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Reactions of nucleophiles with 5-(alkoxy)thianthrenium ions

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ABSTRACT: Reactions of 5-(alkoxy)thianthrenium perchlorates (**1**) with weakly basic nucleophiles Br^-, I^- and PhS^- (X^-) in MeCN and DMSO led to S_N2 substitution, *E2C* elimination, and reaction at sulfonium sulfur to extents depending on the structure of the alkoxy group (RO) in **1** and the nucleophile. Three types of reaction occurred with R = cyclopentyl (**1a**), cyclohexyl (**1b**), *cis*- (**1c**) and *trans*- 4-methylcyclohexyl (**1d**) and cycloheptyl (**1e**), and $X^- = Br^-$ and I^-. That is, S_N2 reaction gave RX and thianthrene 5-oxide (ThO), *E2C* reaction gave cycloalkene and ThO and reaction at sulfonium sulfur gave X_2, thianthrene (Th) and cycloalkanol (ROH). Earlier work with R = Me (**1f**) and Et (**1g**) and $X^- = I^-$, Br^- had shown that only S_N2 reaction occurred. In contrast with reactions of halide ions, reactions of PhS^- with **1b–g** occurred only at sulfonium sulfur, giving Th, ROH and PhSSPh (DPDS). For comparison with **1**, reactions of Ph_2S^+OMe (**2**) with I^- and PhS^- were carried out. Reaction with I^- gave only $Ph_2S{=}O$ and MeI (S_N2). Reaction with PhS^- gave very little PhSMe (S_N2) but mainly Ph_2S, MeOH, and DPDS from reaction at sulfonium sulfur. The differences in nucleophilic pathways (PhS^- vs Br^- and I^-) in reactions with **1** and **2** are attributed to differences in thiophilicities of the nucleophiles. The thiophilicity of PhS^- dominates its reactions with **1** and **2**. The direction toward products (Th, ROH and DPDS) in these reactions is compounded by the ease of displacement of alkoxide from **1** and **2** by PhS^-, and the ease with which, subsequently, thiophilic PhS^- attacks sulfenyl sulfur in the resulting phenylthiosulfonium ion. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: alkoxysulfonium ions; nucleophilic reactions; thiophilic reactions

INTRODUCTION

Alkoxysulfonium salts have been known for about 60 years, since the first one was prepared by Meerwein.[1–3] Meerwein's method, the alkylation of a sulfoxide, is in fact the one frequently used for preparing methoxy- and ethoxysulfonium salts, utilizing commonly available trimethyl- and triethyloxonium salts as alkylating agents.[4] Recently, we found that thianthrene cation radical perchlorate ($Th^{\cdot+}ClO_4^-$) reacts easily with a variety of primary and secondary alcohols (Scheme 1), permitting the isolation of crystalline 5-(alkoxy)thianthrenium perchlorates (**1**).[5–7] The availability of these salts allowed us to begin a systematic study of their reactions with nucleophiles. We found, for example, with the use of ^{18}O labeling, that water reacted with 5-(cyclohexyloxy)thianthrenium perchlorate at sulfonium sulfur, producing thianthrene 5-oxide (ThO) and cyclohexanol.[5] Reactions of **1** containing acyclic primary and secondary alkyl groups (R) with bromide and iodide ions were different, however. The major products were alkyl halide and ThO [Scheme 2, Eqn. (1)]. The products and the rates of reaction (with primary and isopropyl R) indicated that these reactions were S_N2 displacements. Small amounts of two side reactions were also observed. One [Eqn. (2)] was an elimination that gave alkene and ThO, and the other [Eqn. (3)] was reaction at sulfonium sulfur that gave thianthrene (Th), halogen and the alcohol (ROH).[7]

We have continued with studies of reactions of nucleophiles with **1** and report here the reactions of **1a–e** with Br^- and I^- (Scheme 2) in which R is cyclopentyl (**1a**), cyclohexyl (**1b**), *cis*- (**1c**) and *trans*-4-methylcyclohexyl (**1d**) and cycloheptyl (**1e**). As shown in Scheme 2, these reactions encompassed substitution [Eqn. (1)], elimination [Eqn. (2)] and halogen formation [Eqn. (3)]. We also studied reactions of **1b–e** with thiophenoxide ion (PhS^-). In contrast with halide ion reactions, those with PhS^- occurred only at sulfonium sulfur, with the formation of Th, cycloakanol (ROH) and diphenyl disulfide (X_2 = DPDS). For comparison with reactions of **1** having cycloalkyl R, we studied also reactions of 5-(methoxy)- (**1f**) and 5-(ethoxy)thianthrenium perchlorate (**1g**) with PhS^-. For further comparison with reactions of **1**, we studied reactions of methoxydiphenylsulfonium tetrafluoroborate (**2**) with I^- and PhS^-.

Studies of reactions of alkoxysulfonium ions with nucleophiles are by no means new. The largest systematic

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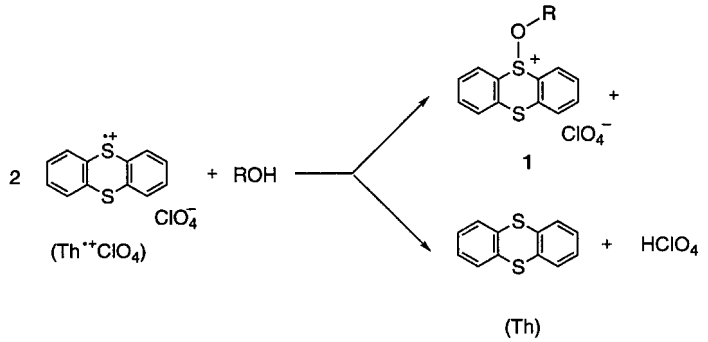
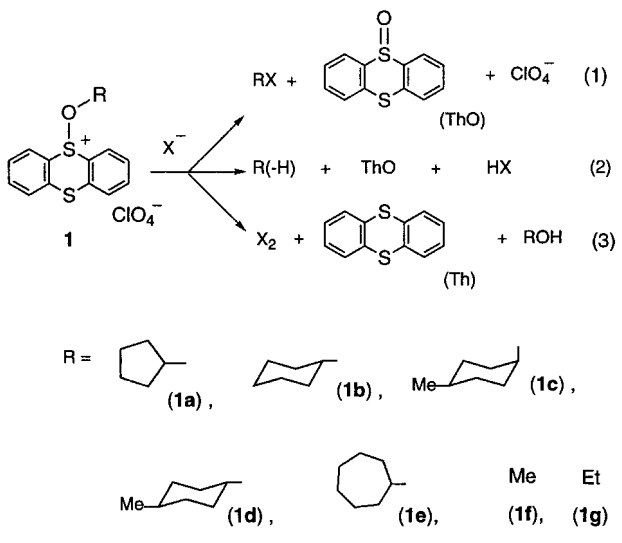


