

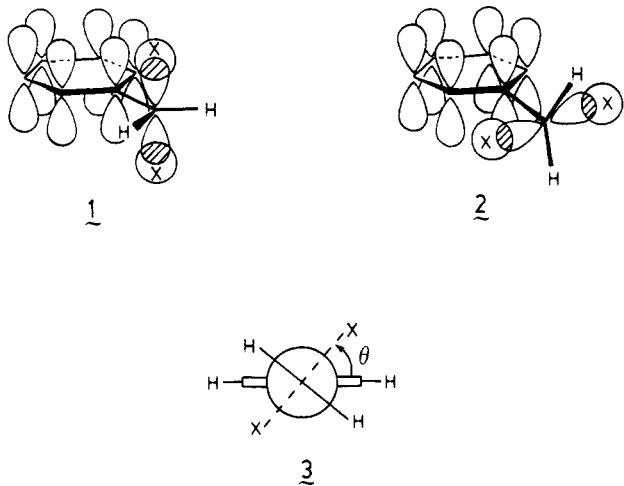
Nucleophilic Substitution Factors. 1. Coplanar vs. Orthogonal Bimolecular Substitution at a Benzylic Carbon. X-ray Structure of 2-Isobutyl-1,3-dihydrobenzo[*c*]thiophenium Perchlorate

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Abstract: A stereoelectronic effect in bimolecular nucleophilic substitution at a benzylic center has been observed in the rates of reaction of thiourea in dimethyl-*d*₆ sulfoxide with a series of sulfonium perchlorates with differing degrees of constraint in the orientation of the reacting C-S⁺ bond with respect to the plane of the aromatic ring. The substrates and their relative rates (at 37 °C, unless otherwise noted) are as follows: (a, highly constrained) 2-ethyl-1,3-dihydrobenzo[*c*]thiophenium perchlorate (**4b**), 1.00, and 2-isobutyl-1,3-dihydrobenzo[*c*]thiophenium perchlorate (**4c**), 2.8; (b, partly constrained) 2-ethyl-3,4-dihydro-1*H*-2-benzothiopyranium perchlorate (**7**), 45 (at 82 °C); (c, unconstrained) *S,S*-dibenzyl-*S*-ethylsulfonium perchlorate (**5b**), 8.1 × 10³. An (8 × 10³)-fold rate difference was also observed between *S,S*-dibenzyl-*S*-ethylsulfonium tetrafluoroborate (**5a**) and 2-ethyl-1,3-dihydrobenzo[*c*]thiophenium tetrafluoroborate (**4a**) with potassium thiocyanate-18-crown-6 in acetonitrile-*d*₃. Analysis of these rate differences, taken with inspection of molecular models which show that the observed rate differences are not adequately accounted for by simple nonbonding or angle strain effects, clearly indicates a dihedral angle dependent factor consistent with π -overlap between p-orbitals on the aromatic ring and the carbon atom undergoing substitution. The "orbital-overlap factor" is estimated to increase the reactivity of the benzylic center in **5b** (4 × 10³)-fold relative to that of the corresponding ethyl group (in **21**). A single-crystal X-ray analysis on **4c** showed the salt crystallizes in space group *P*2₁/*n*, unit cell dimensions *a* = 17.382 (1) Å, *b* = 9.1731 (6) Å, *c* = 8.7828 (3) Å, and β = 91.7 (2)°, with *Z* = 4. On the basis of 2054 unique data with *F*² > 2 σ , full matrix refinement converged at *R* = 0.044 for 232 variables. There is a dihedral angle of 3.8° between the C2,S,C9 plane and the plane of the aromatic ring consistent with the observed low reactivity of the benzylic center and the present analysis. The entropies of activation for benzylic substitution of the cyclic and acyclic substrates (**4b**, **4c**, and **5b**) with thiourea in Me₂SO-*d*₆ are very similar (-12 ± 1 cal mol⁻¹ K⁻¹), in contrast to the great ΔS^\ddagger difference reported for an analogous α -carbonyl system by Bartlett and Trachtenberg; the origin of this difference is discussed.

It has been known since early in the century that bimolecular nucleophilic substitution takes place more readily with benzyl chloride than ethyl chloride, for example.¹ To account for the general phenomenon of accelerated benzylic substitution, Dewar² and Streitwieser³ suggested that the transition state in a benzylic substitution was stabilized by π -bond overlap that may arise if the nuclei and p-orbitals are arranged as in **1**. This picture has



found general acceptance and has been supported by more detailed MO analysis, and it is therefore perhaps surprising to realize that when we began our study the only experimental support put forward to justify the notion was the set of results which prompted it in the first place. Implicit in the π -overlap picture is the idea

that the alternative arrangement shown in **2** must lack the stabilization attributed to **1** and hence that any benzylic substitution constrained to react by way of a transition state like **2** would proceed more slowly than that of an ordinary, unconstrained analogue. Although Bartlett and Trachtenberg tested this basic idea for a substitution α to a carbonyl group in a classic study more than 30 years ago,⁵ the carbonyl reaction has complicating features not present in the benzylic system,⁶ and the latter, to our knowledge, has not been the subject of any corresponding experimental study. Accordingly, in this paper we describe kinetic and X-ray crystallographic observations on a constrained system and appropriate models that provide both experimental evidence for, and approximate assessment of, the stereoelectronic orbital-overlap factor in benzylic substitution.⁹ A preliminary report

(4) (a) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, 1975; pp 256 ff. (b) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 3531-3539.

(5) Bartlett, P. D.; Trachtenberg, E. N. *J. Am. Chem. Soc.* **1958**, *80*, 5808-5812.

(6) Complicating features in α -carbonyl substitution include (a) the uncertainty about the site of nucleophilic attack, i.e., whether at the α -carbon, the carbonyl carbon, or somewhere between,⁷ and (b) the dependence of the " α -carbonyl effect" on the nucleophile, illustrated, for example, by the *inversion* in the relative rates of reaction of phenacyl bromide and MeI on changing from thiourea to Et₃N.⁸

(7) For summaries see ref 5 and also: (a) Bordwell, F. G.; Brannen, W. T. *J. Am. Chem. Soc.* **1964**, *86*, 4645-4650. (b) Ross, S. D.; Finkelstein, M.; Petersen, R. C. *J. Am. Chem. Soc.* **1968**, *90*, 6411-6415. (c) Thorpe, J. W.; Warkentin, J. *Can. J. Chem.* **1973**, *51*, 927-935.

(8) Halvorsen, A.; Songstad, J. *J. Chem. Soc., Chem. Commun.* **1978**, 327-328.

(9) One apparently unrecognized piece of evidence in support of this picture may be found in the chemistry of *O*-ethylphthalidium tetrafluoroborate, which is reported (experimental part only) to react with NaI in CH₃CN to give mainly the product of ethyl transfer (phthalide and EtI) and only a low yield of the product of benzylic attack (ethyl 2-(iodomethyl)benzoate, identified by its lachrymatory properties!); Meerwein, H.; Borner, P.; Fuchs, O.; Sasse, H. J.; Schrodt, H.; Spille, J. *Chem. Ber.* **1956**, *89*, 2060-2079. In our hands this experiment gave an approximately equimolar mixture (as judged by ¹H NMR) of the two sets of products: Tsang, G. T. Y. M. Sc. Thesis, University of Western Ontario, London, Canada, 1984. The high reactivity of the starting material hampered both handling and kinetic studies, and we turned to another system for our more detailed study.

(1) Slaton, A.; Twiss, D. F. *J. Chem. Soc.* **1909**, 95, 93-103. See also: Conant, J. B. et al. *J. Am. Chem. Soc.* **1924**, *46*, 232-252; *J. Am. Chem. Soc.* **1925**, *47*, 476-488; *J. Am. Chem. Soc.* **1925**, *47*, 488-501.

(2) Dewar, M. J. S. "The Electronic Theory of Organic Chemistry"; Oxford University Press: Oxford, 1949; p 73.

(3) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; pp 11-29.

