N^{α}-Benzyloxycarbonyl-N^{ϵ}-*tert*-butyloxycarbonyl-L-lysine isopropyl ester (21) was prepared from **11** in the manner described for the preparation of the corresponding N^{α}-ethoxycarbonyl compound **26** in 88% yield: IR 3260 (m), 1685 (s, b) cm^{-1}; NMR δ 1.25 (d, 6 H, J = 6 Hz) 1.46 (s, 9 H), 1.1-2.05 (m, 6 H), 3.06 (m, 2 H), 4.24 (m, 1 H), 4.85 (d, 1 H), 4.97 (heptet, 1 H, J = 7 Hz), 5.07 (s, 2 H), 5.62 (d, 1 H, J = 8 Hz), 7.24 (s, 5 H); $[\alpha]^{23}_D$ +2.6° (c 2, CH_2Cl_2). Anal. Calcd for $C_{22}H_{34}N_2O_6$: C, 62.5; H, 8.1; N, 6.6. Found: C, 62.3; H, 8.0; N, 6.6.

N^{α}-Benzyloxycarbonyl-L-lysine isopropyl ester (23) was prepared from the corresponding N^{ϵ}-t-Boc derivative **21** by the method employed for the preparation of N^{α}-benzyloxycarbonyl-L-lysine (**9**), affording **23** as a light yellow oil in 93% yield: IR (neat), 3330 (s), 1720 (s, b) cm^{-1}; NMR δ 1.21 (d, 6 H, J = 7 Hz), 1.05-2.04 (m, 8 H), 2.62 (m, 2 H), 4.23 (m, 1 H), 4.93 (heptet, 1 H, J = 7 Hz), 5.17 (s, 2 H), 5.77 (b d, 1 H), 7.28 (s, 5 H); $[\alpha]^{23}_D$ +4.9° (c 1, CH_2Cl_2).

Determination of Optical Purity of Lysine Transamination Products. The α-aminoadipic acids were fused (170 °C, 30 min) to afford 2-piperidone-6-carboxylic acid as a crystalline solid in 85% yield: mp 105-107 °C; IR (mull) 3345 (m), 2500 (m), 1725 (s) cm^{-1}; NMR δ 1.6-2.25 (m, 4 H), 2.18 (t, 2 H, J = 6 Hz), 4.12 (t, 1 H, J = 6 Hz); $[\alpha]^{23}_D$ -15.8° (c 1, 1 N NaOH). Anal. Calcd for $C_6H_9NO_3$: C, 50.3; H, 6.3; N, 9.8. Found: C, 50.2; H, 6.3; N, 9.6.

The 2-piperidone-6-carboxylic acid was then converted to its acid chloride by treatment with oxalyl chloride (105 mol %) and DMF (5 mol %) in CH_2Cl_2 at room temperature for 1 h. (+)-α-Phenylethylamine was then added, and the resulting amide, after the usual extractive isolation, was analyzed by HPLC. This procedure was also repeated with racemic α-aminoadipic acid to establish the resolution and detection limits of the diastereomeric amides: HPLC, 1:1 CH_2Cl_2/isooctane; D-2-piperidone-6-carboxamide, R_t 35.5 min; L-2-piperidone-6-carboxamide, R_t 38.5 min.

The pipecolic acids were converted to their corresponding N-ethoxycarbonyl derivatives. Preparation of their acid chlorides and subsequent conversion to diastereomeric amides with (+)-α-phenylethylamine were readily achieved as described above: 1:1 CH_2Cl_2/isooctane; D-N-ethoxycarbonylpipecolic acid amide, R_t 19 min; L-N-ethoxycarbonylpipecolic acid amide, R_t 21.5 min.

In each instance, with limits of detection established as less than 1%, none of the D diastereomer was observed. Hence the transamination sequence as well as the following transformations were achieved with complete retention of stereochemistry at the lysine α-carbon.

Registry No. 4, 82228-89-5; **9**, 2212-75-1; **10**, 2418-95-3; **11**, 2389-60-8; **11** dicyclohexylammonium salt, 2212-76-2; (*S*)-**14**, 1118-90-7; (*S*)-**17**, 3105-95-1; **21**, 82228-90-8; **23**, 47307-39-1; **24**, 82228-91-9; **25**, 82228-92-0; **26**, 82228-93-1; **27**, 82228-94-2; pyridine-4-carboxaldehyde, 872-85-5; methyl benzenesulfonate, 80-18-2; *tert*-butyl 7-α-hydroxydeacetoxycephalosphoranate, 63599-56-4; *tert*-butyl 7-aminodeacetoxycephalosphoranate, 33610-06-9; N-benzyloxycarbonyl-D-glucosamine, 16684-31-4; β-1,3,4,6-tetra-O-acetyl-2-N-benzyloxycarbonyl-D-glucosamine, 35946-66-8; α-1,3,4,6-tetra-O-acetyl-2-N-benzyloxycarbonyl-D-glucosamine, 82264-19-5; 3,4,6-tri-O-acetyl-D-glucosone, 82228-95-3; (*S*)-2-piperidone-6-carboxylic acid, 34622-39-4; pentylamine, 110-58-7; pentanal, 110-62-3; cyclohexylamine, 108-91-8; cyclohexanone, 108-94-1; α-phenylethylamine, 98-84-0; acetophenone, 98-86-2; β-phenylethylamine, 64-04-0; phenylacetaldehyde, 122-78-1; 1,3,4,6-tetra-O-acetyl-α-D-glucosamine, 17460-45-6.

One-Electron Chemical Reductions of Phenylalkylsulfonium Salts

Peter Beak* and Thomas A. Sullivan

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801.
Received December 7, 1981

Abstract: Twenty-two arylalkylsulfonium salts have been reduced with potassium in graphite in tetrahydrofuran and the sulfide products identified. Two trialkylsulfonium salts did not reduce under these conditions. Comparison of the sulfides from a series of monophenylalkylsulfonium salts reveals a leaving-group propensity of benzyl > secondary > primary > methyl > phenyl in a ratio of 28:(6.0 ± 0.3):1.0:(0.53 ± 0.09):<0.05. The cleavage ratio is shown to be independent of the electron source and the homogeneity of heterogeneity of the reaction in two cases. Multiplicative transitivity of the above ratios is not observed, although the same qualitative order is found for other comparisons. These results are interpreted in terms of the initial formation of a π-ligand radical anion sulfonium cation, which undergoes cleavage to a carbon radical and a sulfide. This appears to be the first evidence for this type of structure in a sulfur system. Leaving-group propensities different from the above order are observed in reductions of diphenylsulfonium and benzo-fused sulfonium salts, and rationales are offered. The intermediates in these reactions appear to be different from those involved in radical additions to, or displacements on, sulfur.

The prospect that one-electron reductions of sulfonium salts could serve as a convenient source of a variety of radicals, along with the possibility that one-electron reductions of sulfonium salts could explain reactions attributed to other pathways, prompted our investigation of the chemical reduction of a series of sulfonium salts.

Most of the one-electron reductions of sulfonium salts that have been reported are electrochemical studies[1-9] in which, with some exceptions,[4,9] an irreversible one-electron transfer is followed by reactions with cathodic material and/or the formation of a carbon radical and a sulfide. The radicals are converted to products by further reaction and/or reduction. A similar formation of radicals has also been noted in reactions of triarylsulfonium salts with potential nucleophiles.[10]

(1) Bonner, W. A. *J. Am. Chem. Soc.* **1952**, *74*, 5078.
(2) Luttringhaus, A.; Machatzke, H. *Liebigs Ann. Chem.* **1964**, *671*, 165.
(3) Colichman, E. L.; Love, D. L. *J. Org. Chem.* **1953**, *18*, 40.
(4) McKinney, P. S.; Rosenthal, S. *J. Electroanal. Chem.* **1968**, *16*, 261.
(5) Finklestein, M.; Peterson, R. C.; Ross, S. D. *J. Electrochem. Soc.* **1963**, *110*, 422.
(6) Chambers, J. Q.; Maupin, P. H., II; Liao, C. S. *J. Electroanal. Chem.* **1978**, *87*, 239.
(7) (a) Wagenknecht, J. H.; Baizer, M. M. *J. Electrochem. Soc.* **1967**, *114*, 1095. (b) Wagenknecht, J. H.; Baizer, M. M. *J. Org. Chem.* **1966**, *31*, 3885. (c) Baizer, M. M. *Ibid.* **1966**, *31*, 3847.
(8) Grimshaw, J. In "The Chemistry of the Sulfonium Group"; Stirling, C. M., Ed.; Wiley: New York, 1981; Chapter 7.
(9) Hall, E. A. H.; Horner, L. *Phosphorus Sulfur* **1981**, *9*, 273.
(10) (a) Knapczyk, J. W.; Lai, C. C.; McEwen, W. E.; Calderon, J. C.; Lubinkowski, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1188. (b) Rossi, R. A.; Bunnett, J. F. *Ibid.* **1974**, *96*, 112. (c) Nickol, S. L.; Kampmeier, J. A. *Ibid.* **1973**, *95*, 1908. (d) Chung, S. K.; Sasamoto, K. *J. Chem. Soc., Chem. Commun.* **1981**, 346.