Scheme 1

studies have been in reactions of hydroxide ion, alkoxide ions and alcohols with methoxy- and ethoxysulfonium ions (since those studies were used in characterizing the exchange of alkoxy ligands at the sulfur atom), the racemization of sulfoxides and the oxidation of alcohols to aldehydes and ketones.[2,4,8–12] As far as we are aware, systematic or deliberate studies of reactions of alkoxysulfonium ions with halide ions have not been reported. Reactions of chloride and bromide ion with particular alkoxysulfonium ions, coincidental, for example, with, and arising from studies of, oxidations of alcohols, have been reported,[13–16] and we shall refer further to these reactions. We shall refer further, also, to the reduction of sulfoxides by HI[17] and the role of halide ions in the racemization of sulfoxides,[18] and in the exchange of ethoxide groups in an ethoxysulfonium ion.[19] Reports of reactions of alkoxysulfonium ions with thiolate ions are also not numerous. Oae and Kim[20] have reported the reaction of ethoxydiphenylsulfonium tetrafluoroborate with *p*-tolyl thiolate and Kobayashi and co-workers[21,22] have reported reactions of arylmethylmethoxysulfonium salts with PhS^-. We shall refer to these reactions also. We have been unable to find any other reports of reactions of thiolate ions with alkoxysulfonium salts.



Scheme 2

RESULTS AND DISCUSSION

Reactions with I^- and Br^-

Reactions were carried out in dry acetonitrile (MeCN). The source of I^- was KI. Two sources of Br^- were used. Because KBr is not sufficiently soluble in MeCN, it was used, as one of the sources, in the presence of 18-crown-6 (18C6). A second source was tetrabutylammonium bromide (TBAB). Reaction products, except I_2 and Br_2, were assayed with quantitative gas chromatographic (GC) analysis. Because salts such as **1a–g** decompose when injected into a hot gas chromatograph inlet,[5] it was necessary to ensure that reaction was complete before the final assay was made. To do that, assays of the reaction mixture solution were made at timed intervals until, when reaction appeared to be complete, completion was verified by injecting a small amount of aqueous K_2CO_3 into the reaction solution. Salts such as **1a–g** are converted into ThO and ROH by aqueous K_2CO_3. Therefore, completion of reaction with halide ion was indicated by invariant assay before and after injection of aqueous K_2CO_3. In Tables 1 (for I^-) and 2 (for Br^-) only the final assay of the dry reaction solution is reported. Iodine was assayed by titration of an aliquot of solution after addition of aqueous K_2CO_3. Assay of Br_2 could not be made directly, and therefore it was assayed after conversion into I_2 by addition of KI.

Reactions with I^-. Six products are listed in Table 1: cycloalkene (ene), cycloalkyl iodide (RI), ThO, Th, cycloalkanol (ROH) and I_2. The amount of ene was small (6.6%) and the amount of RI large (89%) from **1e**. In contrast, the amount of ene was large (about 50%) and RI small (2–6%) from **1b** and **c**. From **1a**, 21% of ene and 55% of RI were obtained, whereas from **1d**, the amounts were approximately 35 and 38%. It is apparent that **1e**

Table 1. Products of reactions of **1a**–**e** with KI

Compound	Product (%)						
	ene	RI	ThO	Th	ROH	I_2[a]	Ratio[b]
1a	21	55	78	19	[c]	17	0.97
1b	53	6.0	55	44	43	43	1.07
1c[d]	52	2.5[e]	52	48	46	47	1.05
1d[f]	35	38	76	23	21	23	0.96
1e	6.6	89	95	5.4	tr	5.3	1.01

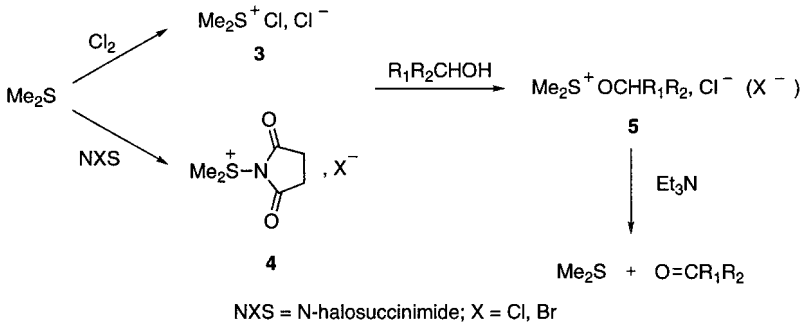
[a] Yield (%) based on starting amount of **1**.
[b] Sum of (ene + RI)/ThO.
[c] Peak overlapped with solvent.
[d] Average of two experiments. Errors in tabulated averages were 2.0 (ene), 0.6 (RI) and 1.0 (all other products.
[e] Assay based on response factor for *cis*-(4-methyl)iodocyclohexane because pure *trans* isomer could not be prepared.
[f] Average of two experiments. Errors in tabulated averages were 1.0 (ene and I_2), 2.0 (RI and Th), 3.0 (ThO) and 4.0 (ROH).

behaved much like a primary salt[7] in undergoing mainly S_N2 displacement, whereas **1a** and **d** to some extent, and **1b** and **c** to major extents, succumbed to elimination.

