have been caused by inadvertent oxidation of iodide ion. The DPDS that was found in reactions of NaSPh is also attributed to concomitant oxidation of PhS^-.

It is, of course, not possible to say that PhS^-, that we have deemed to be so thiophilic, does not react at sulfonium sulfur. Its thiophilicity suggests that this reaction should occur with formation of a sulfurane [**9**, Eqn. (4)], but if that does occur it must be in an unfruitful, reversible way.



9

Is it possible that a sulfurane *is* formed, and through ligand coupling[18] leads to what we have diagnosed as an S_N2 product? We have no direct evidence for the formation of **9** and indirect evidence that leads us to argue on two counts against its leading to RSPh. First, there is no reason to expect that ligand coupling in the reactions of **5** would occur exclusively or preferentially with the benzyl group. If ligand coupling was made feasible by the formation of **9**, both methyl and benzyl groups would be able to participate in it. In the case of **5c**, even the phenyl group could be displaceable, forming diphenyl sulfide. Second, with ligand coupling, the cyclohexyl group in **3h** and **4b** would appear only as cyclohexyl phenyl sulfide. There is no reason to believe that the *E*2*C* reaction we observe could occur within **9**. The parallel of our reactions with **3g** and **h** and cycloalkyl tosylates[10b] and the similarities in our results with **3g**–**i** and the cycloalkyl bromides and tosylates are also indicative of S_N2/*E*2*C* rather than another route.

Nevertheless, we made several attempts to verify an S_N2 route to RSPh in the reactions of PhS^- with **3**. In the first, we set out to measure and compare the rates of reaction of **3a** (methyl) and **3e** (neopentyl) with PhS^- by NMR spectroscopy. We used DMSO-d_6 rather than MeCN-d_3 as solvent because of the poor solubility of NaSPh in the latter. We were able to measure the rate of reaction of **3a** but reaction of **3e** was too slow to measure. Consequently, we resorted to a qualitative, competitive reaction between **3a** and **e** for a deficiency of PhS^-. In that case, all of **3a** reacted rapidly forming **7** and MeSPh, while the amount of **3e** remained unchanged. Thereafter, the methyl group of remaining **3a** was slowly transferred to solvent with the formation (deduced from the NMR) of d_6-Me_2SO^+Me. We saw no change in the NMR spectrum of **3e** to suggest the presence of a sulfurane **9**. We conclude that the result of the competitive reaction is also diagnostic of an S_N2 pathway.

More direct evidence for an S_N2 pathway was sought with the preparation of a 5-(alkyl)thianthrenium salt in which the alkyl group would undergo inversion of configuration in an S_N2 reaction and retention of configuration in ligand coupling. We chose first to alkylate **7** with *cis*- and *trans*-4-methylcyclohexyl formates. However, whereas we had no difficulty in alkylating **7** with cyclohexyl formate, we were repeatedly unsuccessful with the 4-methyl derivatives. Last, we turned to alkylation with (*S*)-2-butyl formate, $[\alpha]_D = +7.9°$, made from (*S*)-(+)-2-butanol, $[\alpha]_D = +13°$. Alkylation of **7** to give the expected 5-[(*R*)-2-butyl] thianthrenium triflate gave a product with a very low rotation, namely $[\alpha]_D = +0.9°$, suggesting that the 2-butyl group was mostly racemic. Reaction of the product with PhS^- gave 2-BuSPh also with a very low rotation, namely, $[\alpha]_D = +0.8°$. The positive rotation is consistent with the formation of (*S*)-2-BuSPh ($[\alpha]_D = +16°$) and thus consistent with an S_N2 pathway, but the results are not considered to be strong enough for a reliable diagnosis.

In conclusion, although we have not been able to provide direct evidence against ligand coupling, all the evidence we have is supportive of S_N2 (and *E*2*C*) reactions of **3**–**5**.