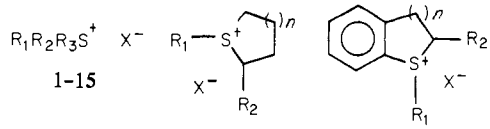
0002-7863/82/1504-4450$01.25/0

Comparison of electrochemical and chemical reductions could be informative. In a recent report, Hall and Horner note that the ratios of thioethers formed electrochemically from sulfonium salts depends on the potential, the solvent, and the electrode material.[9] They report that reduction of diphenylmethylsulfonium perchlorate in acetonitrile by several electrochemical methods gives 75–100% diphenylsulfide, with thioanisole as the only other product. However, the same sulfonium salt gives 83–89% thioanisole and 11–17% diphenyl sulfide on reduction with sodium amalgam in methanol while reduction of this salt with the radical anion of benzonitrile in benzonitrile gives only diphenyl disulfide.

Our results are consistent with the majority of the electrochemical studies. We find that arylalkylsulfonium salts undergo one-electron chemical reductions to give sulfides and hydrocarbon products consistent with homolytic cleavage of a formally valence-expanded intermediate. We postulate this intermediate to be a π-ligand radical anion sulfonium cation. For diarylsulfonium and benzo-fused sulfonium salts, however, some modification of this picture is required.

Results

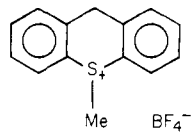
Three general types of sulfonium salts defined structurally as acyclic (**1–15**), cyclic (**16–19**), and benzofused cyclic (**20–24**) were studied.



1-15

16-19

20-23

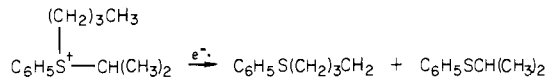


24

Syntheses of Sulfonium Salts. The syntheses of the trialkyl-, dialkylaryl-, alkyldiaryl-, and triarylsulfonium salts usually were achieved by reaction of the appropriate sulfide with an alkylating agent.[11] The synthesis of 1-phenylthiaindan hexafluorophosphate (**23**) was achieved by displacement of methoxide from 1-methoxythiaindan fluoborate with phenyl Grignard.

Sulfonium Salt Reductions. In general, reduction of the sulfonium salts with KC_8[13] in tetrahydrofuran (THF) gives the sulfides and, in the cases where hydrocarbon products were isolated, the coupling, disproportionation, or hydrogen abstraction products that would be expected from reactions of the carbon radical produced by homolytic cleavage of the intermediate **25** as shown in eq 1. The products are compiled in Tables I–III. Product structures are based on comparison with authentic materials and/or elemental analyses and ^{1}H NMR, IR, and mass spectral analyses. In cases where inseparable mixtures were obtained, gas chromatographic analysis (GC) with authentic compounds as standards was used for quantitation in most cases, and gas chromatography–mass spectrometry (GC–MS) was used as an additional criterion for product characterization. Integration of unique absorbances in the ^{1}H NMR spectra of product mixtures was also used to confirm the assignments.

If adequate material balances are obtained, relative leaving-group propensities can be determined from the ratio of the sulfide products. The reduction of phenyl-*n*-butylisopropylsulfonium fluoborate (**4**) provides an example of the selectivity in these cleavages. Upon reduction with 1.1 equiv of KC_8 in THF, **4**



4 87.4 ± 1.4% 14.6 ± 0.6%

undergoes cleavage of the isopropyl group to afford phenyl *n*-butyl sulfide in 87.4 ± 1.4% yield, while loss of the *n*-butyl radical provides phenyl isopropyl sulfide in 14.6 ± 0.6% yield. In this case, then, there is a (6.0 ± 0.3):1 preference for loss of a secondary group over a primary group.

The heterogeneous nature of KC_8 simplifies the separation of products, but it opens the possibility that surface effects could complicate interpretation of the results. For this reason, comparisons of reductions between KC_8 and homogeneous reductions with potassium aromatic radical anions[14] were performed for **4** and **13**. The results, presented in Table I, show reasonable correspondence, although the possible error in the yield of phenyl isopropyl sulfide from **4** is large due to coelution of naphthalene under a variety of chromatographic conditions. In the case of **13**, the heterogeneous reduction produces 2-phenylethyl phenyl sulfide in 97% yield along with 72% 1,4-diphenylbutane, 13% ethylbenzene, and 9% styrene, while the homogeneous reduction gives 97% 2-phenylethyl phenyl sulfide, 71% ethylbenzene, and 7% 1,4-diphenylbutane. Apparently there is a negligible effect of the conditions on the cleavage but a major effect on the fate of the cleaved group. Reasonably, there is substantial dimerization under the heterogeneous conditions where the radicals are produced in a high local concentration on the graphite, but hydrogen abstraction predominates under homogeneous conditions in THF.

A control reduction performed on 1,4-bis(phenylthio)butane as a representative sulfide product, with 2.2 equiv of KC_8 in THF for 1 h, gave quantitative recovery of the sulfide. Accordingly the sulfide products of reduction of the sulfonium salts are stable to the reaction conditions.[15]

Acyclic Sulfonium Salts (1–13). The product distributions of sulfides and hydrocarbons from the reduction of 14 acyclic sulfonium salts are listed in Table I. The failure of the trialkyl salts **10** and **19** to reduce indicates the requirement for a phenyl group on the positive sulfur to effect reduction. Product ratios from the acyclic monophenyl sulfonium salts **1**, **2**, **4**, and **9** show the relative ease of cleavage of groups bonded to sulfur to be benzyl > secondary > primary > methyl ≫ phenyl in a ratio of 28:(6.0 ± 0.3):1.0:(0.53 ± 0.09):(<0.05), respectively.

The cleavage ratios were tested for consistency and transitivity by reduction of two phenylmethyl secondary alkylsulfonium salts, **6** and **7**. Reduction of **6** affords thioanisole and phenyl 2-pentyl sulfide in a ratio of (20.0 ± 5.1):1. Reduction of **7** produces thioanisole and a trace of phenyl isopropyl sulfide, giving a ratio of >30:1. The difference of these ratios from one another and from the value of (11.3 ± 2.5):1 expected on the basis of the above series shows that neither consistency nor multiplicative transitivity applies to the cleavage ratios. Accordingly, the ratios of cleavage propensities given above should not be used for quantitative predictions of product ratios in other cases nor would more general values be obtained by examining more overlapping series. The transition-state energy differences that might give rise to the observed variation are small, and the qualitative order is more important than an exact quantitative comparison, although the observed differences can be rationalized (vide infra).

An initial goal of this work was the formation of carbon radicals for efficient addition to carbon–carbon double bonds. However, attempts to intramolecularly trap an alkyl radical with an olefinic chain or aromatic ring in the cases of **3**, **5**, **8**, and **13** were un-

(11) In order to produce salts that were soluble in THF we sometimes replaced the anion of the sulfonium salt with hexafluorophosphate by a metathesis reaction with ammonium hexafluorophosphate. The difficulties encountered in sulfonium salt synthesis and purification are well documented.[12]

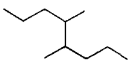
(12) Roush, D. M.; Price, E. M.; Templeton, L. K.; Templeton, D. H.; Heathcock, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 2971.

(13) Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2126.

(14) (a) Bayer, E.; Ruedorff, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1972**, *27*, 1336. (b) Bank, S.; Platz, M. *Tetrahedron Lett.* **1973**, 2097.

(15) Sulfides can be cleaved under some reducing conditions. (a) Screttas, C. G.; Screttas, M. M. *J. Org. Chem.* **1978**, *43*, 1064. (b) Truce, W. E.; Breiter, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 1621. (c) Gerdil, R.; Lucken, E. A. C. *J. Chem. Soc.* **1963**, 5444. (d) Day, R. A.; Underwood, A. L. "Quantitative Analysis"; Prentice Hall: Englewood Cliffs, NJ, 1967; p 64.

Table I. Products of Reduction of Acyclic Sulfonium Salts 1-15[a]

	R_1	R_2	R_3	products	% yield	order of cleavage	cleavage ratio
1	Ph	Me	Et	PhSMe	60.9 ± 2.2[b]	1° > Me	(1.98 ± 0.25):1
				PhSEt	30.8 ± 2.8		
1				PhSMe	48.7 ± 3.0	1° > Me	(1.78 ± 0.21):1
				PhSEt			
2[c]	Ph	Me	*n*-Bu	PhSMe	73 ± 10[b,d]	1° > Me	(2.6 ± 0.6):1
				PhS*n*-Bu			
3[c]	Ph	Me	$CH_2CH_2CH{=}CH_2$	PhSMe	67[e]	1° > Me	
				$PhSCH_2CH_2CH{=}CH_2$	21		
4	Ph	*n*-Bu	*i*-Pr	PhS*n*-Bu	87.4 ± 1.4[b,f]	2° > 1°	(6.0 ± 0.3):1
				$PhSCH(CH_3)_2$	14.6 ± 0.6		(5.7 ± 0.2)1[g]
4[h]				PhS*n*-Bu	85.1 ± 5.2[b]	2° > 1°	(5.7 ± 1.2):1
				PhS*i*-Pr	6.1 ± 17		
							
5[j]	Ph	$CH_2CH_2CH{=}CH_2$	*i*-Pr	$PhSCH_2CH_2CH{=}CH_2$	32.0 ± 2.4	2° > 1°	
				PhS*i*-Pr	20.0 ± 1.2		
6[j]	Ph	Me	$CH_3(CH_2)_2CHCH_3$	PhSMe	92.0 ± 7.6[b,k]	2° > Me	(20.0 ± 5.1):1
				$PhSCH(CH_3)CH_2CH_2CH_3$	4.6 ± 0.8		
					31.1 ± 2.0		
							