The duality of pathways, substitution and elimination, reported in Table 1 (and Table 2), and occuring to a much lesser extent in our earlier work, parallels competing substitution and elimination that was uncovered in reactions of alkyl halides and tosylates with weakly basic nucleophiles about 40 years ago. The elimination reaction is a lesser known but well recognized part of the spectrum of *E*2 eliminations. When first reported by Winstein *et al.*[23] with cyclohexyl substrates, it was called, for want of a better understanding, the 'merged' mechanism, connoting an elimination that occurred in a pathway destined for S_N2 substitution. Thus, this elimination accompanied S_N2 reactions of weakly basic, good nucleophiles, and gave rise to the classification, albeit somewhat controversially, *E*2*C* elimination.[24–26] This is the elimination that iodide ion causes in reactions with **1a–e**, much more pronounced than was obtained in our earlier work with primary and acyclic secondary alkyloxy groups.[7] The data in Table 1 show that *E*2*C* reaction becomes more competitive with S_N2 on going from cycloheptyl to cyclopentyl and, lastly, cyclohexyl alkyl groups. Reactions with the cyclohexyl compounds **1b–d** are particularly striking in that they parallel results reported years ago for cyclohexyl halides and tosylates. That is, Winstein *et al.*[23] noted that *cis*-4-*tert*-butylcyclohexyl tosylate gave more ene than the *trans* isomer in reactions with I^-, Br^- and PhS^-. Eliel and Haber[27] found in reactions with PhS^- that the rate of elimination from *cis*-4-*tert*-butylcyclohexyl bromide was 66 times faster than from the *trans* isomer. In those *cis* substrates, the leaving group is axially oriented. That is also the orientation of the thianthreniumoxy group in the ring of **1c**,[6] and Table 1 shows that more ene (52%) is obtained from the **1c** than from its *trans* isomer, **1d** (35%). Thus, **1c** and **d** have the characteristics of *E*2*C* reactions observed earlier with much simpler substrates. It is noticeable that the amounts of ene and RI formed also from the cyclohexyloxy salt (**1b**) are similar to those formed from **1c** rather than **1d**, which has an equatorial thianthreniumoxy group. At first sight, this was puzzling, since the dominant orientation of the thianthreniumoxy group in cyclohexyl ring of **1b** is equatorial.[6] However, **1b**, but not **1c** and **d**, undergoes ring inversion in solution, and at room temperature approximately 30% has the axially oriented thianthreniumoxy group.[6] We deduce, therefore, that the axial conformer reacts in the *E*2*C* mode more rapidly than the equatorial conformer, as found by earlier workers with simpler systems, thus leading **1b** into a pattern of reaction comparable to that for **1c**. It is apparent that, in S_N2/*E*2*C* terminology, ThO is a good leaving group, and that the cyclopentyl and cycloheptyl rings of **1a** and **e** allow more easily for S_N2 displacement than the cyclohexyl systems **1b**–**d**. We have not been able to find studies of or references to *E*2*C*-type reactions with cyclopentyl and cycloheptyl derivatives comparable to those of cyclohexyl halides and tosylates.

Reactions that give RI and ene must also give ThO [Eqns (1) and (2)]. Therefore, the sum of the yields of RI and ene should equal the yield of ThO. That this is reasonably correct in our results is shown by the ratio (RI + ene)/ThO in Table 1.

Earlier, we noted that although we have not been able to find systematic studies of reactions of halide ions with alkoxysulfonium salts in the literature, reactions of chloride and bromide ions with particular alkoxysulfonium ions had been reported by Corey and co-workers.[13–16] The reactions originated in studies of oxidation of primary and secondary alcohols through the agency of an alkoxydimethylsulfonium ion (**5**) formed *in situ* from a chlorosulfonium chloride (**3**) and/or succinimidosulfonium chloride and bromide (**4**, Scheme 3). Corey and coworkers noted that in some cases oxidation was accompanied by or superseded by halogenation, with the formation of R_1R_2CHX and Me_2SO. For example, when the succinimido chloride **4** was used, benzhydrol and 2-cyclohexenol gave the corresponding alkyl chlorides rather than the ketones.[13] Reaction at −25 °C with

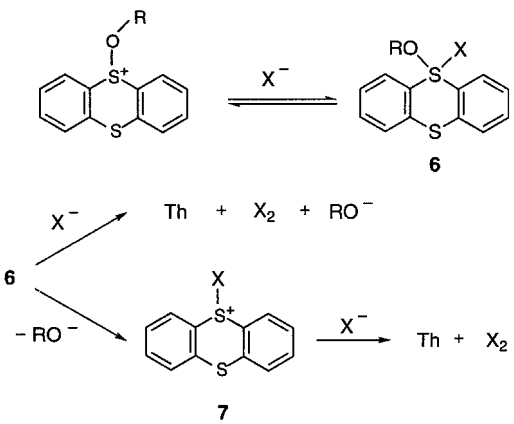


NXS = N-halosuccinimide; X = Cl, Br

Scheme 3

benzhydrol, 2-cyclohexenol and benzyl alcohol in the absence of triethylamine gave, in fact, >95% yields of alkyl chlorides.[14] Analogously, geraniol was converted into geranyl bromide with the use of *N*-bromosuccinimide. Corey and co-workers attributed alkyl halide formation to cases in which the sulfoxonium ion intermediate (**5**, Scheme 3) is relatively unstable[14] and contains alcohols which correspond with stabilized carbocations.[13,15]

An analogous chlorination has been reported by Johnson and Jones[29] in the formation of alkoxysulfonium ions by the oxidation of sulfides with *tert*-butyl- and isopropyl hypochlorites at −78 °C. The initial *tert*-butoxy- and isopropyloxysulfonium chlorides were found to be too unstable to be isolated, but could be stabilized into isolable hexachloroantimonates by the addition of antimony chloride. Without this stabilization the initial salts decomposed into sulfoxide and *tert*-butyl- and isopropyl chloride; quantitative data for chloroalkane formation were not provided. Obviously, the formation of *tert*-butyl chloride could not be from an S_N2 displacement and, by analogy, isopropyl chloride was not formed in that way either. The mechanism of chloroalkane formation in these cases remains unidentified.



Scheme 4

It is evident that our reactions of **1** with iodide (and bromide) ion differ from the halogenations accompanying these oxidation reactions. That is, our first report of alkyl halide formation was with examples of **1** that were not unstable in solution and that contained primary and acyclic secondary alkyl groups unlikely to represent stabilized carbocations. In those reactions the rates of formation of primary alkyl halides clearly fitted S_N2 characteristics. Furthermore, 5-(neopentyloxy)thianthrenium perchlorate failed to give neopentyl- or any other alkyl iodide, a finding that was consistent with S_N2 characteristics of alkyl iodide formation. In our present work, the behavior of the cyclohexyloxy salts **1b**–**d** fit clearly into the $S_N2/E2C$ duality of earlier reports. In only one respect are Corey and co-workers' results analogous to ours, and that is that saturated alcohols, ordinarily inert to conversion into halides in competition with oxidation, could be converted during lengthy reaction times in the absence of triethylamine. Thus, cyclohexylmethanol gave 43% of the chloride after 100 h at 5 °C, while cyclohexylmethanol and 2-phenylethanol gave 70% of the bromides after 36 h at 20 °C in reaction with derivative **4**.[14] These reactions would appear to be S_N2 displacements analogous to ours. Corey and co-workers commented that the use of reagents derived from other sulfides may extend the scope of their halogenation reaction. Our use of the isolable alkoxythianthrenium salts fulfils that prognosis, at least insofar as primary and acyclic secondary alkyl groups are concerned. Suited also to halide formation is the methoxydiphenylsulfonium ion (**2**), which as the tetrafluoroborate gave methyl iodide and diphenyl sulfoxide quantitatively in reaction with iodide ion (see Experimental section).