EXPERIMENTAL

The following compounds used as GC controls and/or for other preparations were obtained from commercial sources: methyl, ethyl, isopropyl, neopentyl and cyclohexyl iodide; cyclopentyl, cycloheptyl and benzyl bromide; methyl and ethyl phenyl sulfide; and methyl and ethyl formate. The preparations of cyclohexyl phenyl sulfide and cyclopentyl and cycloheptyl iodide were described earlier.[2] Acetonitrile was dried by distillation from P_2O_5 and again from $CaCl_2$; methylene chloride was dried by distillation from P_2O_5, and DMSO by boiling over CaH_2 followed by distillation under reduced pressure. Column A used for all compounds except MeI, Me_2S and cyclopentene was 10% OV-101 on 80-100-mesh Chromosorb-W HP, 4 ft × 1/8 in i.d. stainless steel (SS). The column was held at 50 °C for 2 min and ramped to 250 °C at 12 ° min^{-1}. The three compounds listed were assayed on a column (B) of 20% BEEA on 60–80-mesh Chromosorb P AW, 8 ft × 1/8 in i.d. SS held at 50 °C for 2 min and ramped to 100 °C at 6 °C min^{-1}. In each case the GC injector was set at 250 °C and the detector at 300 °C.

Preparation of 5-(alkyl)thianthrenium triflates. An example is given with **3a**. To a stirred mixture of 1.08 g of Th (5.0 mmol) and 600 mg (10.0 mmol) of methyl formate, cooled in an ice-bath, was added 2.5 ml of trifluoromethanesulfonic acid (triflic acid). The mixture was removed from the ice-bath and stirred for 10 h at room temperature, after which it was poured into 100 ml of water. The resulting suspension was extracted with 3×100 ml of dichloromethane. The combined dichloromethane solution was concentrated to 10 ml and poured into 200 ml of diethylether to give 1.16 g (3.05 mmol, 61 %) of **3a**, m.p. 176–178 °C. ^{1}H NMR, 300 MHz (CD_3CN) (*J* in Hz throughout) δ: 8.116, dd(d), 2H, *J* = 7.90, 1.30 (ave), 0.267 (upfield peaks split only); 7.947, dd(d), 2H, *J* = 7.98, 1.07 (ave), 0.228 (upfield peak split only); 7.806, td, 2H, *J* = 7.69 (ave), 1.41 (ave); 7.697, td, 2H, *J* = 7.69 (ave), 1.35 (ave); 3.160, s, 3H. ^{13}C NMR, δ: 136.875, 135.501, 134.547, 131.328, 130.658, 119.587, 25.610.

Attempts to prepare 5-(methyl)thianthrenium perchlorate by reaction of Th with methyl chloroformate and perchloric acid failed.

5-(Ethyl)thianthrenium triflate (**3b**) was prepared similarly, using 2.16 g (10.0 mmol) of Th and 1.48 g (20.0 mmol) of ethyl formate. The first precipitate from pouring the dichloromethene solution into diethylether was a yellow oil. This was dissolved in dichloromethane, cooled in an ice–salt bath and a small amount of diethylether was added, with scratching, giving 740 mg (1.88 mmol, 19%) of pale yellow **3b**, m.p. 65–67 °C. ^{1}H NMR, 300 MHz (CD_3CN), δ: 8.098, dd, 2H, *J* = 7.95, 1.05 (ave); 7.945, dd, 2H, *J* = 7.95, 1.05 (ave); 7.829, td, 2H, *J* = 7.73 (ave), 1.40 (ave); 7.706, td, 2H, *J* = 7.65 (ave), 1.40 (ave); 3.674, q, 2H, *J* = 7.35 (ave); 1.179, t, 3H, *J* = 7.35 (ave). ^{13}C NMR, δ: 136.889, 135.714 135.353, 131.274, 130.593, 117.721, 37.115, 9.828.