7	Ph	Me	*i*-Pr	PhSMe	~99[m]	2° > Me	>30:1
				PhS*i*-Pr	trace		
8[c]	Ph	Me	$PhCH_2CHCH_3$	PhSMe	42[n]		
9[c]	Ph	Me	$PhCH_2$	PhSMe	*o*	$PhCH_2$ > Me	~15:1
				$Ph(CH_2)_2Ph$			
10[c]	*t*-Bu	Me	Me		*p*		
11[c]	Ph	Me	$(CH_2)_4S^+PhMe$	PhSMe	20[m]	Me > 1°[q]	
				$PhS(CH_2)_4SPh$	40(56[m])		
12	*p* MeC_6H_4	*p*-MeC_6H_4	*p*-MeC_6H_4	$(p\text{-}MeC_6H_4)_2$	43.6[s,t]		
				$(p\text{-}MeC_6H_4)_2S$	66.8[t]		
				PhMe	17.2[b]		
13	Ph	$PhCH_2CH_2$	$PhCH_2CH_2$	$PhSCH_2CH_2Ph$	97.2[b]	1° > Ph	≳97:3
				$Ph(CH_2)_4Ph$	72.1		
				PhEt	12.7		
				$PhCH{=}CH_2$	8.6		
13[u]				$PhSCH_2CH_2Ph$	96.6[b]	1° > Ph	≳97:3
				$Ph(CH_2)_4Ph$	7.3		
				PhEt	71		
				$PhCH{=}CH_2$			
14	Ph	Ph	Me	Ph_2S	43.8 ± 4.6[b]	Ph > Me	(3.4 ± 2.2):1
				PhSMe	36.5 ± 3.8		
				PhSEt	26.5 ± 2.0		
15	Ph	Ph	Et	Ph_2S	50.1 ± 2.8[b]	Ph ≈ 1°	~1:1
				PhSEt	46.2 ± 3.2		
				PhS*s*-Bu	3.7 ± 6.0		

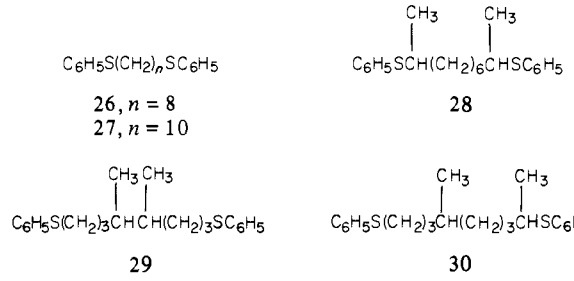
[a] All conditions are standard as described in the Experimental Section. [b] GC yield. [c] As BF_4^- salt. [d] These errors are large due to separation problems. [e] 3-h reduction time; yields are based on NMR of isolated mixture; some loss due to evaporation is possible. [f] Isolated yield was 85%. [g] This ratio is based on NMR integration after removal of solvent in vacuo. [h] Homogeneous reduction with $K^+Nap^{-}\cdot$. [i] Proposed structure based on GC-MS. [j] As BPh_4^- salt. [k] Yields normalized to 100% to correct for recovery of 15.6% 56. [l] Proposed structure based only on GC retention time; yield assumes a response factor equal to that of nonane. [m] Crude yield. [n] Gas evolution noted during reaction; some elimination and/or ylide formation possible. [o] No toluene detected by GC, ratio of products. [p] No reduction under standard conditions, 10 was recovered. [q] Anomalous-see text. [r] NMR of crude mixture. [s] A substantial amount of tar was also produced. [t] % yield calculated by using weight % in the nonvolatile products. [u] Homogeneous reduction with potassium(dimethylamino)naphthalene radical anion.

successful although the cleavage order is again consistent with the above order. The bis sulfonium salt **11** shows an unexpectedly high loss of the methyl group. Reduction of the triarylsulfonium salt **12** does show cleavage of a sulfur aryl bond.

Cyclic Sulfonium Salts (16–19). Reduction of the cyclic sulfonium salts **16–18** was studied to determine the effect of constraint of sulfur to a ring on the course of the reaction. The products of reduction are listed in Table II. For phenyltetramethylenesulfonium hexafluorophosphate (**16**) and phenylpentamethylenesulfonium hexafluorophosphate (**17**) primary cleavage to give 1,8-bis(phenylthio)octane (**26**) and 1,10-bis(phenylthio)decane (**27**), respectively, was the only reaction observed. These products are presumably dimers from the primary radical, and less than 5% of the products that could result from hydrogen abstraction by these radicals is present.

Ratios of secondary and primary cleavage in a cyclic system were obtained with stereoisomers of 1-phenyl-2-methyltetrahydrothiophenium hexafluorophosphate (**18**). The salt **18a** was a mixture of isomers with a cis:trans ratio of 13:87 while **18b** was a 70:30 mixture. The products of reduction consisted of phenyl 2-pentyl sulfide and the sulfides **28–30** as a mixture, which was characterized by ^1H NMR and mass spectra as well as an elemental analysis. A 2:1 ratio of secondary to primary cleavage is obtained with **18a** while a 10:1 ratio is observed for **18b**. This difference for formally identical leaving groups again indicates a lack of a transitive quantitative leaving-group effect; however, the cleavage of a secondary group favored in both cases is similar to that for the acyclic cases.

Reduction of Diphenylsulfonium Salts (14 and 15). Reduction of diphenylethylsulfonium hexafluorophosphate (**15**) as shown in



$C_6H_5S(CH_2)_nSC_6H_5$

26, $n = 8$
27, $n = 10$

28

29

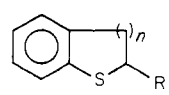
30

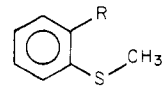
Table I produces phenyl ethylsulfide from phenyl cleavage in 50.1 ± 2.8% yield while loss of the ethyl group to generate diphenyl sulfide proceeds in 46.2 ± 3.2% yield. These yields indicate a secondary:phenyl cleavage ratio of approximately 1:1. A more accurate ratio could be obtained if the small amount of diphenyl-2-butylsulfonium cation formed in the reaction is considered. The latter arises presumably by ethylation of an ylide formed from **15** by a second molecule of **15**. This pathway is indicated by the presence of ca.4% phenyl 2-butyl sulfide detected by GC–MS and has analogy in the literature.[8]

A similar alkyl transfer is observed when diphenylmethylsulfonium hexafluorophosphate (**14**) is reduced. A 26.5% yield of phenyl ethyl sulfide is obtained, apparently due to methyl transfer from **14** to give **15** again via alkylation of an ylide. Thioanisole and diphenyl sulfide, the products of direct cleavage of **14**, were also detected. By appropriate correction it can be determined that a Ph:Me cleavage ratio of (3.4 ± 2.2):1 is observed for **14**.[16] Regardless of the precision of the above ratios, it is evident reduction of diphenylsulfonium salts gives an order of cleavage that is qualitatively different from that observed with the cyclic and acyclic monophenyl salts in which no phenyl cleavage occurs.

Benzo-Fused Sulfonium Salts (20–24). Reductions of the benzo-fused systems **20–24** were undertaken to evaluate the effect of aromatic ring geometry on the outcome of reduction. The results are summarized in Table III.

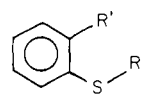
Reduction of 1-methylthiaindan hexafluorophosphate (**20**) provides a 72% yield of thiaindan (**31**) and approximately 2.4% *o*-(methylthio)styrene (**32**). A minimum Me:primary ratio of 2.6:1 can be calculated from this result.





31, $n = 1$, R = H
33, $n = 2$, R = H
39, $n = 1$, R = CH_3

32, R = $CH{=}CH_2$
34, R = $CH_2CH_2CH_3$
35, R = $CH_2CH{=}CH_2$
36, R = $CH{=}CH{-}CH_3$
38, R = $CH_2CH(CH_3)_2$



37, (R = CH_3, R' = $CH_2C(CH_3)H)_2$
40, R = C_6H_5, R = $CH{=}CH_2$
41, R = C_6H_5, R' = CH_2CH_3
42, (R = C_6H_5, R' = $(CH_2)_2)_2$

(16) In order to determine the fraction of the reaction which proceeds via electron transfer, it was necessary to use the previously determined cleavage ratio of **15**. Apparently 53.0 ± 1.9% of the starting material is used up in the ylide route; 26.5 ± 0.9% forms the ylide and another 26.5 ± 0.9% is used in the displacement reaction to form **15**. The displacement accounts for a 26.5% yield of diphenyl sulfide. Cleavage of **15** accounts for an additional 13.2 ± 1.0% yield of diphenyl sulfide and the observed phenyl ethyl sulfide. The combined yields of diphenyl sulfide at this point comprise 90.6 ± 14.5% of the experimentally determined yield. The remaining 47.0 ± 1.9% of the starting sulfonium salt **14** apparently can suffer cleavage to diphenyl sulfide or thioanisole. The observed amount of thioanisole in the product mixture would indicate that 77.5 ± 11.1% of the intermediate loses a phenyl radical. With the assumption that the remaining 22.5 ± 11.1% of the reaction proceeds vis loss of a methyl radical, a Ph:Me cleavage ratio of (3.4 ± 2.2):1 can be calculated.