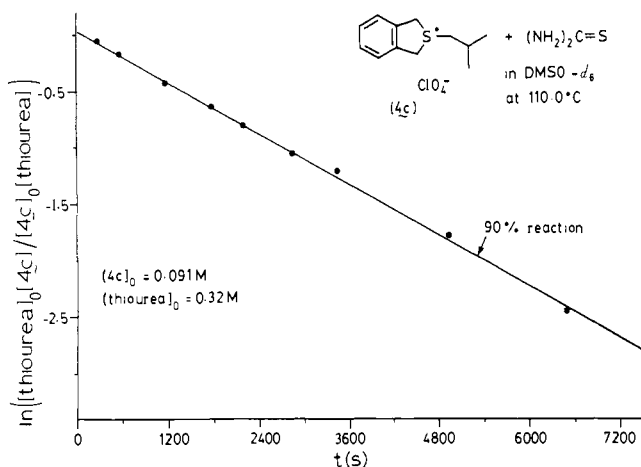
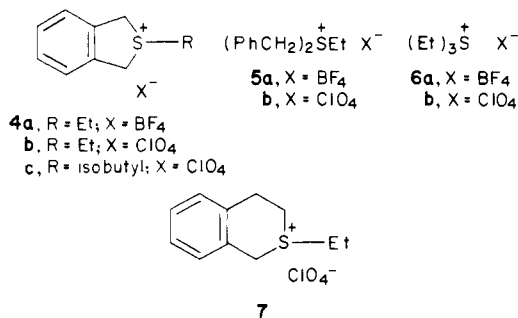


Figure 1. Second-order rate plot for the reaction of 2-isobutyl-1,3-dihydrobenzo[*c*]thiophenium perchlorate (**4c**) with thiourea in dimethyl-*d*₆ sulfoxide at 110 °C.

of the first stage of this study has already appeared.¹⁰

Formulas **1** and **2** illustrate the two extreme relationships between the nuclei of the aromatic ring and those of the reacting groups. In **1** the (ideally straight) line joining the attacking atom of the nucleophile (Nu), the carbon atom being substituted (C), and the departing atom of the leaving group (Lg) is *orthogonal* to the plane defined by the plane of the aromatic ring, whereas in **2** the Nu-C-Lg line is *coplanar* with the aromatic carbons.¹¹ Referring to **3**, "orthogonal" describes the arrangement in which θ is 90° and "coplanar" that in which θ is 0°.

As substrates we chose 2-alkyl-1,3-dihydrobenzo[*c*]thiophenium salts (**4**), with the *S,S*-dibenzyl-*S*-ethylsulfonium and triethylsulfonium analogues (**5** and **6**) for comparison; in addition, we looked briefly at 2-ethyl-3,4-dihydro-1*H*-2-benzothiopyranium perchlorate (**7**), the six-membered ring homologue of **4b**.



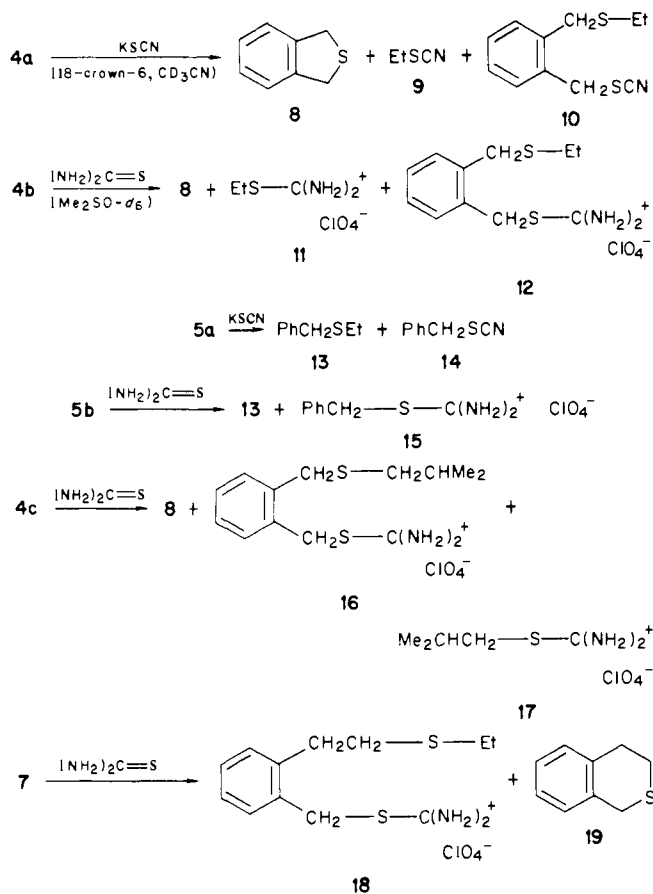
Results and Discussion

Product and Kinetic Studies. Compounds **4–7** were made from the corresponding symmetrical or heterocyclic sulfides by alkylating with either triethyloxonium tetrafluoroborate or isobutyl [2]betylate perchlorate.¹² Sulfonium salt **4a** reacted cleanly with potassium thiocyanate and 18-crown-6 in acetonitrile to give a mixture containing dihydroisothianaphthene (**8**), ethyl thiocyanate (**9**), and the ring-opened product **10** in yields, as determined by NMR integration, of about 80, 80, and 20%, respectively; the reaction of **4b** with thiourea in dimethyl sulfoxide proceeded similarly, yielding **8** (75%) and ethylthiouronium perchlorate (**11**, 75%) along with some **12** (25%), the product of benzylic attack.

(10) King, J. F.; Tsang, G. T. Y. *J. Chem. Soc., Chem. Commun.* **1979**, 1131–1132.

(11) The geometry may be defined with respect to the orientation of either relevant nuclei or the interacting orbitals. While recognizing that the latter may have had greater currency, we have adopted the former description as closer to phenomenological and thus less likely to need change with advances in theory. Our definition yields a simple mnemonic: *coplanar* or *constrained* vs. *orthogonal* or *ordinary*.

(12) Me₂CHCH₂OSO₂CH₂CH₂N⁺Me₃ ClO₄⁻: King, J. F.; Loosmore, S. M.; Aslam, M.; Lock, J. D.; McGarrity, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 7108–7122.



By contrast, the dibenzylethylsulfonium salts (**5a** and **5b**) gave only benzyl ethyl sulfide (**13**) and either benzyl thiocyanate (**14**) or benzylthiouronium perchlorate (**9**) with no sign of dibenzyl sulfide or either ethyl thiocyanate (**9**) or ethylthiouronium perchlorate (**11**). As expected, thiourea attacked the isobutylsulfonium salt **4c** chiefly at the benzylic carbon to form **16** (85–90%), though there was also some reaction at the isobutyl group to give **8** and isobutylthiouronium perchlorate (**17**) (10–15%). The identity of the products was confirmed by comparison of spectra with those of authentic specimens obtained by independent synthesis. Reaction of the six-membered cyclic sulfonium salt (**7**) with thiourea in Me₂SO-*d*₆ gave a reaction product which consisted largely of a material showing NMR singlets at 7.33 and 4.54 ppm, a partly obscured multiplet around 2.5–3.5 ppm, and a triplet at 1.20 ppm, fully consistent with ring-opened structure **18**; in addition, small peaks at 7.18 and 3.73 ppm, consistent with the presence of about 5% of **19** in the product, were also clearly in evidence. Control experiments showed both observed and possible alternative products to be stable to the reaction conditions; we conclude that the products are those of kinetic control and the product ratios correspond to rate ratios.