Table 1 lists three more products, Th, ROH and I_2. These come from a third type of reaction of compounds **1** with halide ion, namely reaction at the sulfur atom (Scheme 4). This reaction was observed to a small extent in our earlier work,[7] but is seen here to be significant in reactions of the cycloalkoxy derivatives. It occurs to the greatest extent with **1b** and **c**, in which, seemingly, S_N2 displacement is the most difficult. Thus, reaction at sulfur, as with elimination, competes with the S_N2

Table 2. Products of reactions of **1a, b** and **e** with bromide ion

Compound	Source[a] of Br^-	Product (%) ene	RBr	RBr_2	ThO	Th	ROH	Br_2	Ratio[b]
1a	TBAB	tr	89	—[c]	94	5.1	—[d]	6.2	0.95
1a	KBr–18C	1.5	89	—[c]	100	3.5	—[d]	2.0	0.91
1b[e]	KBr–18C	3.9	4.2	43	55	45	45	8.2	0.93
1e[f]	TBAB	1.0	89	—[c]	93	8.9	1.3	9.6	0.97
1e[g]	KBr–18C	0	97	—[c]	97	5.1	3.7	—[c]	1.00

[a] TBAB is tetrabutylammonium bromide; KBr–18C is potassium bromide + 18−crown-6.
[b] Sum of (ene + RBr + RBr_2)/ThO.
[c] Not sought or measured.
[d] Peak overlapped with solvent.
[e] Average of two experiments. Errors in tabulated averages were 2.4 (ene), 0.6 (RBr), 1.0 (RBr_2 and ThO), 2.0 (Th), 3.0 (ROH) and 4.8 (Br_2).
[f] Average of two experiments. Errors in tabulated averages were 1.0 (ene), 5.0 (RBr), 3.0 (ThO), 4.1 (Th), 1.3 (ROH) and 3.4 (Br_2).
[g] Average of two experiments. Errors in tabulated averages were 1.0 (RBr), 2.0 (ThO), 0.3 (Th) and 1.8 (ROH).

reaction. Reaction at sulfur should give equal amounts of Th, ROH and I_2, and this is borne out by the data in Table 1.

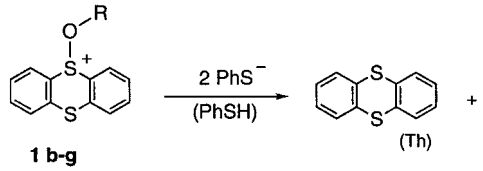
Reactions with Br^-. These reactions were with **1a, b** and **e**, and the source of bromide ion was either potassium bromide in the presence of 18-crown-6 or tetrabutylammonium bromide. In analogy with iodide ion reactions, three pathways were observed (Scheme 2). The dominant pathway with the cyclopentyloxy (**1a**) and cycloheptyloxy (**1e**) derivatives was bromoalkane formation. This was the minor pathway with the cyclohexyloxy derivative (**1b**). Instead, elimination and reaction at sulfonium sulfur were the major fates of **1b**. A complication in the reaction of **1b** was the addition of Br_2, formed as in Eqn. (3), to cyclohexene formed as in Eqn. (2) (Scheme 2), giving *trans*-1,2-dibromocyclohexane, designated RBr_2 in Table 2. It is possible that small amounts of dibromocycloalkane were formed also from **1a** and **e** but we did not search for those products. In terms of stoichiometry, therefore, the sum of the yields of ene, RBr and RBr_2 should equal the yield of ThO. We have expressed that equality as a ratio in Table 2. Also, the yields of Th and ROH should each equal the sum of the yields of Br_2 plus RBr_2. This is also shown to be approximately the case in Table 2.

The summary, then, of our reactions of **1** with I^- and Br^- and of methoxydiphenylsulfonium ion with I^- is that S_N2 displacement of an alkyl group prevails until inhibited by structural features of the alkyl group, whereupon *E2C* reaction and reaction at sulfur become significant. Reaction at sulfur is shown in Scheme 4 to lead to a sulfurane (**6**). The sulfurane itself may react with halide ion, or as proposed by others in other reactions, 17a,b may lead to a halosulfonium ion (**7**), from which products are formed. The loss of an alkoxy group from an alkoxysulfonium ion in reaction with a nucleophile has been described as facile in even the early work of Meerwein.[30] We are unable to distinguish between the two pathways.

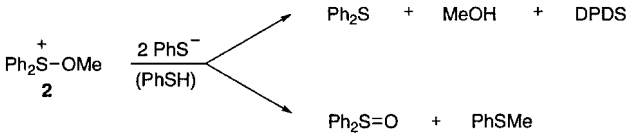
Reactions of halide ions at the sulfur atom of oxysulfonium ions, with concomitant formation of a sulfurane intermediate, have been proposed earlier. Examples include the racemization of sulfoxides by HCl[18a] and the exchange of a sulfoxide's oxygen atom with water, catalyzed by HCl.[18b] Landini and co-workers,[17a,b] interestingly, found that iodide ion in perchloric acid solution caused the reduction of sulfoxides, whereas bromide and chloride ions under the same condition caused only racemization. In all of these cases, reaction was initiated by the attack of halide ion at the sulfur atom of the protonated sulfoxide, that attack being, in fact, identified as the rate-determining step.[17a,b] Our results differ a little from those of Landini and co-workers in that both iodide and bromide ion caused to some extent what is in effect the reduction of compounds **1**, whereas only iodide caused the acid-catalyzed reduction of sulfoxides.[17a] The same workers reported an order in thiophilicities of the halide ions, Cl^-, Br^-, I^- as 1:3:87. Similar ordering in the thiophilicities of halide ions have been listed by Kice[31] for catalyses of reactions of nucleophiles at sulfenyl and sulfynyl sulfur atoms. In analogy with such cases we might expect in our reactions that iodide would give much more Th and halogen than bromide ion in reactions with **1**. That expectation is seen only in reactions of **1a**, however. It may be that the expected order in thiophilicities is compromised by the complexity of our competing reaction systems.