Table II. Products of Reduction of Cyclic Sulfonium Salts 16–19[a]

	R_1	R_2	n	products	% yield	order of cleavage
16	Ph	H	1	26	99[b]	1° > Ph
				PhS-*n*-Bu	trace	
17[c]	Ph	H	2	27	87[d]	1° > Ph
18a[e]	Ph	Me	1	PhS-2-pentyl	6	2° > 1°
				PhS-1-pentyl	14	
				28, 29, 30	52	
18b[b]	Ph	Me	1	PhS-1-pentyl	43	2° > 1°
				28, 29, 30	33	
19[g]	Me	H	2	*h*		

[a] Conditions are standard as described in the Experimental Section unless otherwise noted. [b] Pure by NMR, low purified yield (47%) due to hydrocarbon nature of the product. [c] 0.5 h at 0 °C in DME. [d] Pure by NMR, low isolated yield (30%) as in *b*. [e] cis:trans ratio was 13:87; coupling product ratio was 65:35 αCH_2:$\alpha CHCH_3$ by NMR. [f] cis:trans ratio was 70:30; coupling product ratio was 79:21 αCH_2:$\alpha CHCH_3$ by NMR. [g] BF_4 salt. [h] No reduction under standard conditions or in either PhCl at room temperature for 5 h or in THF at reflux for 15 min.

Reduction of the 1-methylthiachroman salt **21** gives thiachroman (**33**) in 97.5% yield and trace amounts of sulfide assigned structures **34**, **35**, and/or **36** on the basis of GC–MS. The yields of the latter products, which could have arisen by cleavage of the primary group and/or elimination, are less than 2%. The >20:1 ratio of preferential cleavage of a methyl group over both the aryl and primary carbon is consistent with the order observed for **20**.

Reduction of 1,2-dimethylthiaindan hexafluorophosphate (**22**) provides *d*-, *l*-, and *meso*-**37** as a mixture of diastereomers in 13.3% yield. A ^1H NMR spectrum of the product mixture and GC–MS are consistent with a mixture of **34–39** in which comparable amounts of secondary and methyl cleavage occur but pure products were not obtained. Presumably **38** arises by methyl transfer prior to reduction.

Reduction of 1-phenylthiaindan hexafluorophosphate (**23**) was accomplished with both KC_8 and K^+ $Nap^{-\cdot}$. With KC_8 an 8.8 ± 0.9% yield of **31** was produced via loss of a phenyl group. The rest of the reaction proceeded by primary cleavage leading to **40**, **41**, and **42**. These yields indicate an apparent (10.3 ± 1.4):1 preference for primary cleavage relative to phenyl cleavage. When $K^+Nap^{-\cdot}$ is used as the reducing agent for **23**, the olefin **40** is formed in 45% yield. Since none of the corresponding hydrocarbon **41** was detactable by GC, disproportionation is provisionally ruled out as a source of the olefin, which is considered to arise by elimination from **23**. The products of reduction, radical coupling, and phenyl cleavage, **42** and **31**, are obtained in 35 ± 2% and 15.3 ± 3% yield, respectively. If the elimination reaction leading to **40** is discounted, the apparent primary:Ph cleavage ratio is (2.3 ± 1.0):1. The difference in product ratios under different reducing conditions, which is in contrast to the reductions of **9** and **13**, appears to be mechanistically informative and will be discussed (vide infra).

Reduction of *S*-(methylthio)xanthenium hexafluorophosphate (**24**) with KC_8 gives 60% thioxanthene and 9% 9-(methylthio)-xanthene. The formation of the latter appears to again involve an ylide–alkylation sequence, but the reductive loss of a methyl group from **24** is substantial and different for the preferential phenyl loss observed with the acyclic analogue **14**. In general, these benzo-fused cases show cleavages that are qualitatively different from those observed with the monophenyl cyclic and acyclic sulfonium salts.

Discussion

The above results establish that these chemical reductions of arylsulfonium salts proceeds via one-electron reduction to give ultimately sulfides and carbon radicals, as outlined in eq 1. The

$$R_1R_2R_3S^+ \xrightarrow{e^-} \underset{\mathbf{25}}{R_1R_2R_3S\cdot} \rightarrow R_1R_2S + R_3\cdot \qquad (1)$$

stoichiometry of the reaction requires 1 equiv of the KC_8 reducing

Table III. Products of Reduction of Benzo-Fused Sulfonium Salts 20–24[a]

	R_1	R_2	n	products	% yield	order of cleavage	ratio
20	Me	H	1	31	72[b]	Me > 1°	>2.6:1[c]
				32	2.4 ± 0.5		
21	Me	H	2	33	97.5[d]	Me ≫ 1°	>20:1[c]
				34	trace[e]		
				35 or 36	trace		
22	Me	Me	1	37	13.3[f]	2° ~ Me	
				34–39	[g]		
23	Ph	H	1	31	8.8 ± 0.9[i]	1° > Ph	(10.3 ± 1.4):1[j]
				40	15.4 ± 1.5		
				41	15.6 ± 1.6		
				42	59.4		
23	Ph	H	1	31	15.3 ± 3[i]	1° > Ph	(2.3 ± 1.0):1[k]
				40	<5		
				41	45 ± 5		
				42	35 ± 2		
24				thioxanthene 9-(methylthio)-xanthene	60[l]		

[a] Conditions are standard as described in the Experimental Section unless otherwise noted. [b] GC yield. [c] Minimum value. [d] Isolated yield with traces of 34 and 35 or 36. [e] Identified by GC-MS only. [f] Isolated, pure yield. [g] Mixture of 34–38 inseparable, identification based on GC-MS and ^{1}H NMR spectra. [h] Isolated as a mixture of 31, 39, and 40, on the basis of NMR integration with a 10% error limit. [i] Assumes no elimination as a source of 40. [j] Homogeneous reduction with $K^+Nap^-\cdot$. [k] Assumes elimination as the source of 40. [l] Based on ^{1}H NMR and mass spectra of a mixture of 42 and 43.

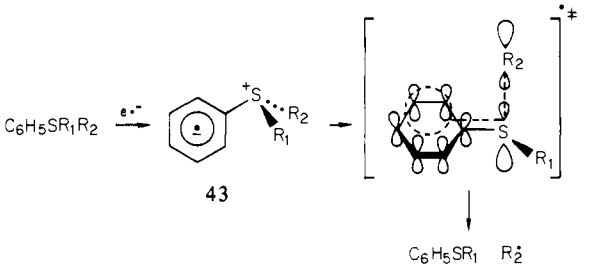
agent. The sulfides are observed directly, and the other products, when isolated, are those expected for radical coupling and disproportionation. The radical pathway is consistent with most of the electrochemical work[1-3,5-9] as well as the reduction of triarylsulfonium salts[10] and the cleavage of a benzylsulfonium salt with zinc.[12,17] In many of the previous studies, a valence-expanded species, **25**, has been postulated as an intermediate although concerted cleavage has also been suggested.[1-9] The possible structures for **25** range from a π-ligand radical anion sulfonium cation that would be tetrahedral to σ, π, or 3-center 3-electron radical species with trigonal-bipyramidal geometry.[18] We suggest the formation of a π-ligand radical anion sulfonium cation provides a reasonable explanation for most of the present results.

Monophenylsulfonium Salts. The relative leaving-group propensities for the salts **1–10**, **13**, and **16–18** in Tables I and II are as expected for a carbon radical as a leaving group. Thus the benzyl:secondary:primary:methyl:phenyl leaving-group ratios of 28:6:1:0.5:<0.05 compare favorably with the radical reduction of bromides by tri-*n*-butyltin hydride, where a ratio of 23:(2.7–1.0):1:0.024 is observed for benzyl:secondary:primary:phenyl groups[19] and with the ratio of 1.7–0.7:1:0.1 for formation of secondary:primary:methyl radicals from fragmentation of tetralkyltin cation radicals.[20]

The proposed mechanism is shown in Scheme I. Transfer of one electron to the phenyl LUMO of the tetrahedral sulfonium salt gives **43**, which is a π-ligand radical anion sulfonium cation that undergoes cleavage to a sulfide and a carbon radical. The alkylsulfonium salts do not reduce because the low-lying LUMO is required to accept an electron. The transition state for cleavage may be envisioned to involve overlap of the singly occupied molecular orbital of the aromatic ring with the σ^* orbital of the bond being broken homolytically, as shown in Scheme I. Thus the selectivity of cleavage is determined primarily by the relative energies of incipient radicals, although relief of steric strain appears to play a role.

The lack of consistency and transitivity in the cleavage ratios may be attributed to differences in strain, with the bulkier group

Scheme I



being preferentially cleaved both because of lengthening of the most crowded bond and because in the conformation in which the smaller group is leaving there would be eclipsing between the phenyl ring and the larger group. The difference noted between **6** and **7** and between **18a** and **18a** can be rationalized on that basis.[21] Tetrahedral π-ligand phosphoranyl radicals analogous to **43** have been observed, but this appears to be the first claim of these species for sulfur.[2]

Diphenyl- and Benzo-Fused Salts. In the case of the diphenyl and benzo-fused salts, the apparent leaving-group propensities are different from those observed for the monophenyl salts and do not parallel the incipient radical stabilities. These results can be rationalized in at least two ways. In the cases of the diphenyl salts **14** and **15**, the relatively favorable phenyl loss could be attributed to eclipsing strain that favors the transition state for phenyl cleavage from the π-ligand radical anion sulfonium cation. Alternatively, if the initially formed π-ligand species (**43**) is converted to a trigonal bipyramid (**44**), the more electronegative phenyl groups would be preferentially apical and cleavages would occur by loss of an apical group.[18] Our reduction of **14** corresponds reasonably well to the chemical reduction of the same sulfonium species with sodium amalgam in methanol reported by Hall and Horner. Comparisons involving **14** may be suspect, however, because of the possibility of methyl group displacement, a reaction that we observed to involve ca. 50% of **14** under our conditions.