5-(Isopropyl)thianthrenium triflate (**3c**), m.p. 75–76 °C, was obtained in 94% yield from reaction of Th with isopropyl formate. ^{1}H NMR, 200 MHz (CD_3CN), δ: 8.098, dd, 2H, *J* = 7.76, 1.50 (ave); 7.946, dd, 2H, *J* = 7.93, 1.45 (ave); 7.845, td, 2H, *J* = 7.58 (ave), 1.43 (ave); 7.716, td, 2H, *J* = 7.58 (ave), 1.56 (ave); 4.469, sept, 1H, *J* = 6.73 (ave); 1.273, d, 6H, *J* = 6.69 (ave).

5-(2-Butyl)thianthrenium triflate (**3d**), m.p. 61–62 °C, was obtained in 40% yield from alkylation of Th with 2-butyl formate. ^{1}H NMR, 300 MHz (CD_3CN), δ:8.090 and 8.055, overlapping dd, 2H, *J* = 7.88, 1.42 (ave) and 7.82, 1.32 (ave); 7.951, dd, 2H, *J* = 7.97, 1.29 (ave); 7.841, td, 2H, *J* = 7.58 (ave), 1.37 (ave); 7.712 and 7.164, overlapping td, 2H, *J* = 7.66 (ave), 1.26 (ave) and 7.73 (ave), 1.24 (ave). 200 MHz, δ:4.402, sextet, 1H, *J* = 6.54 (ave); 1.600, quintet, 2H, *J* = 7.10 (ave); 1.214, d 3H, *J* = 6.89; 0.953, t, 3H, *J* = 7.36 (ave).

5-(Cyclopentyl)thianthrenium triflate (**3g**), 85% yield, m.p. 90–92 °C after reprecipitation from dichloromethane. ^{1}H NMR, 200 MHz (CD_3CN), δ:8.114, dd, 2H, *J* = 7.77, 1.40 (ave); 7.945, d, 2H, *J* = 7.81; 7.835, td, 2H, *J* = 7.62 (ave), 1.18 (ave); 7.707, td, 2H, *J* = 7.55 (ave), 1.36 (ave); 4.707, m (mainly q), 1H, *J* = 6.0 (ave); 1.936–1.66, m, overlapping solvent peaks.

5-(Cycloheptyl)thianthrenium triflate (**3i**), 17%, m.p. 70–71 °C after reprecipitation from dichloromethane. ^{1}H NMR, 200 MHz (CD_3CN), δ: 8.807, dd, 2H, *J* = 7.73, 1.38 (ave); 7.951, dd, 2H, *J* = 7.83, 1.46; 7.832, td, 2H, *J* = 7.62 (ave), 1.52 (ave); 7.707, td, 2H, *J* = 7.54 (ave), 1.50 (ave): 4.501, m. 1H: 1.759–1.441, m. 12H.

5-(Benzyl)thianthrenium triflate (**3f**). Thianthrene (864 mg, 4.0 mmol) and benzyl bromide (684 mg, 4.0 mmol) were dissolved in 20 ml of dichloromethane. The solution was stirred while 514 mg (2.0 mmol) of silver triflate was added. After 3 h of stirring the mixture was filtered into 80 ml of dry diethylether. The precipitated product was reprecipitated from MeCN with diethylether, giving 560 mg (1.23 mmol, 61%) of **3f**, m.p. 87–88 °C. ^{1}H NMR 200 MHz (CD_3CN), δ: 4.935, s, 2H; the NMR spectrum of **3f** in the aromatic region was a series of overlapping multiplets, δ 7.987–7.058, from the thianthrenium and phenyl rings. Also, **3f** tended to decompose slowly in MeCN so that the aromatic region was further complicated by a small amount of thianthrene and the departed benzyl group. Attempts to alkylate Th with benzyl formate failed.