Reactions with PhS^-

Reactions were carried out in MeCN and DMSO over a period of 2 h. Completion of reaction was verified in some cases by following separately the disappearance of the sulfonium ion with NMR spectroscopy. A small excess of sodium thiophenoxide (PhSNa) over the amount of sulfonium salt (**1** and **2**) was used, corresponding to the stoichiometry of Schemes 5 and 6. Thiophenol (PhSH), approximately equivalent to the amount of



Scheme 5



Scheme 6

Table 4. Products of reaction of 5-methoxy- (**1f**) and 5-ethoxythianthrenium perchlorate (**1g**) with PhSNa

			Product (%)[a]			
Run	Compound	Solvent	ROH[b]	Th	DPDS[d]	ThO
1	**1f**	DMSO	98	99	104	1.7
2	**1f**	MeCN	105	99	105	2.5
3	**1g**	DMSO	96	99	102	1.0
4	**1g**	MeCN	[c]	95	103	4.2

[a] Average of three assays in each run. The average errors for assays of ROH, Th and ThO were: (run 1) 0.05, 1.7, 0.18; (run 2) 0.93, 0.30, 0.15; (run 3) 0.03, 1.3, 0.22; (run 4) –, 0.12, 0.18. In all experiments the molar ratio of PhSNa to **1** was ca 2.5, and PhSH equivalent to the amount of PhSNa was also used.
[b] On column E.
[c] EtOH overlapped the solvent in GC traces.
[d] After separation by column chromatography; GC on column A. Yield is based on the stoichiometry of Scheme 5.

PhSNa, was included in all runs. Unless PhSH was used, large amounts of sulfoxide (ThO from **1**, Ph_2SO from **2**) were formed. (Insofar as using added PhSH is concerned, we found that this was the practice in one of the earlier studies,[27] but not in others. Where E2C occurred, of course, thiol was formed *in situ*, as pointed out by Cook *et al.*[32] with *p*-nitrothiophenoxide and by Bordwell and Mrozack[33] with *p*-methoxythiophenoxide. Routine use of an excess of PhSH was noted by Arnone *et al.*[34] in studies of $S_{RN}1$ reactions.) In the presence of PhSH the products of reaction were substantially only alkanol (ROH), the parent sulfide (Th from **1**, Ph_2S from **2**) and diphenyl disulfide (DPDS). None of the S_N2 product (PhSR) was obtained from reactions of **1** and only small amounts from reactions of **2**. PhSH itself did not react with the alkoxysulfonium salts. The results are listed in Tables 3–5. In these Tables, the yields of products, except DPDS, are from GC analyses of reaction solutions. Because an excess of PhSNa and PhSH was used, the yields of DPDS were assayed by GC but only after PhSH and unused PhSNa had been removed as described in the Experimental section. We were able to assay without difficulty the formation of cycloalkanols from reactions of **1b–e** in MeCN, and of MeOH and EtOH from reactions of **1f** and **g** and **2** in DMSO. Direct assay of MeOH and EtOH from reactions of **1f** and **g** and **2** in MeCN were not possible, apparently because of the insolubility of NaOMe and NaOEt in MeCN. These alkoxides were not converted into the alcohols in these circumstances. Conversion resisted the addition of a large excess of PhSH, and was achieved only with the addition of a small amount of water (0.2 ml) to the reaction solution (10 ml) after reaction was complete. Assay of MeOH by GC was then successful and is reported in Tables 4 and 5. Assay of EtOH was not possible even with this treatment because the GC peak overlapped that of MeCN. Some control experiments on the fate of sodium alkoxides in MeCN are included in the Experimental section. We conclude that the formation of cycloalkanol from **1b–e** in MeCN was driven to completion by reaction of PhSH with soluble

Table 3. Products of reaction of **1b–e** with PhSNa

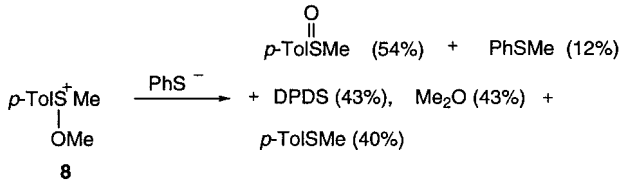
		Product (%)[a]			
Run	Compound	ROH[b]	Th[b]	DPDS[b,c]	ThO[d]
1	**1b**	99	94	105	5.1
2	**1c**	101	94	100	7.7
3	**1d**	96	96	103	3.7
4	**1e**	96	97	99	6.2

[a] Average of two experiments with **1b–d** and three with **1e**. All experiments were in MeCN at room temperature.
[b] Errors in tabulated averages were 1–5.
[c] After separation by column chromatography; GC on column A. Yield is based on the stoichiometry of Scheme 5.
[d] Errors in tabulated averages were 3.3 (**1b**), 4.1 (**1c**), 1.6 (**1d**) and 1.0 (**1e**).

Table 5. Products of reaction of methoxydiphenylsulfonium tetrafluoroborate (**2**) with PhSNa

		Product (%)				
Run	Solvent	MeOH[a]	Ph_2S[b]	DPDS[c]	Ph_2SO[b]	PhSMe[b]
1	MeCN	98	98	110	tr	1.6
2	DMSO	94	89	102	9.7	3.1

[a] Column E was used. An average of three assays is given with errors 2.1% (run 1) and 1.0% (run 2). MeOH was found in run 1 only after adding 0.2 ml of water to the suspension before assay. MeOH was found and assayed in run 2 without addition of water.
[b] Column A was used. An average of three assays is given with errors in yields (%) for Ph_2S, Ph_2SO, PhSMe, respectively, of 0.80,–, 0.03 (run 1) and 0.40, 0.17, –(run 2).
[c] After separation by column chromatograph; GC on column A. Yield is based on the stoichiometry of Scheme 6.



8

Scheme 7

alkoxide. The formation of MeOH and EtOH from **1f** and **g** and **2** in DMSO was similarly driven or may have been driven to completion by small amounts of water in the incompletely dried solvent.