For the benzo-fused systems **20**, **21**, **22**, and **24**, the presence of the five-membered ring would preferentially place the exocyclic group in the position to be cleaved, in agreement with the ob-

(17) Hyde, J. S.; Breslow, R.; DeBoer, C. *J. Am. Chem. Soc.* **1966**, *88*, 4763.

(18) For an excellent summarizing discussion of the evidence that sulfuranyl radicals are trigonal bipyramids, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Laegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753 and references cited therein.

(19) Rogers, H. R.; Hill, *J. Am. Chem. Soc.* C. L.; Fujiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. **1980**, *102*, 217. Menapace, L. W.; Kuivila, H. G. *Ibid.* **1964**, *86*, 3047.

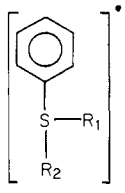
(20) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 2654.

(21) The case of **11** still appears anomalous. It is possible that there is an association between the phenyl anion and the remote sulfur to make a cyclic species in which an exocyclic or apical methyl is cleaved, that the positively charged sulfonium group inhibits cleavage, or that an additional intermediate is formed by interaction between the sulfurs.[22]

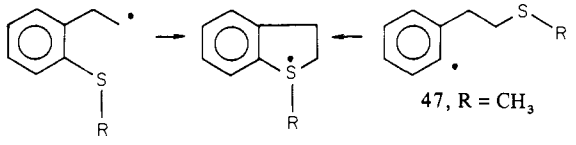
(22) Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200.

servations for **20**, **21**, and **24**. Thus, the difference between the benzo-fused and monophenyl cases, **20** and **1**, may be considered to reflect stereoelectronic control in the cleavage of the π-ligand intermediate. The case of **22** appears to be anomalous in that comparable amounts of exo- and endocyclic cleavage occur. That anomaly is not resolved by including formation of a trigonal-bipyramidal species at a rate competitive with cleavage, although that would be favored by the five-membered ring and is possible for all the benzo-fused cases.[18,23] Alternative formulation of the intermediates as equilibrating trigonal bipyramids does not offer a more consistent explanation of the results.

The cleavage of **23** could occur via a species in which the exocyclic phenyl group is the radical anion. The case of **23** is worth further consideration because it allows evaluation of the possibility that the apparent leaving-group propensities in the benzo system are disguised by a ring-opening–displacement sequence. If the ring-opened radical **45** undergoes $S_{H'}$ displacement to cleave the exocyclic group, a ratio of sulfides and thereby of leaving-group propensities would be obtained that would not reflect the relative transition-state energies of the initial cleavage. In fact, such a process has been observed by Kampmeier et al. for intermediates corresponding to those produced for endocyclic cleavage of **20** and **23**.[24] Kampmeier finds that when **45** and **46** are generated



44



45, R = C_6H_5
46, R = CH_3

47, R = CH_3

directly, displacement and hydrogen atom abstraction occur to comparable extents.[25] Since in the present work the reductions of **20** and **23** give different amounts of exocyclic cleavage, at least one of these reductions does not involve a ring-opening–displacement sequence. If it is assumed that the ring opening of **23** followed by displacement occurs, it becomes possible to explain the difference in primary:phenyl cleavage of ~10:1 and 2:1 observed in the heterogeneous and homogeneous reductions. Presumably, in the former case the radical is produced in high concentration on a surface, and dimerization is faster than hydrogen atom abstraction or displacement, which predominate under the homogeneous conditions. Thus in the latter the apparent ratio of leaving-group cleavages involves more displacement than the heterogeneous reaction. We cannot, however, assess the quantitative extent of ring-opening–displacement sequences for **23**. Since **20** apparently does not follow this route, the leaving-group ratio for that case is not perturbed by a ring-opening–displacement sequence, and the difference between the benzo-fused and acyclic monophenyl cases is considered to reflect initial cleavage preferences.

An interesting aspect of the present reductions of the benzo-fused sulfonium salts is that the reaction intermediates seem to be different from those generated by Kampmeier, who observed exclusive displacement of the exocyclic group.[24] Thus, for example, radicals **46** and **47** gave thiaindan as a common product but the different uncyclized products expected for trapping the radicals.

The π-ligand tetrahedral formulation of **43** as the species involved in these reductions is different from the trigonal-bipyramidal geometry assigned to sulfuranyl radicals.[18] Structural definition of the sulfuranyl radicals is generally based on cases in which these species are produced by addition of a radical to divalent sulfur, a process in which trigonal-bipyramidal geometry is preferred.[18,26] In contrast, the reduction reaction involves a tetrahedral precursor accepting an electron into a phenyl LUMO in a process that must be close to the diffusion limit.[27]

Experimental Section

Methods. Gas chromatography was performed on a Varian Series 1800 gas chromatograph; four to six injections were made of both a mixture of authentic compounds with an internal standard and the product mixture with the internal standard added. Integration was performed by cutting and weighing the peaks. After determination of the response factors, a standard error analysis was performed; two standard deviations were used to ensure that the reported values are at the 95% confidence limit. When ^{1}H NMR was used as a means of quantitation, the error of integration is estimated to be ±5% unless otherwise noted. Melting points and boiling points are likewise uncorrected. Infrared spectra were recorded neat or as Nujol mulls. Chemical shifts for ^{1}H NMR are reported in δ relative to an internal tetramethylsilane standard. Elemental analyses were performed by J. Nemeth and associates. Mass spectra were obtained from a Varian MAT CH-5 spectrometer by J. Wrona or R. Milberg under the supervision of C. Cook. Gas chromatographic–mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois.

Materials. THF was dried by distillation from sodium benzophenone ketyl. All the sulfonium salts used in reductions were recrystallized several times and gave sharp melting points, good elemental analyses, and clean NMR spectra unless otherwise noted. Potassium/graphite was obtained from Alfa/Ventron as a gold solid and used without further purification. Potassium naphthalenide was prepared by stirring a freshly cut piece of potassium in a THF solution of naphthalene for approximately 1 day before use.

The reference compounds phenyl *n*-butyl sulfide, phenyl *n*-pentyl sulfide, phenyl 2-pentyl sulfide, phenyl 3-butenyl sulfide, phenyl isopropyl sulfide, thiaindan, thiachroman, 2-methylthiaindan, *o*-(ethylthio)anisole, *o*-ethyldiphenyl sulfide, and *o*-(phenylthio)styrene were prepared by standard methods and characterized by ^{1}H NMR and mass spectrometry. The details of these procedures appear in the supplementary material.

Phenylethylmethylsulfonium Hexafluorophosphate (1). Ethyl iodide (4.2 g, 26 mmol) was added to a solution of 2.48 g (20 mmol) of thioanisole and 3.89 g (20 mmol) of $AgBF_4$ in 100 mL of CH_2Cl_2 at 0 °C, and the mixture was stirred for 1.5 h. Filtration to remove the yellow precipitate of AgI followed by removal of solvent in vacuo provided a brown oil, which was washed with hexane and concentrated in vacuo to yield 5.43 g of the tetrafluoroborate of **1** as a brown oil. This was dissolved in DMF and filtered to remove residual Ag^0, and an aqueous solution of NH_4PF_6 was added to provide white crystals. Filtration afforded 3.68 g of material, which was recrystallized from aqueous EtOH to give 1.27 g of **1**. A second crop was obtained from both the original filtrate and the mother liquor by evaporation of water. A total of 4.33 g (73% pure yield) of **1** was finally obtained after the combined crops were recrystallized from $CCl_4/CHCl_3$: mp 113.5–115 °C; ^{1}H NMR ($(CD_3)_2CO$) δ 8.2–8.0 (m, 2 H, *o*-Ar H), 7.9–7.6 (m, 3H, *m*- and *p*-Ar H), 3.85 (q of d, 2 H, J = 7 Hz, diastereotopic CH_3CH_2S), 3.5 (s, 3 H, SCH_3), 1.4 (t, 3 H, J = 7 Hz, CH_2CH_3); IR (mull) 2900, 1440, 1420, 1380, 1375, 1345, 1330, 1285, 1260, 1080, 1050, 987, 930, 900–800, 785, 760, 695 cm^{-1}. Anal. ($C_9H_{13}F_6PS$) C, H, S.

Phenylmethyl-*n*-butylsulfonium Fluoborate (2). Addition of 1.48 g (0.01 mol) of trimethyloxonium fluoborate to 1.66 g (0.01 mol) of phenyl *n*-butyl sulfide in 25 mL of CH_2Cl_2 followed by stirred for 0.25 h and

(23) Roberts, B. P. In "Advances in Free Radical Chemistry"; Williams, G. H., Ed.; Heyden and Son: Philadelphia, 1980; Vol. 6, p 225. See also: Bentrude, W. G. *Phosphorus Sulfur* **1977**, *3*, 109. Solodovnikov, S. P.; Bubnov, N. N.; Prokof'ef, A. I. *Russ. Chem. Rev. (Engl. Transl.)* **1980**, *49*, 3.

(24) (a) Kampmeier, J. A.; Evans, T. R. *J. Am. Chem. Soc.* **1966**, *88*, 4096. (b) Kampmeier, J. A.; Jordan, R. B.; Liu, M. S.; Yamanaka, H.; Bishop, P. J. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, DC, 1978; Chapter 16.