5-(Neopentyl)thianthrenium perchlorate (**3e**). To a stirred suspension of 630 mg (2.0 mmol) of $Th^{+\cdot}ClO_4^-$ in 2 ml of MeCN was added dropwise a solution of 342 mg (1.0 mmol) of dineopentylmercury in 5 ml of MeCN. The mixture was stirred until the color of $Th^{\cdot+}$ had disappeared. The solvent was removed in a rotary evaporator and the residue was dissolved in dichloromethane. That solution was shaken with 1% aqueous LiCl, separated, concentrated to about 5 ml and poured into dry diethylether to precipitate 235 mg (0.61 mmol, 61%) of **3e**, m.p. 125–127 °C (decomp.). ^{1}H NMR, 200 MHz (CD_3CN), δ:8.141 dd, 2H, *J* = 7.82, 1.42 (ave); 7.982, dd, 2H, *J* = 7.89, 1.229 (ave); 7.813, td, 2H, *J* = 7.62 (ave), 1.52 (ave); 7.695, td, 2H, *J* = 7.60 (ave), 1.42 (ave); 3.710, s, 2H; 1.040, s, 9H.

5-(Cyclohexyl)thianthrenium triflate (**3h**) was prepared from 5.0 mmol of Th, 10.0 mmol of cyclohexyl formate and 2.5 ml of triflic acid. The product was reprecipitated from dichloromethane with ether three times, giving 1.86 g (4.15 mmol, 83%) of **3h**, m.p. 80–81 °C. ^{1}H NMR, 200 MHz (CD_3CN), δ:8.057, dd, 2H, *J* = 7.76, 1.33; 7.947, dd, 2H, *J* = 7.89, 1.29 (ave); 7.834, td, 2H, *J* = 7.63 (ave), 1.37 (ave); 7.701, td, 2H, *J* = 7.56 (ave), 1.44 (ave); 4.310, quintet, 1H, *J* = 7.38 (ave); 1.817–1.753, m, 2H; 1.664–1.544, m, 5H; 1.413–1.268, m 3H.

Diphenylmethylsulfonium triflate (**4a**). Reaction of 930 mg (5.0 mmol) of diphenyl sulfide, 600 mg (10.0 mmol) of methyl formate and 2.5 ml of triflic acid gave 1.56 g (4.46 mmol, 89%) of **4a**, m.p. 95–97 °C. ^{1}H NMR, 200 MHz (CD_3CN), δ: 7.968–7.903, m, 4H; 7.695–7.580, m, 6H; 3.688, s, 3H. Lit. m.p. 94–97.5 °C,

from alkylation of diphenyl sulfide with methyl iodide and silver triflate.[19]

Cyclohexyldiphenylsulfonium triflate (**4b**), prepared similarly to **4a**, pale yellow solid after two precipitations from dichloromethane, m.p. 96–98 °C. ^{1}H NMR, 200 MHz (CD_3CN), δ:7.982–7.939, m, 4H; 7.845–7.684, m, 6H; 4.535, br m, 1H; 1.995–1.840, br m, overlapping solvent; 1.759–1.407, br m, 7H. Compound **4b** was obtained as a semi-solid by Kang and Ku in the reaction of cyclohexyl phenyl sulfide with diphenyliodonium triflate.[20]

*Preparation of benzylsulfonium perchlorates (**5**).* The method of Aggarwal *et al.* was used.[8] To a solution of 2.0 mmol of sodium perchlorate in a minimum amount of acetone were added 2.0 mmol of a dialkyl sulfide and 2.0 mmol of alkyl halide. The solution was stirred for 2 days at room temperature. The solid that formed was filtered off, the filtrate was evaporated under reduced pressure and the residue was dissolved in a small amount of dichloromethane. The solid that remained was filtered off and diethylether was added to the filtrate to precipitate the product.

Benzyldimethylsulfonium perchlorate (**5a**), from dimethyl sulfide and benzyl bromide, 75%, m.p. 104–105 °C. ^{1}H NMR, 200 MHz (CD_3CN), δ: 7.461, s, 5H; 4.722, s, 2H; 2.907, s, 6H.