The rates of these reactions were measured by following the disappearance of appropriate NMR peaks due to the starting material. The rate constants were obtained from second-order rate plots, which gave good straight lines to at least 75% reaction for the reactions with thiourea (>90% for those of **4b**, **4c**, and **5b**; see Figure 1 for a typical plot). The observed second-order rate constants are summarized in Table I; the rate constants for the reaction of **7** are less accurate than the others owing to signal overlap in the spectra. The reactions with KSCN and 18-crown-6 were not as clean as those with thiourea and presented further difficulties arising from the rather limited solubility of the crown ether in CD₃CN. The rate constants obtained with this system are therefore also less accurate than those from the reactions of the corresponding substrates in thiourea-Me₂SO; they are included here because they clearly show the same pattern as that displayed by the latter system, thereby confirming the generality of the main results of this study. Table II gives the percentages of reaction

Table I. Observed Rate Constants in the Reactions of Sulfonium Salts with Nucleophiles

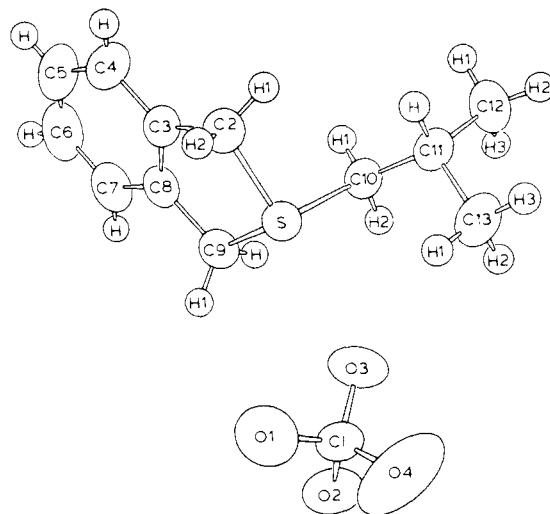
substrate	[substrate], M	[nucleophile], M	<i>T</i> , °C	<i>k</i> ₂ , M ⁻¹ s ⁻¹
(a) Reactions with Thiourea in Dimethyl- <i>d</i> ₆ Sulfoxide				
4b	0.108	0.99	37.0	1.02 × 10 ⁻⁶
4b	0.123	0.99	37.0	1.24 × 10 ⁻⁶
4b	0.087	0.56	110.0	2.32 × 10 ⁻³
4b	0.101	0.49	110.0	2.35 × 10 ⁻³
4c	0.098	0.90	37.0	8.27 × 10 ⁻⁷
4c	0.098	1.03	37.0	8.23 × 10 ⁻⁷
4c	0.123	1.22	37.0	7.72 × 10 ⁻⁷
4c	0.099	0.98	37.0	8.83 × 10 ⁻⁷
4c	0.098	0.83	82.0	1.12 × 10 ⁻⁴
4c	0.104	1.04	82.0	1.15 × 10 ⁻⁴
4c	0.087	0.56	110.0	1.57 × 10 ⁻³
4c	0.102	0.49	110.0	1.45 × 10 ⁻³
4c	0.091	0.32	110.0	1.62 × 10 ⁻³
4c	0.094	0.40	110.0	1.43 × 10 ⁻³
4c	0.098	0.17	110.0	1.33 × 10 ⁻³
4c	0.099	0.24	110.0	1.50 × 10 ⁻³
5b	0.058	0.31	36.5	2.15 × 10 ⁻³
5b	0.060	0.30	37.0	2.19 × 10 ⁻³
5b	0.058	0.31	47.8	6.51 × 10 ⁻³
5b	0.059	0.25	57.1	1.55 × 10 ⁻²
5b	0.064	0.27	57.3	1.55 × 10 ⁻²
6b	0.105	1.01	37.0	2.78 × 10 ⁻⁷
6b	0.132	0.76	37.0	2.71 × 10 ⁻⁷
7	0.097	0.81	82.3	1.1 × 10 ⁻³
7	0.094	0.82	83.0	1.6 × 10 ⁻³
(b) Reactions with KSCN in CD ₃ CN Saturated (~0.14 M) with 18-Crown-6				
4a	0.12	0.12	37.0	4.9 × 10 ⁻⁶
4a	0.11	0.11	37.0	6.4 × 10 ⁻⁶
4a	0.10	0.10	59.0	1.6 × 10 ⁻⁴
4a	0.12	0.13	59.0	1.0 × 10 ⁻⁴
5a	0.12	0.12	37.0	9.5 × 10 ⁻³
5a	0.18	0.19	37.0	6.1 × 10 ⁻³
5a	0.10	0.10	37.0	7.6 × 10 ⁻³
5a	0.09	0.09	37.0	8.1 × 10 ⁻³
5a	0.09	0.09	37.0	6.8 × 10 ⁻³
6a	0.11	0.12	59.0	2.5 × 10 ⁻⁵

at the benzylic center, as determined by NMR integration, and also the derived rate constants for reaction at the benzylic and alkyl positions; Table III shows the activation parameters derived from these rate constants for **4b**, **4c**, and **5b**.

Table II. Percentages of Benzylic Attack and Derived Rate Constants for the Reaction of Sulfonium Salts with Nucleophiles

substrate	<i>T</i> , °C	benzylic attack, ^a %	rate constants M ⁻¹ s ⁻¹ ^b		
			<i>k</i> ₂	<i>k</i> _b	<i>k</i> _r
(a) Reactions with Thiourea in Dimethyl- <i>d</i> ₆ Sulfoxide					
4b	37.0	24	1.13 × 10 ⁻⁶	1.36 × 10 ⁻⁷	8.59 × 10 ⁻⁷
4b	82.0	(25) ^c	(1.78 × 10 ⁻⁴)	2.23 × 10 ⁻⁵	1.33 × 10 ⁻⁴) ^d
4b	110.0	25	2.34 × 10 ⁻³	2.95 × 10 ⁻⁴	1.75 × 10 ⁻³
4c	37.0	92	8.26 × 10 ⁻⁷	3.80 × 10 ⁻⁷	6.6 × 10 ⁻⁸
4c	82.0	90	1.14 × 10 ⁻⁴	5.13 × 10 ⁻⁵	1.1 × 10 ⁻⁵
4c	110.0	85	1.48 × 10 ⁻³	6.30 × 10 ⁻⁴	2.2 × 10 ⁻⁴
5b	36.5	(100)	2.15 × 10 ⁻³	1.08 × 10 ⁻³	
5b	37.0	(100)	2.19 × 10 ⁻³	1.10 × 10 ⁻³	
5b	47.8	(100)	6.51 × 10 ⁻³	3.26 × 10 ⁻³	
5b	57.1	(100)	1.55 × 10 ⁻²	7.75 × 10 ⁻³	
5b	57.3	(100)	1.55 × 10 ⁻²	7.75 × 10 ⁻³	
5b	82.0	(100)	(1.25 × 10 ⁻¹)	6.25 × 10 ⁻²) ^d	
6b	37.0	(0)	2.75 × 10 ⁻⁷		9.2 × 10 ⁻⁸
7	82.3	94	1.1 × 10 ⁻³	1.0 × 10 ⁻³	6 × 10 ⁻⁵
7	83.0	95	1.6 × 10 ⁻³	1.5 × 10 ⁻³	8 × 10 ⁻⁵
(b) Reactions with KSCN in CD ₃ CN Saturated with 18-Crown-6					
4a	37.0	19	5.7 × 10 ⁻⁶	5 × 10 ⁻⁷	4.6 × 10 ⁻⁶
4a	59.0	18	1.3 × 10 ⁻⁴	1 × 10 ⁻⁵	1.1 × 10 ⁻⁴
5a	37.0	(100)	7.6 × 10 ⁻³	3.8 × 10 ⁻³	
6a	59.0	(0)	2.5 × 10 ⁻⁵		0.8 × 10 ⁻⁵

^a Average value of those obtained by NMR integration at the end of each kinetic run. ^b *k*₂ is the measured second-order rate constant (see Table I, mean value of multiple determinations at one temperature); *k*_b and *k*_r are statistically corrected rate constants for attack at the benzylic and alkyl (ethyl or isobutyl) positions, respectively. ^c By interpolation. ^d Estimated from the activation parameters.

**Figure 2.** Structure of 2-isobutyl-1,3-dihydrobenzo[*c*]thiophenium perchlorate (**4c**) showing the numbering scheme.

It is immediately evident from these results that the constrained substrates, **4** and **7**, react at the benzylic center much more slowly than the unconstrained model (**5**), i.e., that the coplanar reaction is much slower than orthogonal benzylic substitution. The *S*-ethylthiophenium salts (**4a** and **4b**), for example, react 8 × 10⁻³ times more slowly than the corresponding models (**5a** and **5b**) with either potassium thiocyanate-18-crown-6 in acetonitrile or thiourea in Me₂SO (at 37 °C).