(25) Kampmeier, J. A., private communication, 1981.

(26) (a) Copper, J. W.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1977**, 228. (b) Gara, W. B.; Roberts, B. P. *J. Chem. Res., Miniprint* **1977**, 1748. (c) Gara, W. B.; Roberts, B. P.; Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C. *Ibid.* **1977**, 152. (d) Gara, W. B.; Roberts, B. P. *J. Organomet. Chem.* **1977**, *135*, C20.

(27) (a) Dorfman, L. M. *Acc. Chem. Res.* **1970**, *3*, 224. (b) Garst, J. F. *J. Am. Chem. Soc.* **1971**, *4*, 400. (c) Bank, S.; Juckett, D. A. *Ibid.* **1975**, *97*, 567 and references cited therein.

removal of solvent in vacuo produced 2.78 g of a yellow oil. Attempted crystallization from $CHCl_3$/ether provided 2.62 g (98%) of **2** as an oil: ^1H NMR ($(CD_3)_2CO$) δ 8.5–8.3 (m, 2 H, *o*-Ar H), 8.2–7.9 (m, 3 H, *m*- and *p*-Ar H), 4.0 (t, 2 H, J = 7 Hz, SCH_2), 3.55 (s, 3 H, SCH_3), 2.0–1.4 (m, 4 H, $CH_2CH_2CH_3$), 0.9 (t, 3 H, J = 6 Hz, CH_2CH_3); IR (neat) 3600, 2950, 1470, 1450, 1420, 1340, 1290, 1200–950, 760, 690 cm^{-1}.

Anal. ($C_{11}H_{17}BF_4S$) C, H.

Similar procedures were used for the preparation of the other sulfonium salts, although variation in solvents, reaction times, metathesis, and temperature were required for many cases. The details of these preparations appear in the supplementary material. The reactants, yields, and characterizations of the products are summarized in the following section.

Phenylmethyl(3-butenyl)sulfonium fluoborate (3) was prepared in quantitative yield from phenyl 3-butenyl sulfide and trimethyloxonium fluoroborate: mp 72–75 °C; ^1H NMR ($(CD_3)_2CO$) δ 8.1 (m, 2 H, *o*-Ar H), 7.9–7.6 (m, 3 H, *m*- and *p*-Ar H), 6.1–5.6 (m, 1 H, $CH{=}CH_2$), 5.3–5.0 (m, 2 H, $CH{=}CH_2$), 4.1–3.8 (m, 2 H, SCH_2), 3.45 (s, 3 H, SCH_3), 2.6–2.3 (m, 2 H, $CH_2CH{=}CH_2$); IR (melt) 3000, 1700, 1650, 1480, 1450, 1330, 1290, 1200–960, 940, 760, 690 cm^{-1}. Anal. ($C_{11}H_{15}BF_4S$) H, S. Calcd: O, 49.65. Found: C, 48.97.

Phenylisopropylbutylsulfonium hexafluorophosphate (4) was prepared from phenyl butyl sulfide, 2-bromopropane, and $AgBF_4$ in 29% yield: mp 83–85 °C; ^1H NMR (CD_2Cl_2) δ 7.8 (s, 5 H, Ar H), 4.05 (m, 1 H, $CHMe_2$), 3.6 (t, 2 H, J = 7 Hz, SCH_2), 1.6 and 1.3 (d, 6 H, J = 7 Hz, $CH(CH_3)_2$); IR (melt) 2950, 1690, 1540, 1260, 1240, 1165, 1100, 1060, 1000, 950, 930, 900–800, 740, 680 cm^{-1}. Anal. ($C_{13}H_{21}F_6PS$) C, H. S.

Phenylisopropyl(3-butenyl)sulfonium tetraphenylborate (5) was prepared from phenyl 3-butenyl sulfide, 2-bromopropane, and $AgBF_4$ in 19.2% yield: mp 128–131 °C; ^1H NMR (CD_2Cl_2) δ 7.9–6.5 (m, 25 H, Ar H), 5.7–4.7 (m, 3 H, $CH{=}CH_2$), 3.1 (m, 1 H, J = 7 Hz, $CHMe_2$), 2.6 (t, 2 H, J = 7 Hz, SCH_2), 2.2–1.7 (m, 2 H, CH_2CH_2CH), 1.2 (d, 3 H, J = 7 Hz, $(CH_3)_2CH$), 0.9 (d, 3 H, J = 7 Hz, CH_3); IR (film) 3000, 1950, 1890, 1820, 1755, 1645, 1575, 1440, 1260, 1180, 1130, 1060, 1030, 990, 928, 843, 790–670 cm^{-1}.

Anal. ($C_{37}H_{39}BS$) H. Calcd: C, 84.39. Found: C, 82.41.[28]

Phenylmethyl(2-pentyl)sulfonium tetraphenylborate (6) was prepared from phenyl 2-pentyl sulfide and trimethyloxonium fluorborate in 68.7% yield: mp 125–127 °C dec; ^1H NMR ($(CD_3)_2CO$) δ 8.0–7.6 (m, 5 H, Ar H), 7.5–7.2 (m, 8 H, BPh_4 *o*-H), 7.1–6.7 (m, 12 H, *m*- and *p*-H of BPh_4^-), 3.9 (m, 1 H, $CH(CH_3)CH_2R$), 3.1 (s, 3 H, SCH_3), 1.9–0.8 (m, 10 H, $CH_3CH(CH_2)_2CH_2)_2CH_3$); IR (mull) 2900, 1575, 1460, 1380, 1265, 1180, 1150 1065, 1030, 1000, 970, 850, 745, 735, 708, 680 cm^{-1}.

Anal. ($C_{36}H_{39}BS$) C, H, S.

Phenylmethylisopropylsulfonium hexafluorophosphate (7) was prepared from thioanisole, 2-bromopropane, and $AgBF_4$ in 35% yield: mp 83–86 °C; ^1H NMR ($CDCl_3$) δ 7.9–7.5 (m, 5 H, Ar H), 4.2–3.6 (m, 1 H, $CH(CH_3)_2$), 3.2 (s, 3 H, SCH_3), 1.6 (d, 3 H, J = 7 Hz, $CH(CH_3)_2$), 1.3 (d, 3 H, J = 7 Hz, $CH(CH_3)_2$); IR (melt) 3000, 1700, 1575, 1440, 1410, 1250, 1160, 1070, 980, 930, 900–800, 760, 685 cm^{-1}. No further purification was attempted.

Anal. Calcd for ($C_{10}H_{15}F_6PS$): C, 38.47; H, 4.84; S, 10.27. Found: C, 39.48; H, 4.62; S, 11.02.

Phenylmethyl(1-phenyl-2-propyl)sulfonium hexafluorophosphate (8) was prepared from 1-phenyl-2-(phenylthio)propane and trimethyloxonium fluoroborate: ^1H NMR ($(CD_3)_2CO$) δ 8.1 (m, 2 H, *o*-C_6H_5S), 7.8 (m, 3 H, *m*- and *p*-C_6H_5S), 7.2 (m, 5 H, Ar H), 4.5–4.0 (m, 1 H, SCH), 3.5 (s, 3 H, SCH_3), 3.0 (m, 2 H, $PhCH_2$), 1.45 (d, 1.4 H, J = 7 Hz, $CHCH_3$); IR (neat) 3100, 1750, 1620, 1595, 1500, 1480, 1420, 980, 900–800, 750, 710, 690 cm^{-1}.

Anal. ($C_{16}H_{19}F_6PS$), H, S. Calcd: C, 49.48. Found: C, 49.07.

Phenylmethylbenzylsulfonium fluoborate (9) was prepared from phenyl benzyl sulfide[29] and trimethyloxonium fluoborate in 91% yield: mp 120–121 °C; ^1H NMR (CD_2Cl_2) δ 7.6 (m, 5 H, C_6H_5S), 7.1 (m, 5 H, Ar H), 4.8 (m, 2 H, $PhCH_2$, diastereotopic), 3.3 (s, 3 H, SCH_3); ^1H NMR ($(CD_3)_2CO$) 8.1–7.85 (m, 2 H, *o*-C_6H_5S), 7.8–7.6 (m, 3 H, *m*- and *p*-C_6H_5S), 7.35 (br, 5 H, Ar H), 5.15 (m, 2 H, $PhCH_2$), 3.5 (s, 3 H, SCH_3); IR (mull) 3000, 1600, 1460, 1380, 1340, 1280, 1190, 1160–1000, 1000, 980, 940, 930, 840, 780, 755, 720, 700, 680 cm^{-1}.

Anal. ($C_{14}H_{15}BF_4S$) C, H, S.

Dimethyl-*tert*-butylsulfonium fluoborate (10) was prepared from *tert*-butyl methyl sulfide and trimethyloxonium fluoborate in 98% yield: mp ca. 200 °C dec.; ^1H NMR ($(CD_3)_2CO$) δ 3.05 (s, 3 H, SCH_3), 1.70 (s, 9 H, $(CH_3)_3C$); IR (C_4Cl_6) 3000, 1510–1370, 1160–1010 cm^{-1}.

Anal. ($C_6H_{15}BF_4S$) C, H, S.

***S,S'*-Dimethyl-1,4-bis(phenylthio)butane fluoborate (11)** was prepared from 1,4-bis(phenylthio)butane and trimethyloxonium fluoborate in 70% yield (**11**): mp 182–183 °C ^1H NMR ($(CD_3)_2SO$) δ 8.0–7.85 (m, 4 H, *o*-Ar H), 7.8–7.6 (m, 6 H, *m*- and *p*-Ar H), 3.6 (m, 4 H, SCH_2), 3.4 (s, 6 H, SCH_3), 1.4 (m, 4 H, CH_2CH_2); IR (mull) 2900, 1290, 1200–950, 760, 690 cm^{-1}.