Dibenzylmethylsulfonium perchlorate (**5b**), from benzyl methyl sulfide and benzyl bromide, 68%, m.p. 120–121 °C. ^{1}H NMR, 200 MHz (CD_3CN), δ:7.530–7.482, m, 4H; 7.394–7.314, m, 6H; 4.849, d, 2H, J = 12.6; 4.693, d, 2H, J = 12.6; 2.692, s, 3H. Lit. m.p. 122 °C, and diastereotopic benzylic CH_2 ^{1}H NMR, 60 MHz (DMSO-d_6), δ: 5.32, d, 2H, J = 13.0; 5.16, d, 2H, J = 13.0.[21]

Benzylmethylphenylsulfonium perchlorate (**5c**), from thioanisole and benzyl bromide, 4 days of stirring, 6.4%, m.p. 132–133 °C. ^{1}H NMR, 200 MHz (CD_3CN), δ: 7.791–7.605, m, 5H; 7.434–7.321, m, 3H; 7.193, d, 2H, J = 7.49; diastereoptopic CH_2, 4.878, d, 1H, J = 12.8; 4.691, d, 1H, J = 12.6; 3.169, s, 3H. Lit. m.p. 115–117 °C, ^{1}H NMR, 60 MHz (acetone-d_6), δ: 8.00–7.57, m, 5H; 7.25, br s, 5H; 5.10, d, 2H, J = 4.4; 3.41, s, 3H.[22] The triflate salt had a ^{1}H NMR spectrum (CD_3CN) similar to that of **5c**.[23]

Sulfides. Sulfides were prepared as follows. Benzyl phenyl sulfide was prepared by stirring a mixture of benzyl bromide (2.8 g, 16 mmol) and thiophenol (1.5 g, 14 mmol) with Cs_2CO_3 (4.6 g, 14 mmol) under argon for 48 h. The mixture was poured into 50 ml of 2 M NaOH. Extraction with diethylether gave 2.5 g (12.5 mmol, 89%) of product, m.p. 37–38 °C. Lit. m.p. 40–41 °C.[24,25]

Phenyl isopropyl sulfide, 82%, from reaction of isopropyl iodide with PhSNa in MeCN solution was purified on a column of silica gel. The product was an oil[26] that gave a single GC peak. ^{1}H NMR, 200 MHz (CD_3CN), δ:7.423–7.362, m, 2H; 7.331–7.173, 2m, 3H; 3.374, heptet, 1H, J = 6.66; 1.291, d, 6H, J = 6.66.

Neopentyl phenyl sulfide, 62%, obtained as an oil from reaction of neopentyi iodide with sodium thiophenoxide was purified on a column of silica gel, and had a satisfactory ^{1}H NMR spectrum.[27]

2-Butyl phenyl sulfide, 36%, obtained from reaction of 2-butyl iodide with NaSPh in MeCN had one GC peak after purification on a column of silica gel. ^{1}H NMR, 200 MHz ($CDCl_3$), δ: 7.419–7.358, m, 2H; 7.325–7.159, m, 3H; 3.163, sextet, 1H, J = 6.63 (ave); 1.598, m, 2H; 1.272, d, 3H, J = 6.69; 1.007, t, 3H, J = 7.36 (ave).

(*S*)-2-Butyl phenyl sulfide. (*R*)-2-Butyl iodide (assumed configuration[28]) was prepared by reaction of (*S*)-2-butanol with NaI and Me_3SiCl in MeCN following the procedure of Olah *et al.*[29] The reaction solution was diluted with diethylether and the ether solution was washed successively with water, sodium thiosulfate solution and brine, and dried over Na_2SO_4. The ether solution was concentrated to a small volume and used for reaction with NaSPh in MeCN. Work-up and chromatography on silica gel gave 2.3% of (*S*)-(+)-2-butyl phenyl sulfide, with a single GC peak and $[\alpha]_D$ (room temperature) in MeCN +15.3°. A second preparation, 16% yield, had $[\alpha]_D$ = +17.3°.