Structure Description. The crystals of **4c** are built up from discrete cations and anions, since the shortest nonbonded contact between cations is 2.39 (5) Å between H2C2 and H1C12, whereas between cations and anions values of 2.41 (3) between O4 and H2C9 and 2.61 (3) Å between O3 and H2C10 are observed. An illustration showing the atom numbering scheme is given in Figure 2, while a stereoview of the salt is presented as Figure 3; in each, atoms are drawn as 50% probability thermal ellipsoids. A selection of bond distances and bond angles is given in Table IV.

The perchlorate anion was well-behaved during the refinement, and the final geometry is unexceptionable, with bond distances ranging from 1.396 (4) to 1.423 (2) Å and bond angles from 107.7 (2) to 112.3 (2)°. The geometry of the cation has been determined with an entirely satisfactory degree of accuracy, and the dimen-

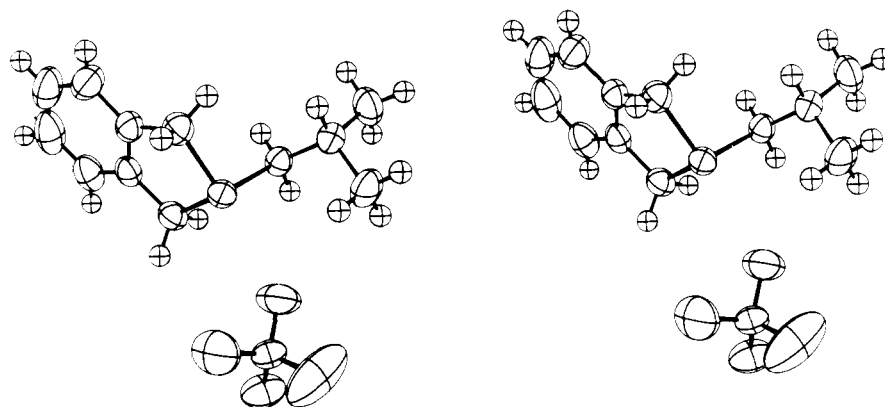


Figure 3. Stereoview of 2-isobutyl-1,3-dihydrobenzo[*c*]thiophenium perchlorate (**4c**).

Table III. Activation Parameters^a for the Reactions of Sulfonium Perchlorates with Thiourea in Dimethyl-*d*₆ Sulfoxide

substrate	ΔH_2^\ddagger	ΔS_2^\ddagger	ΔH_6^\ddagger	ΔS_6^\ddagger	ΔH_r^\ddagger	ΔS_r^\ddagger
4b	24.0	-8.4	24.2	-12.1	24.0	-9.1
4c	23.5	-10.6	23.3	-12.9	25.4	-9.7
5b	18.9	-9.8	18.9	-11.3		

^a Obtained from a least-squares fit of $\ln(k/T)$ vs. $1/T$. ΔS^\ddagger values refer to 37 °C. ΔH^\ddagger values are in kcal mol⁻¹; ΔS^\ddagger , in cal mol⁻¹ K⁻¹. Subscripts are those of the corresponding rate constants (Table 11) used to obtain these parameters.

sions so obtained are consistent, both within the molecule itself and with other studies in the literature. Moreover, all 17 H atoms were located, and refined with isotropic Debye parameters. The C-H bond lengths varied from 0.89 (4) to 1.05 (4) Å; angles involving H atoms at sp²-hybridized C atoms varied from 119 (2) to 122 (2)° and at sp³-hybridized atoms not included in the five-membered ring from 105 (1) to 115 (3)°.

The structural chemistry of sulfonium salts was reviewed in 1981 by Perozzi and Paul in a detailed article.¹³ In each analysis, where S is bonded to three C atoms, it adopts a trigonal-pyramidal geometry as observed in the present study. In comparison with the structures in the review¹³ the geometry observed in the present study is notable for two reasons, the small C2-S-C9 angle of 95.7 (1)°, the smallest found, and the distance of the S atom from the plane formed by the three bonded C atoms, 0.85 Å, the largest seen. Both of these may be attributed to constraints resulting from inclusion of the S atom in a five-membered ring. Perozzi and Paul also presented Newman projections showing the torsion angles in several of the structures reviewed. Data for **4c**, where the sulfur atom is part of a five-membered ring, are given in Table SI.⁴⁸ The isopropyl group on C10 is almost exactly anti (178°) to C9, whereas the C10-C11 bond is almost orthogonal (87°) to the C2-S bond.

The closest approach of the sulfonium center to the perchlorate anion is S...O3 at 3.080 (3) Å. Given the generally accepted van der Waals radii for S and O of 1.75 and 1.40 Å, respectively, this distance may be taken¹³ to indicate a significant interaction, though weaker, perhaps, than that of 3.006 (3) Å observed in an aminosulfonium salt. However, the three X-S-O3 bond angles involving X = C2, C9 and C10 respectively are 171.7 (1), 76.1 (1), and 80.0 (1)°, which would indicate no directional preference for a strong, interionic, electrostatic interaction.

From the viewpoint of the mechanistic study the most important feature of the structure is given by the weighted least-squares planes (presented in full in Table SII). The plane formed by C2, C9, S is at an angle of 3.8° to plane of the arene fragment;¹⁴ the C-S⁺ bond is thus close to coplanarity with the benzene ring,

(13) Perozzi, E. F.; Paul, I. C. In "The Chemistry of the Sulphonium Group"; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; pp 15-77.

(14) Note that C2 and C9 are not quite coplanar with the aromatic ring, but, with reference to Figure 3, are slightly in front of the ring while the sulfur atom is slightly behind. The C2, C3, C8, C9 plane, makes a 2.5° angle with the aromatic ring and hence a 6.3° angle with C9, S, C2 plane.

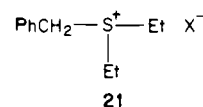
thereby making **4c** an appropriate substrate for displaying the effect of a minimal contribution from the orbital-overlap factor.

A second feature is the clear indication of strain in the five-membered ring, shown not only by the small C2-S-C9 angle mentioned above but also by the similarly contracted other internal angles of the five-membered ring. Cleavage of one of the ring C-S⁺ bonds might be expected to relieve some of this strain and hence show steric acceleration. This has been demonstrated¹⁵ in reactions of simple saturated five-membered cyclic sulfonium salts; making the reasonable assumption that the methyl transfer has much the same rate whether a five- or six-membered heterocycle is the leaving group, we may estimate from the results of Eliel et al.^{15a} that such ring strain generates an acceleration of about 25-30 times.

Finally, we note that except for a short distance between the sulfur and H1C13 atoms (2.77 (4) Å), all pairs of atoms not bonded to each other or to the same atom are separated by distances close to or greater than the sum of the van der Waals radii. The short H...S separation may influence the reactivity of **4c**, as noted below.

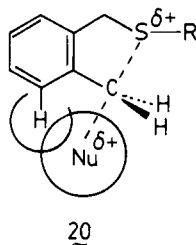
The Need for the Orbital-Overlap Factor. It is clear that the greater rate of reaction at the benzylic center in **5** vs. that in **4** and **7** is nicely consistent with the incursion of an orbital-overlap factor displaying the expected dependence on the dihedral angle, θ . This stereoelectronic effect, however, is not the only conceivable influence determining the rates of these reactions—the possible nonbonding repulsion between the attacking nucleophile and the ortho hydrogen shown in **20**, for example, is obviously another—and, accordingly, a more detailed analysis of our results is required.

To this end the following rate factors are defined with respect to the rate of the same reaction of the corresponding *ethyl* group (cf. ref 3), specifically, the reaction at one of the ethyl groups in **21**: (a) a dihedral angle dependent "orbital-overlap" factor,



symbolized as f_θ and defined as the rate difference (acceleration) that may be assigned to orbital-bond overlap that is observed between the reaction of a benzylic substrate and that of the ethyl group in **21**; (b) a "nonbonding repulsion factor", f_{nb} , arising from the interaction of the attacking nucleophile with the hydrogen ortho to the methylene group undergoing coplanar attack, as illustrated in **20**; (c) a "ring-strain factor", f_r , the effect of differences in ring strain between starting material and the transition state when one of the ring C-S⁺ bonds in a cyclic substrate is being broken (as mentioned above the occurrence of ring-strain acceleration has been clearly demonstrated¹⁵ in simple analogues of **4** and is to be expected in the reaction of **4** itself from the

(15) (a) Eliel, E. L.; Hutchins, R. O.; Mebane, R.; Willer, R. L. *J. Org. Chem.* **1976**, *41*, 1052-1057. See also: (b) Garst, M. E.; McBride, B. J. *J. Org. Chem.* **1983**, *48*, 1362-1366.



evidence for ring strain provided by the X-ray crystallographically determined structure).