Anal. ($C_{18}H_{24}B_2F_8S_2$) C, H, S.

Tri-*p*-tolylsulfonium Fluoborate (12). Metathesis of the chloride salt with $NaBF_4$ allowed isolation of **12**: mp 161–65 °C (lit.[30] mp 163–164 °C); ^1H NMR ($(CD_3)_2SO$) 7.75 (m, 12 H, Ar H), 2.5 (s, 9 H, $ArCH_3$).

Anal. Calcd for ($C_{21}H_{21}BF_4S$: C, 64.30; H, 5.40. Found: C, 63.06; H, 5.34.[31]

Phenylbis(2-phenylethyl)sulfonium hexafluorophosphate (13) was prepared from phenyl phenethyl sulfide, phenethyl bromide, and $AgBF_4$ in 63.4% yield: mp 77.5–79.5 °C; ^1H NMR ($(CD_3)_2CO$) δ 7.8 (m, 5 H) C_6H_5S), 7.2 (m, 10 H, $C_6H_5CH_2$), 4.1 (t, 4 H, J = 7 Hz, SCH_2), 3.0 (t, 4 H, J = 7 Hz, $PhCH_2$); IR (mull) 2900, 950, 935, 900–800, 745, 700, 685 cm^{-1}.

Anal. ($C_{22}H_{23}F_6PS$) C, H, S.

Diphenylmethylsulfonium hexafluorophosphate (14) was prepared from diphenyl sulfide and trimethyloxonium fluoroborate in quantitative yield: mp 68–70 °C. ^1H NMR (D_2O) δ 7.9 (m, 10 H, ArH), 3.8 (s, 3 H, SCH_3); IR (melt) 3050, 1480, 1450, 1420, 1075, 990, 900–800, 750, 680 cm^{-1}.

Anal. ($C_{13}H_{13}F_6PS$) C, H, S.

Diphenylethylsulfonium hexafluorophosphate (15) was prepared from diphenyl sulfide, ethyl iodide, and $AgBF_4$ in 74% yield: mp 115–116 °C; ^1H NMR ($(CD_3)_2CO$) δ 8.2–8.0 (m, 4 H, *o*-C_6H_5S), 7.9–7.6 (m, 6 H, *m*- and *p*-C_6H_5S), 4.4 (q, 2 H, J = 7 Hz, SCH_2CH_3), 1.5 (t, 3 H, J = 7 Hz, CH_2CH_3); IR (mull) 2900, 1575, 1290, 1260, 1180, 1165, 1070, 1000, 975, 900–800, 780, 765, 760, 745, 685 cm^{-1}.

Anal. ($C_{14}H_{15}F_6PS$) C, H, S.

Phenyltetramethylenesulfonium hexafluorophosphate (16) was prepared from ω-bromobutyl phenyl sulfide[32] and $AgPF_6$ in 94% yield: mp 147–149 °C; ^1H NMR ($(CD_3)_2SO$) δ 7.8 (m, 2 H, *o*-Ar H), 7.6 (m, 3 H, *m*- and *p*-Ar H), 3.5–4.0 (m, 4 H, SCH_2), 3.3 (m, 4 H, CH_2CH_2); IR (mull) 2900, 1460, 1380, 950–750, 750, 685 cm^{-1}.

Anal. ($C_{10}H_{13}F_6PS$) C, H, P, S.

Phenylpentamethylenesulfonium hexafluorophosphate (17) was prepared from 1-thiophene, 5-bromopentane, and $AgPF_6$ in 42% yield: mp 165–167 °C; ^1H NMR ($(CD_3)_2SO$) δ 7.9 (m, 2 H, *o*-C_6H_5S), 7.6 (m, 3 H, *m*- and *p*-C_6H_5S), 3.8 (m, 4 H, SCH_2), 2.3–1.3 (m, 6 H, $(CH_2)_3$).

Anal. ($C_{11}H_{15}F_6PS$) C, H, P, S.

1-Phenyl-2-methyltetrahydrothiophenium hexafluorophosphate (18a and 18b) was prepared from 1-thiophenyl-4-bromopentane and $AgBF_4$ in 17% yield: mp 69–72 °C; ^1H NMR ($(CD_3)_2CO$) δ 8.1-7.7 (m, 5 H, ArH), 4.7–4.0 (m, 3 H, SCH and SCH_2), 3.0–2.6 (m, 4 H, CH_2CH_2), 1.8 (d, 0.87 H, J = 7 Hz, *trans*-CH_3), 1.3 (d, 2.17 H, J = 7 Hz, *cis*-CH_3), ca. 70% cis and 30% trans; IR (mull) 2900, 1450, 900–800, 760, 690 cm^{-1}.

Anal. ($C_{11}H_{15}F_6PS$) C, H, S.

A second synthesis, at 10 times scaleup, produced a 17.5% yield of **18a**, 87% trans and 13% cis, mp 103–110 °C. The larger percentage of trans isomer is presumably due to the greater number of recrystallizations required for purification.

The assignment of stereochemistry to **18** is based on chemical shift arguments. The methyl group in the cis compound would be expected to appear upfield relative to the trans methyl group due to its position in the shielding cone of the phenyl ring. Two signals are seen in the ^1H NMR spectrum of the mixture of isomers: one doublet at δ 1.65 and a second at δ 1.00. Of the two mixtures made, the one heated longer gave a larger percentage of the downfield peak. If we assume that the trans salt would be thermodynamically favored, this is consistent with the assignment.

Methylpentamethylenesulfonium fluoborate (19) was prepared from pentamethylene sulfide and trimethyloxonium fluoborate in quantitative yield: mp > 200 °C; ^1H NMR ($(CD_3)_2CO$) δ 3.8–3.1 (m, 4 H, SCH_2), 3.0 (s, 3 H, SCH_3), 2.2–1.5 (m, 6 H, $(CH_2)_3$); IR (mull) 1285, 1270, 1260, 1245, 1200–950, 940, 895–840, 815, 768 cm^{-1}.

Anal. ($C_6H_{13}BF_4S$) C, H, S.

1-Methylthiaindan hexafluorophosphate (20) was prepared from thiaindan and methyl fluorosulfonate in 81% yield followed by metathesis with ammonium hexafluorophosphate: mp 130–132 °C; ^1H NMR ($(CD_3)_2SO$) δ 8.1–7.9 (m, 1 H, *o*-ArH), 7.7–7.4 (m, 3 H, Ar H), 4.3–3.4 (m, 4 H, CH_2CH_2), 3.0 (s, 3 H, SCH_3); IR (mull) 2900, 1460, 1450, 1420, 1380, 1320, 1260, 1210, 1030, 985, 900–800, 790, 780, 770, 745 cm^{-1}.

(28) This analysis is low due to the poor quality of the NaBPh used. An elemental analysis revealed only 83.10 wt % C; calcd 84.23%.

(29) Taboury, F. *Bull. Soc. Chim. Fr.* **1904**, *31*, 1183.

(30) LaRochelle, R. W.; Trost, B. M. *J. Am. Chem. Soc.* **1971**, *93*, 6077.

(31) Carbon is low due to a small amount of $NaBF_4$ impurity.

(32) Torii, S.; Matsuyama, Y.; Kawasaki, K.; Uneyama, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2912.

Anal. ($C_9H_{11}F_6PS$) C, H, S.

1-Methylthiachroman hexafluorophosphate (21) was prepared from thiachroman and methyl fluorosulfonate in 54% yield: mp 76–78 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 7.9 (m, 1 H, Ar H), 7.7–7.3 (m, 3 H, Ar H), 4.1–3.4 (m, 2 H, SCH_2), 3.2 (s, 3 H, SCH_3), 3.1–2.8 (m, 2 H, Ar CH_2), 2.5–2.1 (m, 2 H, $CH_2CH_2CH_2$); IR (melt) 3000, 1480, 1430, 1270, 1200 985, 930, 910–800, 780, 760, 740 cm^{-1}.

Anal. ($C_{10}H_{13}F_6PS$) C, H, S.

1,2-Dimethylthiaindan hexafluorophosphate (22) was prepared from 2-methylthiaindan and trimethyloxonium fluoroborate in 24% yield: mp 126–128 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 8.0 (m, 1 H, Ar H *o*- to SMe), 7.8–7.5 (m, 3 H, Ar H), 4.5 (q of d, 1 H $CHCH_3$), 4.25–3.85 (m, 1 H, diastereotopic CH_2), 3.45–2.9 (m, 4 H, SCH_3 and diastereotopic CH_2), 1.5 (d, 3 H, J = 7 Hz, $CHCH_3$); IR (mull) 2900, 1460, 1440, 1380, 1325, 1300, 1200, 1085, 1010, 990, 980, 925, 900–800, 770, 762, 704 cm^{-1}.

Anal. ($C_{10}H_{13}F_6PS$) C, H, S.

1-Phenylthiaindan hexafluorophosphate (23) was prepared by methylation of thiaindan sulfoxide[33] with trimethyloxonium fluoborate and reaction of the product with phenylmagnesium bromide in ether to give 51% of **23**, mp 176–178 °C; ^{1}H NMR ($(CD_3)_2CO$) δ 8.15 (d, 1 H, J = 7 Hz, Ar H *o*- to SPh), 8.0–7.6 (m, 8 H, Ar H), 5.9–4.2 (m, 2 H, SCH_2), 4.0 (m, 2 H, Ar CH_2); IR (mull) 2900, 1460, 1380, 1160, 1000, 890, 880–810, 755, 685 cm^{-1}.