Reactions with 1b–e

Table 3 shows the substantially quantitative formation of cycloalkanol, Th and DPDS. Small amounts of ThO were obtained. In principle, ThO should be formed from either S_N2 displacement of the cycloalkyl group or from *E*2*C* elimination, but no indications of PhSR and ene were found in the GC traces. These reactions of **1b–e** are thus in great contrast with those of the halide ions, in which S_N2 and *E*2*C* were dominant. The reactions are also unlike those of cyclohexyl halides and tosylates with aryl thiolates. For example, Eliel and Haber[27] found almost equal amounts of substitution and elimination in the reactions of PhS^- with bromocyclohexane and *cis*- and *trans*-4-(*tert*-butyl)bromocyclohexane, the ratio of rates for the two reaction types being 1.13, 1.04 and 1.17, respectively. Reaction of *cis*-4-*tert*-butylcyclohexyl tosylate gave 40% of 4-*tert*-butylcyclohexene.[27] The last reaction in the hands of Winstein and co-workers[23] gave 48% of elimination. McLennan[28] obtained 55% of cyclohexene from reaction of PhS^- with bromocyclohexane. We repeated that reaction and confirmed that in our hands, too, large amounts of cyclohexene were formed (see Experimental section). Bordwell and Mrozack[33] reported that, whereas 9-methylfluorene anion led to >90% substitution, and 6-bromo-2-naphthoxide ion led to >90% elimination, in reaction with bromocyclohexane, 4-methoxythiophenoxide ion caused equal amounts of substitution and elimination. Thus, although our compounds **1b–d** can be regarded as cyclohexanes carrying a good leaving group (ThO), they have no propensity to engage in the S_N2 and *E*2*C* reactions that suit a good leaving group. The nucleophilic nature of PhS^- is such that, instead, given the opportunity, it prefers to react with **1b–d** at sulfonium sulfur.

Reactions with 1f and g and 2. Preference for reaction at sulfonium sulfur is also seen in the reactions of PhS^- with **1f,g** (Table 4) and with methoxydiphenylsulfonium tetrafluoroborate (**2**, Table 5). We chose **1f** and **g** because we had found earlier[7] that they underwent almost total S_N2 reaction with I^- and Br^-. In contrast, each gave quantitative amounts of Th, ROH and DPDS in reaction with PhS^-. None of the displacement products, PhSMe and PhSEt, were found. We chose to work with **2** so as to characterize the mode of reaction of simpler alkoxysulfonium salts with PhS^- and I^-. Reaction with I^- (see Experimental section) gave 98–99% of MeI and Ph_2SO, indicative of S_N2 displacement of methyl. Only small amounts of diphenyl sulfide (Ph_2S) were formed, that would be consistent with reaction at sulfur. Reaction with PhS^-, however (Scheme 6), gave predominantly Ph_2S, MeOH and DPDS. About 9% of ThO was formed in reaction in DMSO, suggestive of S_N2 displacement, but only 3.1% of PhSMe was found (Table 5).

Our results show that in contrast with halide ions PhS^- has a strong preference for reaction at sulfur in reactions with **1** and **2**. Oae and Kim[20] found analogously that only Ph_2S (90%) and *p*-tolyl disulfide (80%) were formed when *p*-tolyl thiolate reacted with ethoxydiphenylsulfonium tetrafluoroborate in anhydrous ethanol. The relative thiophilicity of PhS^- compared with halide ions is all the more noteworthy when related to the carbon nucleophilicity of these nucleophiles. For example, the ratio of reactivities PhS^-/I^- in methanol solution toward methyl tosylate (MeOTs) is 321 and toward methyl iodide (MeI) it is 313.[35,36] In sulfolane solution, this ratio of reactivities toward MeI is 37 000.[37] The ratio for displacement of methyl from cobalt-bound methyl in methyl cobalt(III)phthalocyanine in dimethylacetamide solution is 41 000.[37] Intrinsically, therefore, especially in analogy with reaction with MeOTs, one would expect PhS^- to react more easily than I^- (and Br^-) at the alkyl group and displace ThO from **1** and Ph_2SO from **2**. Reaction at both sulfonium sulfur (43%) and carbon (12%) did ocur in reaction of PhS^- with methoxymethyl-*p*-tolylsulfonium tetrafluoroborate (**8**) in dichloromethane (Scheme 7).[21] In that case, methoxide ion, displaced from the methoxysulfonium ion by PhS^-, reacted further with **8** to give dimethyl ether. No such reaction was found in our work.

The collective data show that reaction of PhS^- with the sulfur atom of an alkoxysulfonium ion is very facile. In terms of Scheme 4, the sulfurane (**6**) and phenylthiosulfonium ion (**7**) are formed preferably. Once **7** is formed, furthermore, it must react rapidly with thiolate ion irreversibly. Measurements of thiophilicity of thiolate ions comparable to those of halide ions[17a,31,38] do not seem to have been made, although Kice and Rogers[39] found that SCN^- reacted more rapidly than I^- at the sulfenyl sulfur atom of $PhSS^+(OH)Ph$. Edwards and Pearson[40] noted that, among nucleophiles, RS^- and PhS^- rank high in their ability to break a sulfur-sulfur bond, while Kice[31] deduced that ions such as R_2S^+SPh undergo nucleophilic substitution at sulfenyl sulfur with tremendous alacrity. More recent reports have brought out the very facile, S_N2-like nature of the attack of thiolate ions on the disulfide bond,[41] from which, by comparison, the even more facile S_N2-like displacement of sulfonium

sulfur (e.g. in **7**) by thioloate would be expected. The summation of our work and the earlier reports[20–22] is that thiolate ions react selectively at the sulfonium sulfur atom of alkoxysulfonium ions, facilitated, perhaps, by the facile expulsion of the alkoxy group.[20] Once that occurs, it is followed by another very facile product-forming reaction of thiolate at the sulfenyl sulfur atom of (in our cases) a phenylthiosulfonium ion.