Defining k_b and k_e as rate constants for attack at benzylic and ethyl positions, respectively, and indicating the substrates of reactions by a subscripted structure number, we may write the following:

$$\frac{(k_b)_{5b}}{(k_e)_{21}} = (f_\theta)_{5b}(f_{nb})_{5b} \quad (1)$$

$$\frac{(k_b)_{4b}}{(k_e)_{21}} = (f_\theta)_{4b}(f_{nb})_{4b}(f_r)_{4b}$$

and so

$$\frac{(f_\theta)_{5b}(f_{nb})_{5b}}{(f_\theta)_{4b}(f_{nb})_{4b}(f_r)_{4b}} = \frac{(k_b)_{5b}}{(k_b)_{4b}} = \frac{1.10 \times 10^{-3}}{1.36 \times 10^{-7}} = 8.1 \times 10^3 \quad (2)$$

It is evident from this that if we were to try to account for the much faster benzylic substitution in **5** over **4** without invoking orbital overlap, it would have to be on the basis of a high value of $(f_{nb})_{5b}/(f_{nb})_{4b}(f_r)_{4b}$, but careful examination of molecular models provides no indication of this. Specifically, the nonbonding interactions in the ordinary benzylic reaction of **5** are not evidently much different from those in the corresponding ethyl transfer, and hence $(f_{nb})_{5b}$ cannot be much different from one. If, for the transition states, we assign (a) a C...S^{δ+} bond length of 2.2–2.3 Å, corresponding to a 20–30% bond extension in the transition state,¹⁶ and (b) a preferred C–C...S^{δ+} angle of 90°, and at the same time distort the angles in the five-membered ring to roughly the same extent that they are in the starting material, we obtain a transition state for the benzylic reaction of **4b** with $\theta \approx 30^\circ$ and a puckered five-membered ring in which the eclipsing interactions present in **4** itself are removed; with this model the internuclear separation of the attacking sulfur and the ortho hydrogen is only slightly smaller than that in the corresponding ethyl transfer. By further small distortion of the model (such that one might reasonably imagine that the sum of the torsional and ring strains in the transition state is about the same as that in **4**, and hence $f_r \approx 1$), the S...H internuclear distance can be increased to the same as that estimated for the ethyl reaction. Even though these models only roughly approximate the actual transition states from **4**, **5**, and **6**, they clearly show that there is no basis for assigning more than a part (and probable a small part at that) of the factor of 8×10^3 to the ratio $(f_{nb})_{5b}/(f_{nb})_{4b}(f_r)_{4b}$ and hence that there must be a dihedral angle dependent factor leading to the high reactivity of **5** relative to **4**. We conclude that the orbital-overlap factor is fully concordant not only with the original results it was invoked to explain but also the much more stringent test reported here.¹⁷

In this context we note a recent report by Garst and McBride^{15b} on related reactions of allylic analogues of **4b** and **7** in which it is reported that nucleophilic displacement with ring opening takes place readily (using an enolate anion) with the six-membered unsaturated sulfonium ion whereas the reaction of the five-membered analogue (2,5-dihydrothiophenium fluoroborate) gives only the product of ring opening by an elimination process. With this five-membered cyclic species the lack of nucleophilic sub-

stitution cannot be ascribed to nonbonding repulsions but is in full accord with an orbital overlap picture common to benzylic and allylic nucleophilic substitutions.

The Magnitude of the Orbital-Overlap Factor. To determine the magnitude of $(f_\theta)_{5b}$ we define another factor, f_i , to deal with the small corrections required when the leaving group is not a benzylic ethyl sulfide. The rates of ethyl transfer from **4b** and **6b** (Table II) are in the ratio 10:1, indicating a rate increase of about 3 as each ethyl group is replaced by a benzylic substituent; on this basis we assign $(f_i)_{4b} \approx 3$ and $(f_i)_{6b} \approx 0.3$. Taking $(k_e)_{4b}/(k_e)_{21} = (f_i)_{4b}$ and $(k_e)_{6b}/(k_e)_{21} = (f_i)_{6b}$ with eq 1 and the rate constants in Table II, we obtain

$$\frac{(f_\theta)_{5b}(f_{nb})_{5b}}{(f_i)_{4b}} = \frac{(k_b)_{5b}}{(k_e)_{4b}} = 1.3 \times 10^3$$

and so

$$(f_\theta)_{5b} = \frac{1.3 \times 10^3}{(f_{nb})_{5b}} (f_i)_{4b}$$

$$(f_\theta)_{5b} = \frac{1.2 \times 10^4}{(f_{nb})_{5b}} (f_i)_{6b}$$

Since, as noted above, models show no indication of significant differences in nonbonding interaction energies in benzyl and ethyl transfers, we assign $(f_{nb})_{5b} \approx 1$, and with the f_i values above, obtain, from each of these expressions, $(f_\theta)_{5b} \approx 4 \times 10^3$ for the reaction of sulfonium salts with thiourea in Me₂SO at 37 °C. In the same way we find a rough value of $(f_\theta)_{5b} \approx 10^3$ at 82 °C from the rate constants for **5b** and **7** in this system and, in addition, from the rates of reaction of **4a** and **5a**, $(f_\theta)_{5a} \approx 3 \times 10^3$ for the reaction of potassium thiocyanate–18-crown-6 in CD₃CN at 37 °C.

On examining the rate data for the isobutyl salt (**4c**), we note that k_b for **4c** is 2.8 times that for **4b** and also that the rate of ethyl transfer from **4b** is only about 13 times that of isobutyl transfer from **4c** rather than the more usual factors³ of around 30. These observations are consistently accounted for by assuming that there is a small amount of steric strain in **4c** which is relieved during cleavage of one of the C–S⁺ bonds. As has been noted above, **4c** shows a short H...S distance (conveniently described as a gauche CH₃...S interaction), and it is conceivable that this is somewhat relieved in the transition state for nucleophilic attack.¹⁸ Using $(k_b)_{4c}$, $(k_b)_{5b}$, and $(k_e)_{4b}$ from Table II and incorporating a strain release factor of roughly 3 for the C–S⁺ cleavage reactions of **4c**, we arrive at $(f_\theta)_{5b} \approx 4 \times 10^3$, the same value as that already found above.²⁰

The factor f_θ , which presumably achieves its maximal value in the reactions of simple benzyl derivatives such as **5**, may also be described in terms of a difference in free energy of activation, $\Delta\Delta G^\ddagger_\theta$, of about 5 kcal mol⁻¹. By way of comparison, we note that the difference in heats of hydrogenation of ethylene and styrene (to ethylbenzene), which may be taken as a measure of the analogous (i.e., cross conjugative) π -overlap energy in styrene,

(18) Specifically, by attack (a) C10 (X-ray numbering) extending the C10–S bond or (b) at C2 with a small accompanying contraction of the C9–SC–10 angle, with, in each case, concomitant increase in the H1C13...S separation.

(19) Laur, P. H. "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 3; p 100.

(20) We also note another (probably minor) factor, the polar effect of the aryl substituent in benzylic substitution, f_{pb} , which may arise from the somewhat greater electron-withdrawing power of phenyl vs. methyl groups and which is expected to be independent of the dihedral angle, θ . If we accept Young and Jencks' assignment²¹ of the rate difference between benzyl and *p*-nitrobenzyl halides as due to a polar effect, we may estimate from known²² k and σ^* values that the rate of attack of PhNH₂ on PhCH₂Cl is influenced by polar effects enough to slow the reaction of PhCH₂Cl relative to that of CH₃CH₂Cl by a factor of ~0.4. Since f_{pb} would appear in the denominator of eq 1, a factor of ~0.4 for f_{pb} in the sulfonium salt–thiourea reaction would increase the estimated value of f_θ accordingly.