Anal. ($C_{14}H_{13}F_6PS$) C, H, S.

***S*-Methylthioxanthenium hexafluorophosphate (24)** was prepared from thioxanthene and trimethyloxonium fluoroborate in 45% yield: mp 215 °C dec; ^{1}H NMR ($(CD_3)_2CO$) δ 8.2 (d, 2 H, J = 8 Hz, Ar H), 7.8–7.5 (m, 6 H, Ar H), 4.85 (d, 1 H, J = 19 Hz, Ar CH_2), 4.55 (d, 1 Hh, J = 19 Hz, Ar CH_2), 3.5 (s, 3 H, SCH_3); IR (mull) 2900, 1650, 1580, 1450, 1380, 1300, 1280, 1240, 1170, 1100, 1040, 995, 930, 900–800, 880, 765, 730, 705, 695 cm^{-1}.

Anal. ($C_{14}H_{13}F_6PS$) C, H, S.

Reductions with Potassium in Graphite. KC_8 (1.1 equiv, 5.5 mmol) was added to 5 mmol of the sulfonium salt slurried or dissolved in 50–100 mL of dry THF at ambient temperature under nitrogen in a dry system. After 1 h a few drops of water was added to destroy the excess KC_8. Following removal of THF in vacuo, hot hexane was added to the product mixture, and a filtration was performed to separate the material soluble in hot hexane from the graphite and potassium salts. Gas chromatographic analysis was used to identify and quantify the products and GC–MS was used as a second criterion of identity. The solvent was then removed in vacuo to provide the product mixture, which could be analyzed by ^{1}H NMR spectroscopy. Integration of unique absorbances in the spectrum could be used as a method of quantitation. When necessary, a MPLC separation was performed to obtain the pure components.

Homogeneous Reductions with $K^+Nap^{-}\cdot$.[14] A preformed solution of $K^+Nap^{-}\cdot$ in THF was added to a solution or slurry of the sulfonium salt in THF over a period of approximately 10 min. After an additional 10 min of stirring, a few drops of water were added to quench any remaining $K^+Nap^{-}\cdot$. If volatile products were expected, pentane or hexane was used to precipitate the salt and the reaction mixture was analyzed by GC after filtration. A similar procedure was used for homogeneous reductions with $K^+/DIMAN^{-}\cdot$.[14] Yields were calculated from isolated material, integration of gas chromatograms relative to an internal standard, or integration of a ^{1}H NMR spectrum of a product mixture. Products and yields are summarized in Tables I–III.

A control reduction performed on 1,4-bis(phenylthio)butane as a representative sulfide with 2.2 equiv of KC_8 under standard conditions afforded quantitative recovery of the sulfide with no reduction.

Reduction of 1. After a standard reduction of 5 mmol of **1** in 100 mL of THF for 1.25 h, 100 mL of pentane was added to precipitate any unreduced salt. Filtration of this mixture followed by trituration of the precipitate with CH_2Cl_2 and removal of solvent in vacuo afforded no residue of **1**. To the initial filtrate was added 0.353 g of nonane as an internal standard, and gas chromatographic analysis was performed on a 5 ft × $^1/_8$ in. column packed with 15% SE-30 on Varaport-30 programmed at 70 °C for 2 min and then 10 °C min^{-1} to 130 °C. Response factors were determined for authentic samples of thioanisole and phenyl ethyl sulfide relative to nonane and used to calculate the yields as 60.9 ± 2.2% and 30.8 ± 2.8%, respectively. GC/MS and ^{1}H NMR spectra confirmed the product assignments, and integration of the ^{1}H NMR spectrum corroborated the yields.

A second reduction of **1** was performed due to the low mass balance above. This was allowed to stir for 3 h before working up as for the first reaction. The yields in this case were 48.7 ± 3.0% and 27.3 ± 1.6%, respectively. The ^{1}H NMR spectrum of the product mixture corroborated the assignments and yields.

Reductions of 2–24 are summarized in the supplementary material.

1,8-Bis(phenylthio)octane (26) obtained from reduction of **16** was a solid, mp 82–83 °C (lit.[34] mp 83 °C). A second crop of 0.13 g was obtained from an ethanol/water recrystallization for a total yield of 47.2%: ^{1}H NMR ($CDCl_3$) δ 7.2 (m, 10 H, Ar H), 2.8 (t, 4 H, J = 7 Hz, SCH_2), 1.8–1.2 (m, 12 H, $(CH_2)_6$); IR (mull) 1575, 1290, 1230, 1100, 1030, 900, 735, 690 cm^{-1}; mass spectrum (70 eV), m/e (rel intensity) 330 (100, M^+), 221 (31, M – SPh), 123 (98, $PhS{=}CH_2$), 110 (86, PhSH).

Anal. ($C_{20}H_{26}S_2$) C, H.

1,10-Bis(phenylthio)decane (27) obtained by reduction of **17** was a solid: mp 83–85 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.0 (m, 10 H, Ar H), 2.8 (t, 4 H, J = 7 Hz, SCH_2), 1.8–1.1 (m, 16 H, $(CH_2)_8$); IR (mull) 2900, 1590, 1450, 1230, 1095, 1015, 900, 730, 690 cm^{-1}; mass spectrum (70 eV), m/e (rel intensity) 358 (54, M^+), 249 (12, M – PhS), 123 (64, $PhS{=}CH_2$), 110 (100, PhSH).

Anal. ($C_{22}H_{20}S_2$) C, H.

2,3-Dimethyl-1,4-bis(2-(methylthio)phenyl)butane (37) obtained by reduction of **22** as a mixture of diastereoisomers was a solid: mp 60–75 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–6.9 (br, 8 H, Ar H), 3.2–1.2 (m, 6 H, $CH_2CHCHCH_2$), 2.45 (2 s, 6 H, diastereotopic SCH_3), 0.9 (d, 6 H, J = 7 Hz, $CHCH_3$); IR (film) 2900, 1590, 1460, 1440, 1365, 1325, 1315, 1260, 1070, 1040, 970, 955, 740, 670 cm^{-1}; mass spectrum (70 eV), m/e (rel intensity) 330 (37, M^+), 283 (88 M – SMe), 193 (35), 165 (8, M/2), 137 (100, $C_6H_4(SMe)(CH_2\cdot)$).

Anal. ($C_{20}H_{26}S_2$) C, H.

Acknowledgment. We are grateful for support of this work by the National Science Foundation and the National Institute of Health. Funds for support of the mass spectrometer were provided by GM 27029. We are also grateful to Professor Jack Kampmeier for stimulating discussions and helpful analyses.

Registry No. 1, 82135-72-6; **2**, 82135-73-7; **3**, 82135-75-9; 4, 82135-77-1; **5**, 82135-79-3; **6**, 82149-97-1; **7**, 82135-80-6; **8**, 82135-82-7; **9**, 22900-27-2; **10**, 69652-46-6; **11**, 82135-84-0; **12**, 22743-99-3; **13**, 82135-86-2; **14**, 23686-31-9; **15**, 82135-87-3; **16**, 82135-88-4; **17**, 82135-89-5; *trans*-**18a**, 82135-91-9; *cis*-**18b**, 82135-93-1; **19**, 60715-88-0; **20**, 82135-95-3; **21**, 82135-97-5; **22**, 82135-98-6; **23**, 82136-00-3; **24**, 82149-98-2; **26**, 66919-99-1; **27**, 82136-01-4; **28**, 82136-02-5; **29**, 82136-03-6; **30**, 82136-04-7; (*R*,R**)-**37**, 82136-05-8; (*R*,S**)-**37**, 82136-06-9; **40**, 82137-07-0; $PhSCH(CH_3)CH_2CH_2CH_3$, 13921-08-9; $Ph(CH_2)_2Ph$, 103-29-7; $Ph(CH_2)_4Ph$, 1083-56-3; PhS-1-pentyl, 1129-70-0; thioanisole, 100-68-5; phenyl butyl sulfide, 1126-80-3; phenyl 3-butenyl sulfide, 4285-49-8; 2-bromopropane, 75-26-3; 1-phenyl-2-(phenylthio)propane, 62252-49-7; phenyl benzyl sulfide, 831-91-4; *tert*-butyl methyl sulfide, 6163-64-0; 1,4-bis(phenylthio)butane, 5330-89-2; phenyl phenethyl sulfide, 21213-26-3; diphenyl sulfide, 139-66-2; ω-bromobutyl phenyl sulfide, 17742-54-0; thiophene, 110-02-1; 1-phenylthio-4-bromopentane, 82136-08-1; pentamethylene sulfide, 1613-51-0; thiaindan, 4565-32-6; thiochroman, 2054-35-5; 2-methylthiaindan, 6165-55-5; thiaindan sulfoxide, 26524-83-4; thioxanthene, 261-31-4; 5,6-dimethyloctane, 15869-96-2; potassium (dimethylamino)naphthalene radical anion, 82136-09-2.

Supplementary Material Available: Details of the synthesis of reference compounds and the preparation of other sulfonium salts (23 pages). Ordering information is given on any current masthead page.

(33) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282.

(34) Braun, J. V. *Chem. Ber.* **1909**, *42*, 4541.