Cyclopentyl phenyl sulfide, 71%, was obtained similarly from cyclopentyl bromide as an oil[25,30] with a single GC peak. ^{1}H NMR, 200 MHz (DMSO-d_6), δ: 7.38–7.13, m, 5H; 3.597, m, 1H; 2.09–2.00, m, 2H; 1.82–1.56, m, 6H.

Cycloheptyl phenyl sulfide, 80%, was obtained from cycloheptyl bromide as an oil with a single GC peak. ^{1}H NMR, 200 MHz ($CDCl_3$), δ: 7.392–7.186, m, 5H; 3.340, heptet, 1H, J = 4.40 (ave); 2.079, m, 2H; 1.459–1.777, m, 10H.

Formates. Formates were prepared as follows. Isopropyl formate was prepared in 60% yield by reaction of isopropyl alcohol with formic acid catalyzed by concentrated H_2SO_4, b.p. 62–65 °C. ^{1}H NMR, 200 MHz ($CDCl_3$), δ:8.017, s, 1H; 5.139, sept of d, 1H, J = 6.26, 1.00; [these splittings are similar to these for ethyl formate in the AIST (Agency of Industrial Science and Technology), Japan, database. (http://www.go.jp)], 1.296, d, 6H, J = 6.29. Lit. b.p. 68.8-68.9 °C.[31]

(S)-(+)-2-Butyl formate. A solution of 7.4 g (0.10 mol) of (*S*)-(+)-2-butanol, 10.5 g (0.20 mol) of 88% formic acid and 10.8 g (0.10 mol) of Me_3SiCl in 20 ml of MeCN was stirred at room temperatue for 24 h and poured into water. To this was added solid $NaHCO_3$ until gas evolution stopped. Three extractions with diethylether, work-up and distillation gave 4.7 g (46%) of product, b.p. 90–92 °C, $[\alpha]_D$ in MeCN +7.9 °. This product was used for the attempted preparation of (*R*)-**3d** as described for **3d** itself.

Cyclohexyl formate was prepared by reaction of cyclohexanol (0.15 mmol) with formic acid (0.20 mmol)

and chlorotrimethylsilane (0.15 mmol) in 20 ml of MeCN.[32] The mixture was stirred overnight and poured into water. The aqueous solution was neutralized with solid $NaHCO_3$ and extracted three times with diethyl-ether. After work-up and fractional distillation, the portion of b.p. 30–32 °C (3.5 mmHg) was freed from an impurity on a column of silica gel and had ^{1}H NMR, 200 MHz ($CDCl_3$), δ:8.046, d, 1H, $J = 0.80$, [these splittings are similar to those for ethyl formate in the AIST (Agency of Industrial Science and Technology), Japan, database (http://www.go.jp)]; 4.891, tt, 1H, $J = 8.51$ (ave), 4.31 (ave); 1.906–1.700, m, 4H; 1.600–1.232, m, 6H. Lit. b.p. 94.5–95.0 °C (97–98 mmHg).[33]

Cyclopentyl formate was prepared similarly, b.p. 30–32 °C (6.5 mmHg), ^{1}H NMR, 200 MHz ($CDCl_3$), δ:7.871, s, 1H; 5.139, irreg. m, 1H; 1.754–1.469, irreg. m, 8H.

Cycloheptyl formate was prepared similarly, b.p. 55–58 °C (5 mmHg), ^{1}H NMR, 200 MHz ($CDCl_3$), δ: 8.023, s, 1H; 5.065, hept of d, 1H, $J = 4.29$ (ave), 0.92 (ave). 1.974–1.870, m, 2H; 1.781–1.429, m, 10H.