(21) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288–3294.

(22) Ballistreri, F. P.; Maccarone, E.; Mamo, A. J. *Org. Chem.* **1976**, *41*, 3364–3367. Perrin, D. D.; Dempsey, B.; Serjeant, E. P. "pK_a Prediction for Organic Acids and Bases"; Chapman and Hall: London, 1981; pp 119 and 121.

(16) (a) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *Can. J. Chem.* **1982**, *60*, 1291–1294. See also: (b) DeTar, D. F.; McMullen, D. F.; Luthra, N. P. *J. Am. Chem. Soc.* **1978**, *100*, 2484–2493 and references cited.

(17) Our demonstration of a rate factor dependent on the dihedral angle, θ , does not in itself establish that π -overlap is the basis of the factor. Wolfe et al.,^{16a} for example, point to the possibility of an additional θ -dependent mode of p orbital interaction.

Table IV

atom	atom	distance ^a	atom	atom	distance ^a	atom	atom	distance			
Bond Distances											
C1	O1	1.404 (4)	C4	C5	1.375 (6)	C10	H1C10	0.94 (3)			
C1	O2	1.423 (2)	C4	HC4	0.90 (3)	C10	H1C10	0.94 (3)			
C1	O3	1.419 (2)	C5	C6	1.378 (6)	C10	H2C10	0.98 (4)			
C1	O4	1.396 (4)	C5	HC5	0.89 (4)	C11	C12	1.519 (4)			
S	C2	1.815 (3)	C6	C7	1.377 (5)	C11	C13	1.517 (4)			
S	C9	1.813 (3)	C6	HC6	1.00 (4)	C11	HC11	0.99 (3)			
S	C10	1.813 (2)	C7	C8	1.383 (4)	C12	H1C12	1.01 (4)			
C2	C3	1.506 (4)	C7	HC7	1.03 (4)	C12	H2C12	0.96 (4)			
C2	H1C2	0.96 (3)	C8	C9	1.500 (4)	C12	H3C12	1.00 (4)			
C2	H2C2	1.05 (4)	C9	H1C9	1.01 (3)	C13	H1C13	0.99 (4)			
C3	C4	1.385 (4)	C9	H2C9	0.98 (3)	C13	H2C13	0.99 (5)			
C3	C8	1.377 (4)	C10	C11	1.505 (4)	C13	H3C13	0.93 (4)			
atom	atom	atom	angle ^b	atom	atom	atom	angle	atom	atom	atom	angle
Bond Angles											
O1	C1	O2	111.0 (2)	C4	C5	C6	120.3 (4)	C11	C10	H1C10	113 (2)
O1	C1	O3	108.0 (2)	C4	C5	HC5	119 (3)	C11	C10	H2C10	111 (2)
O1	C1	O4	109.8 (2)	C6	C5	HC5	121 (3)	C11	C10	H2C10	108 (3)
O2	C1	O3	107.7 (2)	C5	C6	C7	120.5 (4)	C10	C11	C12	108.0 (2)
O2	C1	O4	108.0 (2)	C5	C6	HC6	120 (2)	C10	C11	C13	112.1 (3)
O3	C1	O4	112.3 (2)	C7	C6	HC6	120 (2)	C10	C11	HC11	108 (2)
C2	S	C9	95.7 (1)	C6	C7	C8	119.2 (4)	C12	C11	C12	111.4 (3)
C2	S	C10	101.9 (1)	C6	C7	HC7	122 (2)	C12	C11	HC11	106 (2)
C9	S	C10	101.8 (1)	C8	C7	HC7	119 (2)	C13	C11	HC11	110 (2)
S	C2	C3	106.0 (2)	C3	C8	C7	120.4 (3)	C11	C12	H1C12	110 (2)
S	C2	H1C2	104 (2)	C3	C8	C9	116.1 (2)	C11	C12	H2C12	112 (2)
S	C2	H2C2	103 (2)	C7	C8	C9	123.5 (3)	C11	C12	H3C12	106 (2)
C3	C2	H1C2	116 (2)	S	C9	C8	106.1 (2)	H1C12	C12	H2C12	106 (3)
C3	C2	H2C2	113 (2)	S	C9	H1C9	104 (2)	H1C12	C12	H3C12	109 (3)
H1C2	C2	H2C2	113 (3)	S	C9	H2C9	104 (2)	H2C12	C12	H3C12	115 (3)
C2	C3	C4	124.2 (3)	C8	C9	H1C9	118 (2)	C11	C13	H1C13	108 (2)
C2	C3	C8	115.7 (2)	C8	C9	H2C9	116 (2)	C11	C13	H2C13	112 (3)
C4	C3	C8	120.1 (3)	H1C9	C9	H2C9	108 (3)	C11	C13	H3C13	109 (2)
C3	C4	C5	119.5 (4)	S	C10	C11	111.9 (2)	H1C13	C13	H2C13	108 (3)
C3	C4	HC4	119 (2)	S	C10	H1C10	107 (2)	H1C13	C13	H3C13	107 (3)
C5	C4	HC4	121 (2)	S	C10	H2C10	105 (2)	H2C13	C13	H3C13	112 (3)

^a In angstroms. ^b In degrees. Numbers in parentheses are estimated standard deviations in the least significant digits.

is 4.2 kcal mol⁻¹.²³ It should be noted that $\Delta\Delta G^\ddagger_\theta$, in itself, does not give a direct measure of the effect of the orbital overlap in the transition state for the reaction of **5** but rather reflects the difference in overlap energy between the transition state and starting material. In light of the evidence of π -overlap in allylic halides, alcohols, and ethers (the "generalized anomeric effect"²⁴) such an effect may well be present in **5** (in the ground state), and hence the overlap energy in the transition state from **5** may amount to rather more than 5 kcal mol⁻¹.

A further question is how much orbital overlap is there in the reactions of the constrained compounds, **4** and **7**? Although we cannot fully answer the question, the following argument indicates that $(f_\theta)_7$ must be >50 while $(f_\theta)_4$ is probably small (perhaps ~1-10).

The product ratio from the reaction of **7** (at 82.3 °C; see Table II) enables us to write

$$(f_\theta)_7(f_{nb})_7(f_r)_7(f_i)_7 = \frac{(k_b)_7}{(k_c)_7} = 16$$

Taking $(f_i)_7 \approx 0.3$ (leaving group less reactive than a benzylic ethyl sulfide, as discussed above) we get

$$(f_\theta)_7(f_{nb})_7(f_r)_7 \approx 50 \quad (3)$$

From the fact that we observe some of the deethylation products but no sign of any of the material that would arise from ring cleavage by attack at C3, we infer that there is ring strain in the transition state inhibiting ring opening in **7** and hence that $(f_r)_7$

< 1. As mentioned in the previous section, any nonbonding interactions will slow the reaction, hence $f_{nb} \leq 1$, and it thus follows from eq 3 that $(f_\theta)_7 > 50$, i.e., that there is at least some orbital overlap in the transition state from **7**.

Returning to eq 2 and taking $(f_\theta)_{5b} \approx 4 \times 10^3$ and $(f_{nb})_{5b} \approx 1$, as above, we obtain

$$(f_\theta)_{4b}(f_{nb})_{4b}(f_r)_{4b} \approx \frac{4 \times 10^3}{8 \times 10^3} \approx 0.5 \quad (4)$$

The 100-fold smaller value of the $f_\theta f_{nb} f_r$ product in eq 4 relative to that in eq 3 is obviously fully consistent with $(f_\theta)_{4b} \ll (f_\theta)_7$, as one would expect from the greater steric constraints imposed by the five-membered ring system. Since there is no apparent way in which f_θ can be <1, we assign $(f_\theta)_{4b} \geq 1$, and hence $(f_{nb})_{4b}(f_r)_{4b} \leq 0.5$. A simple and consistent picture for the reaction of **4b** that emerges from these points and those already raised in the preceding section is one in which the combination of the nonbonding and ring-strain effects results in only a rather small reduction in rate relative to that ethyl transfer from **21** and in which the overlap factor, $(f_\theta)_{4b}$, is comparatively small, say, between 1 and 10. It must be noted, however, that our observations do not exclude the possibility that the transition states in the reactions of **4** and **7** have extensive orbital overlap in highly distorted, highly strained geometries in which large values of f_θ are compensated by a very small $f_r f_{nb}$ product. Our inspection of molecular models, however, suggests that the contortion required to make such strained species would require more energy than can be provided by the approximately 5 kcal mol⁻¹ (see above) resulting from maximal overlap, but a rigorous exclusion of this possibility would require more accurate tools for assessing these factors than are available to us at present.