EXPERIMENTAL

Solvents were dried as described earlier.[6] Cycloheptanol, iodocyclohexane, bromocyclopentane, bromocyclohexane, bromocycloheptane and *trans*-1,2-dibromocyclohexane were obtained from Aldrich Chemical and cyclopentanol from Arapahoe Chemical. Iodocyclopentane was prepared[42] by reaction of cyclopentanol (1.0 g, 12 mmol) with iodotrimethylsilane (5 g, 25 mmol) in 40 ml of CH_2Cl_2 and was purified by column chromatography on 60–100-mesh silica gel with pentane as eluent, giving 0.62 g (3.16 mmol, 26%) of product with a satisfactory ^{1}H NMR spectrum. Iodocycloheptane was prepared similarly and was distilled after chromatography failed to give a satisfactory product, giving 1.4 g (6.25 mmol, 71%), b.p. 56–57 °C (2 mmHg); lit.[43] b.p. 92 °C (14 mmHg). *cis*-(4-Methyl)iodocyclohexane was prepared from *trans*-4-methylcyclohexanol (830 mg, 7.28 mmol) and iodotrimethylsilane (2.90 g, 14.5 mmol) in 40 ml of $CHCl_3$. Only a small amount of product was obtained after 2 days of stirring, and stirring was continued at room temperature for 20 days. Iodine was removed by washing with sodium thiosulfate and water. Evaporation of the dried solution and distillation gave 460 mg (2.05 mmol, 28%) of product, b.p. 45–46 °C (2 mmHg). The product had a satisfactory ^{1}H NMR spectrum corresponding to the *cis* structure, concordant with the mechanism of formation.[42] Attempts to prepare *trans*-(4-methyl)iodocyclohexane from *cis*-4-methylcyclohexanol gave a mixture of *cis*- and *trans*-iodides. Physical data for the isomeric iodides could not be found in the literature. Cyclohexyl phenyl sulfide was prepared by reaction of iodocyclohexane with PhSNa, and was separated from DPDS by chromatography on a column of silica gel eluted with light petroleum ether, b.p. 37–56 °C. The product[44] had a satisfactory ^{1}H NMR spectrum. Methoxydiphenylsulfonium tetrafluorborate (**2**) was prepared as described earlier.[4] Sodium thiophenoxide (PhSNa) was prepared by reaction of thiophenol (PhSH) with dispersed sodium in boiling diethyl ether under argon. The product (95%) was filtered and washed with dry diethyl ether. It was completely soluble in MeOH and DMSO but only partly soluble in MeCN. For example, 21 mg remained undissolved when 66 mg in 10 ml of MeCN were treated with a sonic vibrator. Similarly, 36% remained undissolved when 18-crown-6 was included in a heated solution. The recovered solid was itself only partly soluble in fresh MeCN. We did not proceed further. The insolubility of PhSNa in MeCN has been noted earlier.[45] Thermogravimetric analysis showed that the PhSNa did not contain volatile material such as water.

*Preparation of **1a–g**.* The preparations of **1b–d, f** and **g** from reactions of thianthrene cation radical perchlorate (**caution**: a warning about explosiveness has been given[46]) have already been decribed.[6,7] Compounds **1a** (66%) and **1e** (69%) were prepared similarly and had m.p. (decomp.) 63–68 and 70–71 °C, respectively. Each had the characteristic aromatic ^{1}H NMR spectrum of a 5-(alkoxy)thianthrenium perchlorate.[6,7] The multiplet for H-1′ of **1a** at δ 5.12 and of **1e** at δ 4.84 were, as expected, approximately 0.8 ppm downfield from the signals of the corresponding alcohols.

Assays of products. Products of reaction (except halogen) of **1a–e** with halide ions were assayed by GC on a Varian Model 3700 gas chromatograph and a Spectra-Physics Model 4290 integrator–recorder. Three stainless-steel packed columns were used, each of 1/8 in i.d.: A, 10% OV-101 on 80–100-mesh Chrom-WHP, 4 ft; B, 10% Carbowax 20 M on Chrom-WHP, 6 ft; C, 10% OV-17 on 80–100-mesh Chrom Q11, 6 ft. Columns A and C were held at 50 °C for 2 min and ramped to 250 °C at 12 °C min^{-1}; column B was heated similarly, but to only 100 °C. Assays of products of reactions with PhSNa were made with column A and with two other columns: D, capillary SE-54 (Supelco No. 2-4001) and E, capillary SPB-20 (Supelco No. 2-4086). Each was 30 m × 0.25 mm i.d., film thickness 0.25 μm. D was heated at 50 °C for 2 min and ramped at 12 °C min^{-1} to 250 °C; E was heated similarly and ramped to 100 °C. In all cases the injector was at 250 °C and detector at 300 °C.

*Reactions of **1** with KI.* An example is given with **1a** (entry 1, Table 1). A solution of **1a** (44.0 mg, 0.110 mmol) and KI (46.9 mg, 0.394 mmol) in 5 ml of MeCN containing both naphthalene and 2-butanone as GC standards was stirred in a septum-capped volumetric flask. Aliquots were taken for GC analysis after 35, 140 and 280 min of stirring, after which 0.3 ml of 2 M K_2CO_3 was injected. Stirring was continued for 2 h and GC analysis was repeated. The products (mmol × 10^2) of the third and fourth (in parentheses) assays were cyclopentene 2.30 (2.20), iodocyclopentane 6.00 (6.00), Th 2.10 (2.13) and ThO 8.60 (8.80). Cyclopentanol was not assayed because its GC peak was too broad and shallow and overlapped with the solvent peak. The third assays are listed in Table 1. An aliquot was taken after the third assay for titration of iodine. For this, 0.3 ml of K_2CO_3 was added to the aliquot and was followed by titration with $Na_2S_2O_3$. Column E was used for all products except cyclopentene, for which column B was used.

Reactions of **1b–e** were carried out similarly with small variations in concentrations and sampling times.

*Reactions of **1** with TBAB.* An example is given with **1a** (entry 1, Table 2). A solution of **1a** (41.6 mg, 0.104 mmol) and TBAB (115 mg, 0.357 mmol) in 5 ml of MeCN containing both naphthalene and 2-butanone as GC standards was stirred in a septum-capped volumetric flask. Aliquots were taken for GC analysis after 10, 50, 120, 285 and 345 min of stirring. Products (mmol $\times 10^2$) after the third and fifth (in parentheses) assays were cyclopentene trace(trace), bromocyclopentane 9.33 (9.29), Th 0.523 (0.530) and ThO, 9.92 (9.79). The fifth assays are listed in Table 2. After 6 h of stirring, 500 mg of KI were added to the solution and the liberated iodine was titrated with $Na_2S_2O_3$. The result is expressed as Br_2 in Table 2. Column B was used for cyclopentene and column C for all other products.

*Reactions of **1** with KBr–18-crown-6.* An example is given with **1b** (part of entry 3, Table 2). A solution of 427 mg (0.103 mmol) of **1b** in 5 ml of a solution that was 0.0717 M in KBr and 0.132 M in 18-crown-6 and containing both naphthalene and 2-butanone as GC standards was stirred in a septum-capped volumetric flask. Aliquots were taken for GC assay after 10, 170, 235 and 370 min. The fourth assay is listed in Table 2. After that assay, 500 mg of KI were added to the solution and iodine was titrated as usual. Column B was used for assaying cyclohexene and column C for all other products.