*Reaction of sulfonium salts (**3** and **4**) with iodide ion.* An example is given with **3a**. In a 10 ml volumetric flask were placed 60.4 mg (0.159 mmol) of **3a**, 67.5 mg (0.407 mmol) of KI, 21.9 mg (0.171 mmol) of naphthalene as GC standard and 10 ml of MeCN. The septum-capped mixture was stirred overnight and was assayed three times for Th (column A) and MeI (column B), giving 0.158 ± 0.002 mmol (99.4%) of Th and 0.146 ± 0.020 mmol (91.8%) of MeI. Reactions of **3b–i** and **4a** and **b** were carried out similarly. In some cases, the reaction solution was noticeably yellow or brown at the end of stirring and in some of these cases the solution was titrated for iodine with aqueous sodium thiosulfate after GC analysis, e.g. with **3e** (entry 9, Table 1) and **3i** (entry 18). In the reaction of **3g**, in which a large amount of ene (cyclohexene, 79%) was formed, three assays were carried out after overnight stirring and three more after a second night's stirring (results in parentheses), giving 78.6 (78.6)% of cyclohexene. 20.1 (20.7)% of cyclohexyl iodide and 103 (103)% of Th.

*Reaction of sulfonium salts (**3** and **4**) with thiophenoxide ion.* An example is given with **3a**, the procedure being similar to that with KI. Compound **3a** (58.2 mg, 0.153 mmol), NaSPh (54.3 mg, 0.411 mmol) and naphthalene (22.2 mg, 0.173 mmol) were used. Assays on column A gave 0.154 mmol (100.7%) of thioanisole and 0.154 mmol (100.7%) of Th. Diphenyl disulfide (0.0193 mmol) was also formed and is attributed, because of the quantitative yields of products, to oxidation of some of the unused thiophenoxide ion, either in solution or in the GC inlet. Reactions of **3b–i** and **4a** and **b** were carried out similarly. In all of these reactions not all of the NaSPh was dissolved. In the reaction of **4b**, column A could not separate diphenyl sulfide (Ph_2S) and cyclohexyl phenyl sulfide. The yields of these compounds were calculated as stated in Table 2.

*Reactions of benzylsulfonium salts (**5**) with bromide and thiophenoxide ions.* The source of bromide ion was mainly KBr in the presence of 18-crown-6 (KBr/18C6). Tetrabutylammonium bromide was used with **5a** but was avoided thereafter because it gave rise to spurious GC peaks. Naphthalene and 2-butanone were used together as GC standards. When **5a** was used the products designated as $PhCH_2SR_1$ and $PhCH_2SR_2$ were the same ($PhCH_2SMe$) so that half of the total yield is entered in each column (entries 1 and 2). The same applies to R_1X and R_2X (MeSPh, entry 2). We were unable to assay MeBr with our columns (entry 1). The experimental procedures were the same as with **3** and **4**.

*Competition between **3a** and **3e** in reaction with thiophenoxide ion.* A solution of 19.6 mg ($5{,}17 \times 10^{-5}$ mol) of **3a** and 19.9 mg (5.16×10^{-5} mol) of **3e** was prepared in 1 g of DMSO-d_6. A solution of 3.11 mg (2.36×10^{-5} mol) of NaSPh was prepared in 1 g of the solvent and the two solutions were mixed. The NMR spectrum recorded after 11 min showed the singlet of MeSPh at 2.47 ppm. Integration of that singlet and of the singlet for the CH_2 group of **3e** at 3.99 ppm showed that 88% of **3a** had been converted into MeSPh. After 18 h no change in the spectrum of **3e** could be found, but the remaining **3a** had transferred its methyl group to the solvent, visible at 3.99 ppm. The singlet of the CH_2 group of neopentyl phenyl sulfide was not seen.

Reactions of cycloalkyl bromides and tosylates with NaSPh. As an example, a solution of 38.6 mg (0.161 mmol) of cyclopentyl tosylate and 50.3 mg (0.381 mmol) of NaSPh in 10 ml of MeCN containing naphthalene and 2-butanone as GC standards was stirred overnight. GC assay gave 97% of cyclopentyl phenyl sulfide and 2% of cyclopentene. Similar reactions were carried out with other cycloalkyl derivatives.

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