General Reactivity and Synthetic Consequences. As has already been pointed out, one obvious result from the present study is that the S_N2 reactivity of a benzylic center can, with sufficient con-

(23) Mortimer, C. T. "Reaction Heats and Bond Strengths"; Pergamon Press: London, 1962; p 55.

(24) (a) Kirby, A. J. "The Anomeric Effect and Related Stereoelectronic Effects at Oxygen"; Springer-Verlag: West Berlin, 1983; pp 20 ff. (b) Lessard, J.; Tan, P. V. T.; Martino, R.; Saunders, J. K. *Can. J. Chem.* **1977**, *55*, 1015-1023. (c) Brown, R. S.; Marcinko, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 5721-5727.

straint, be reduced by a factor of almost 10^4 , i.e., to rather less than that of an ethyl group. Such a substantial rate difference may be expected to lead to qualitatively different behavior between constrained and unconstrained systems, and, in fact may already have been seen in the aqueous chlorination of 1,3-dihydrobenzo[*c*]thiophene (**8**) to form (2-formylphenyl)methanesulfonyl chloride (**22**).²⁵ With unconstrained benzyl sulfides in aqueous acetic acid the usual product, in addition to the sulfonyl chloride, is benzyl chloride and not benzaldehyde.²⁶ The different oxidation levels in the products are readily explained in the present context by simply noting that the presumed chlorosulfonium ion intermediate from unconstrained starting material ($\text{PhCH}_2\text{S}^+\text{ClR}$) is readily cleaved to PhCH_2Cl and RSCl (which then gives RSO_2Cl), whereas the lack of orbital overlap in the transition state from **4** ($\text{R}, \text{X} = \text{Cl}$) (for either $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}1$ opening) should slow the $\text{C}-\text{S}^+$ bond cleavage, thereby permitting an alternative "thionium" ($>\text{C}=\text{S}^+-\text{R}$) ion to α -hydroxy sulfide sequence²⁷ ultimately leading to the aldehyde sulfonyl chloride **22**.

Though the consequences of orbital overlap (or its absence) in ring cleavage are not trivial, the effect may well prove of greater practical synthetic significance in the microscopic reverse process, i.e., cyclization reactions. For example, a cyclization to a five- or six-membered ring involving displacement at a benzylic center may well prove more troublesome than expected owing to competing polymer formation, since the full value of f_{θ} in the latter process may be sufficient to counterbalance the usual entropic assistance of the formation of five- and six-membered rings (particularly if the product of the f_{nb} , f_{r} , and f_{θ} factors in the cyclization is $\ll 1$).

Normality of the Activation Parameters. From Table III we note that the rate differences between the cyclic and unconstrained sulfonium salts appear mostly as differences in the enthalpies of activation, while the entropies of activation are very similar ($-12 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$) and in the usual range for $\text{S}_{\text{N}}2$ reactions.²⁸ This observation would be unremarkable had not Bartlett and Trachtenberg's classic study⁵ yielded very different ΔS^{\ddagger} values for the constrained and unconstrained reactions (specifically, $+25.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ for the reaction of iodide in acetone with 5,7-dinitrocoumarone and $-30.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ for that of their open-chain model). Though our chemical system is not the same as theirs, the difference between the two sets of results, especially when taken with the high positive entropy of activation reported for the dinitrocoumarone reaction, leads us to wonder if they have correctly identified the reaction that they followed. It would seem not unlikely that the true $\text{S}_{\text{N}}2$ reaction of the dinitrocoumarone with iodide ion may be too slow to compete with another, unknown process with quite different activation parameters (possibly one with an initial electron transfer from iodide to the aromatic ring), but Bartlett and Trachtenberg report no experimental information about the products of their reactions, and further speculation at this stage is unwarranted. We would note, however, that though our results may cast doubt on the validity of the activation parameters for the dinitrocoumarone reaction (and hence on any conclusions specifically dependent on them), they do not affect the basic point that the constrained system was found to react more slowly than the unconstrained and hence that the $\text{S}_{\text{N}}2$ reaction α to a carbonyl probably has a stereoelectronic requirement.

Experimental Section

General. Instrumentation: IR, Beckman IR 4520 or Perkin-Elmer 621 using 0.1-mm NaCl or KBr cells; ^1H NMR, Varian T-60 or XL-100 with all chemical shifts from the XL-100 except as noted; MS, Varian MAT-311A; mp, Kofler hot stage (uncorrected). Solvents and reagents: when not otherwise described, reagent grade materials without further purification; triethyloxonium tetrafluoroborate, mp 90–93 °C, lit.²⁹ mp

91–92 °C dec; 2-chloroethanesulfonyl chloride,³⁰ bp 40 °C/0.8 torr.

Simpler Substrates and Authentic Specimens. Triethylsulfonium tetrafluoroborate (**6a**), mp 110–110.5 °C, lit.³¹ mp 105.5 °C, ^1H NMR (CD_3CN) δ 3.22 (6 H, q), 1.40 (9 H, t); triethylsulfonium perchlorate (**6b**) (from **6a** as described below for **4a** \rightarrow **4b**), mp 115 °C, lit.³² mp 111.5–112.5 °C, ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 3.32 (6 H, q), 1.35 (9 H, t); 1,3-dihydrobenzo[*c*]thiophene²⁵ (**8**), mp 22–23 °C, lit.³³ mp 22.5–23.5 °C, ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 7.26 (4 H, s), 4.20 (4 H, s); 3,4-dihydro-1*H*-2-benzothiopyran³⁴ (**19**), ^1H NMR (CDCl_3) δ 7.15 (4 H, s), 3.73 (2 H, s), 3.1–2.75 (4 H, sym m centered at 2.93); benzyl ethyl sulfide²⁶ (**13**), bp 84 °C/4.9 torr, ^1H NMR (CD_3CN) δ 7.30 (5 H, s), 3.72 (2 H, s), 2.42 (2 H, q), 1.18 (3 H, t); dibenzyl sulfide, ^1H NMR (CD_3CN) δ 7.30 (5 H, s), 3.62 (2 H, s); ethyl thiocyanate³⁵ (**9**), bp 76 °C/15 torr, ^1H NMR (CD_3CN) δ 3.02 (2 H, q), 1.46 (3 H, t); MS, *m/e* calcd for $\text{C}_3\text{H}_7\text{NS}$ 87.0143, found 87.0141; benzyl thiocyanate (**14**) (from benzyl mesylate³⁶ and NaSCN in MeOH, 3 h at 25 °C) mp 40–42 °C, lit.³⁷ mp 41 °C; ^1H NMR (CD_3CN) δ 7.42 (5 H, s), 4.23 (2 H, s); MS, *m/e* calcd for $\text{C}_8\text{H}_7\text{NS}$ 149.0299, found 149.0298. *S*-Benzylthiouronium perchlorate (**15**) was made from the chloride in aqueous solution (mp 149–150 °C, made from benzyl chloride and thiourea in refluxing absolute EtOH) by addition of saturated NaClO_4 , mp 181.5–182.5 °C (recrystallized from absolute EtOH–ether); IR (KBr disk) 3390 (m), 3330 (m), 3230 (m), 3180 (m), 1650 (s), 1435 (m), 1090 (vs), 710 (m); ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 9.03 (4 H, br s), 7.39 (5 H, s), 4.47 (2 H, s). Anal. Calcd for $\text{C}_8\text{H}_{11}\text{ClN}_2\text{O}_4\text{S}$: C, 36.03; H, 4.16; Cl, 13.29; N, 10.50; S, 12.02. Found: C, 36.18; H, 4.21; Cl, 13.15; N, 10.42; S, 11.89. *S*-Isobutylthiouronium perchlorate (**17**) was obtained from *S*-isobutylthiouronium tosylate (from thiourea and isobutyl tosylate), mp 154–155 °C, lit.³⁸ mp 156–157 °C, by ion exchange (Rexyn 201 (OH) converted to the ClO_4^- form), viscous liquid, ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 8.95 (4 H, br s), 3.06 (2 H, d), 1.86 (1 H, m), 0.99 (6 H, d). *S*-Ethylthiouronium perchlorate (**11**) was obtained as a viscous liquid from the bromide or tosylate³⁸ by ion exchange as described for **4a** \rightarrow **4b**; ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 8.95 (4 H, br s), 3.16 (2 H, q), 1.28 (3 H, t).