*Reactions of **1** with sodium thiophenoxide in the presence of thiophenol.* An example is given with **1b** (part of entry 1, Table 3). A solution of 71.0 mg (0.171 mmol) of **1b** and 45 µl (48.3 mg, 0.439 mmol) of PhSH in 10 ml of MeCN containing biphenyl as GC standard was stirred with 57.8 mg (0.438 mmol) of PhSNa in a septum-capped volumetric flask for 2 h. The solution was assayed twice on column A giving in mmol (average) 0.169 ± 0.0015 (99%) of cyclohexanol, 0.157 ± 0.0001 (92%) of Th, 0.0029 ± 0.0005 (1.7%) of ThO and 0.215 ± 0.002 (126%, based on the amount of **1b**) of DPDS. Following the GC assays, the solution was poured into 50 ml of 2 M NaOH and the aqueous solution was extracted with 3×25 ml of diethyl ether. The dried ($MgSO_4$) ether solution was evaporated to dryness and the solid residue was placed on a column of silica gel from which 94.3 mg of a mixture of biphenyl, Th and DPDS was eluted with light petroleum. This mixture was dissolved in 5 ml of MeCN and assayed by GC on column A to give 0.148 mmol (87%) of Th and 0.175 mmol (102%, based on **1b**) of DPDS. This assay of DPDS is reported in Table 3.

Similar reactions with **1c–e** were carried out. In some cases, both biphenyl and 2-butanone (for ROH assay) were used as internal GC standards. In these runs, columns A and D were used. Reactions with **1f** and **g** were carried out similarly but in DMSO and MeCN (Table 4).

*Reaction of methoxydiphenylsulfonium tetrafluoroborate (**2**) with sodium thiophenoxide in the presence of thiophenol.* An example is given with entry 2, Table 5. A solution of 71.9 mg (0.237 mmol) of **2** and 60 µl (64 mg, 0.582 mmol) of PhSH in 10 ml of DMSO containing both biphenyl and 2-butanone as GC standards was stirred in a septum-cappped volumetric flask with 76.8 mg (0.582 mmol) of PhSNa for 2 h. The solution was assayed three times on column A, giving in mmol (average) 0.212 ± 0.020 (89%) of Ph_2S, 0.023 ± 0.002 (9.7%) of Ph_2SO, 0.357 ± 0.002 (151%, based on the amount of **2**) of DPDS, 0.00745 ± 0.0009 (3.1%) of PhSMe and 0.222 ± 0.0036 (94%) of MeOH. Following the GC assays, the solution was poured into 50 ml of 2 M KOH and worked up as described earlier to give 105 mg of a mixture of biphenyl, Ph_2S and DPDS. GC assay gave 0.200 mmol (84%) of Ph_2S and 0.242 mmol (102%, based on the amount of **2**) of DPDS. This assay of DPDS is reported in Table 5.

*Reactions of **1b** and **f** and **2** with sodium thiophenoxide in the absence of thiophenol.* The PhSNa was crystallized from ethanol, washed with hexane and dried under vacuum. A solution of 34.0 mg (0.0821 mmol) of **1b** in 5 ml of MeCN containing naphthalene as GC standard was stirred with 35.6 mg (0.0270 mmol) of PhSNa for 2 h. GC assay gave 0.0524 mmol (64%) of Th, 0.0311 mmol (38%) of ThO, 0.0771 mmol (94%) of cyclohexanol and 0.0521 mmol (63%) of DPDS. An analogous reaction with **1f** gave 55% of Th, 43% of ThO and 62% 0f DPDS. The GC peak for MeOH overlapped that for the solvent (column A). Similarly, **2** gave 46% of Ph_2S, 54% of Ph_2SO, 71% of DPDS and 53% of MeOH (column E). These reactions may be compared with those in the presence of PhSH (Tables 3–5).

Reaction of 2 with KI. A solution of 61.6 mg (0.203 mmol) of **2** and 90.8 mg (0.547 mmol) of KI in 10 ml of dry DMSO containing both biphenyl and 2-butanone as GC standards was stirred for 2 h in a septum-capped volumetric flask. CG assay on column A gave 0.198 mmol (98%) of Ph_2SO and 0.200 mmol (99%) of MeI. Traces of MeOH and Ph_2S were also found.

Reaction of bromocyclohexane with sodium thiophenoxide. A solution of 43.3 mg (0.266 mmol) of bromocyclohexane and 91.6 mg (0.694 mmol) of PhSNa in 10 ml of DMSO containing biphenyl as GC standard was stirred for 1 h. GC assay gave 0.172 mmol (65%) of cyclohexene, 0.111 mmol (42%) of cyclohexyl phenyl sulfide and 0.0372 mmol (11%) of DPDS. PhSH was formed but could not be assayed because its GC peak overlapped that of the solvent. Column A was used.

Experiments with sodium alkoxides. (a) NaOMe was prepared as a dry powder from reaction of Na with dry MeOH. A suspension of 13.8 mg (0.256 mmol) of NaOMe

in 10 ml of MeCN containing toluene as GC standard was stirred for 30 min. GC on column E failed to detect MeOH. PhSH (71 mg, 0.645 mmol) was injected into the suspension and stirring was continued for 30 min. GC again failed to detect MeOH. Water (0.2 ml) was injected and stirring was continued for 30 min. A small amount of solid remained. GC gave 0.269 mmol (105%) of MeOH. A similar experiment with 10.5 mg (0.194 mmol) of NaOMe and 1.22 g (11.1 mmol) of PhSH again gave MeOH (0.185 mmol, 95%) only after the addition of 0.2 ml of water. The same type of experiments were carried out with EtSH. With 10.5 mg (0.194 mmol) of NaOMe and 36 μl (0.484 mmol) of EtSH, MeOH (0.192 mmol, 99%) was obtained only after the addition of water. When a larger amount of EtSH (11.2 mmol) was used, MeOH was detectable again only after the addition of water, but assay was thwarted by overlap of the MeOH peak with the very large peak from EtSH.

(b) The sodium salt of cyclohexanol was prepared by heating Na with cyclohexanol under reflux. The white precipitate was filtered, washed with dry diethylether and dried under vacuum. To 20.7 mg (0.170 mmol) of the salt was added 10 ml of dry MeCN containing naphthalene as GC standard. Most of the salt dissoved. After stirring for 30 min, GC assay on column A gave 0.162 mmol (95%) of cyclohexanol. The experiment was repeated with redried (P_2O_5) MeCN and again cyclohexanol (98%) was found without the need to add PhSH or water.

Reaction of 1b with PhSH. A solution of 16.2 mg (0.039 mmol) of **1b** and 28.3 mg (0.257 mmol) of PhSH was made in 3 ml of CD_3CN containing napthalene as GC standard. Reaction (decrease of the peaks of **1b** at 8.4 and 4.54 ppm) had not occurred after 18 h. After the solution had been heated for 1 h at 100 °C, GC showed cyclohexene, ThO, PhSH and DPDS. A solution of **1b** in MeCN gave ThO (105%) and cyclohexene (100%) when injected into the hot GC inlet.

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