2-Ethyl-1,3-dihydrobenzo[*c*]thiophenium Tetrafluoroborate (4a) and Perchlorate (4b). Triethyloxonium tetrafluoroborate (1.7 g, 90 mmol) was added to solution of **8** (1 g, 73 mmol) in dry ethylene chloride (4 mL) and the flask stoppered and shaken on a mechanical shaker at room temperature overnight, whereupon excess solvent was removed under reduced pressure. The grayish solid was recrystallized from absolute EtOH, giving **4a** as white needles, mp 77–78 °C; IR (KBr disk) 1740 (m), 1418 (m), 1294 (m), 1055 (vs), 895 (m), 750 (m) cm^{-1} ; ^1H NMR (CD_3CN) δ 7.47 (4 H, s), 4.99–4.52 (4 H, AB quartet, δ 4.89, 4.62, $J = 16 \text{ Hz}$), 3.14 (2 H, q), 1.35 (3 H, t). Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{BF}_4\text{S}$: C, 47.65; H, 5.20; S, 12.72. Found: C, 47.57; H, 5.39; S, 12.64.

A solution of **4a** (0.58 g, 2.3 mmol) in the minimum amount of methanol was passed down a column of quaternary ammonium ion-exchange resin (Rexyn 203 (OH), Fisher, 10 g, converted to the perchlorate form with 30% perchloric acid) and the resin eluted slowly with further methanol (300 mL). Removal of the MeOH gave **4b** as a white solid (0.59 g, 96%) which recrystallized from absolute EtOH–ether as white needles, mp 90.5–91 °C; IR (KBr disk) 1455 (m), 1408 (m), 1080 (vs), 885 (m), 745 (s), 625 (s) cm^{-1} ; ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 7.56–7.35 (4 H, m), 5.04–4.65 (4 H, AB quartet, δ 4.91, 4.77, $J = 16 \text{ Hz}$), 3.19 (2 H, q), 1.23 (3 H, t). Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_4\text{S}$: C, 45.37; H, 4.95; Cl, 13.39; S, 12.11. Found: C, 45.43; H, 5.08; Cl, 13.35; S, 12.25.

2-(2-Methylpropyl)-1,3-dihydrobenzo[*c*]thiophenium Perchlorate (4c). Isobutyl [2]betylperchlorate was prepared via isobutyl ethenesulfonate (from the alcohol, 2-chloroethanesulfonyl chloride, and Me_2N) to the (dimethylamino)ethanesulfonate ester (with Me_2NH) to the betylate fluorosulfate (with MeSO_2F) to the betylate perchlorate (with NaClO_4) by the general procedure;¹² recrystallization from CH_3CN –ether gave white crystals, mp 141–141.5 °C dec; IR (KBr) 2980 (w), 1480 (m), 1360 (s), 1170 (s), 1080 (vs), 935 (s), 855 (m), 630 (m), 580 (m), 530 (m) cm^{-1} ; ^1H NMR (CD_3CN) δ 4.17 (d, 2 H), 3.78 (s, 4 H), 3.19 (s, 9 H), 2.02 (7, 1 H), 1.00 (d, 6 H). Anal. Calcd for $\text{C}_9\text{H}_{22}\text{ClNO}_7\text{S}$: C, 33.39; H, 6.85; Cl, 10.95; N, 4.33; S, 9.90. Found:

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C, 33.45; H, 6.96; Cl, 10.62; N, 4.54; S, 10.03.

A solution of the betylate (1.82 g, 5.6 mmol) and **8** (3.85 g, 28.1 mmol) in dry acetonitrile (20 mL) was refluxed for 140 h. Upon cooling, the mixture was filtered (to remove the precipitated $\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{SO}_3^-$) and the solvent evaporated. Trituration with dry ether followed by filtration removed the excess **8**, leaving **4c** as a gray solid (0.90 g, 55%); five recrystallizations from absolute ethanol-ether gave the analytical specimen as white crystals, mp 120.5–121 °C; IR (KBr disk) 2980 (m), 1457 (m), 1401 (m), 1080 (vs), 894 (m), 745 (s), 628 (s) cm^{-1} ; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) δ 7.50 (4 H, s), 5.15–4.60 (4 H, AB quartet, δ 4.99, 4.77, $J = 16$ Hz), 3.08 (2 H, d), 2.16 (1 H, m), 1.05 (6 H, d). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{ClO}_4\text{S}$: C, 49.23; H, 5.85; Cl, 12.11; S, 10.95. Found: C, 49.27; H, 6.12; Cl, 12.15; S, 11.14.

S,S-Dibenzyl-S-ethylsulfonium Tetrafluoroborate (5a) and Perchlorate (5b). Dibenzyl sulfide (1.33 g, 6.21 mmol) and triethyloxonium tetrafluoroborate (1.41 g, 7.45 mmol) as in the preparation of **4a** gave **5a** as white needles (from absolute EtOH), mp 94–95 °C; lit.³¹ mp 93.5 °C; IR (KBr disk) 1497 (m), 1460 (m), 1060 (vs), 777 (m), 710 (m), 692 (m), 528 (m); $^1\text{H NMR}$ (CD_3CN) δ 7.46 (10 H, s), 4.52 (4 H, s), 3.15 (2 H, q), 1.25 (3 H, t). The perchlorate (**5b**) was prepared quantitatively from **5a** (as for **4a** \rightarrow **4b**), white crystals from absolute EtOH, mp 108–108.5 °C; lit.³² mp 108.5 °C; IR (KBr) 1498 (m), 1458 (m), 1085 (vs), 777 (m), 710 (s), 692 (s), 628 (s) cm^{-1} ; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) δ 7.45 (10 H, s), 4.74 (4 H, s), 3.26 (2 H, q), 1.19 (3 H, t). Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{ClO}_4\text{S}$: C, 56.05; H, 5.59; Cl, 10.34; S, 9.35. Found: C, 56.12; H, 5.72; Cl, 10.21; S, 9.31.

[2-(Ethylthio)methyl]phenylmethyl Thiocyanate (10) and S-[2-[(Ethylthio)methyl]phenyl]thiuronium Perchlorate (12) and Picrate. [*o*-(Hydroxymethyl)phenyl]methanethiol³⁹ (1 g, 6.5 mmol) was added to a solution of sodium ethoxide in absolute ethanol (from addition of 153 mg of Na metal to the ethanol); ethyl bromide (0.71 g, 6.5 mmol) was dropped in and the mixture let stand for 12 h. Workup gave crude *o*-[(ethylthio)methyl]benzyl alcohol (1.18 g, 100%) as a yellowish oil; IR (neat) 3380 (br, s), 2960 (m), 2920 (m), 2860 (m), 1450 (m), 1265 (m), 1205 (m), 1035 (m), 1000 (s), 765 (s), 730 (s) 615 (m); $^1\text{H NMR}$ (CDCl_3) δ 7.5–7.2 (4 H, m), 4.72 (2 H, s), 3.79 (2 H, s), 3.08 (1 H, br s), 2.44 (2 H, q), 1.21 (3 H, t). Reaction of this thioether-alcohol (0.57 g, 3.1 mmol) with "easy mesyl"³⁶ (1.2 g, 4.5 mmol) and *N,N*-dimethylaminoacetonitrile (20 μL) in dichloromethane (15 mL) and acetonitrile (1.5 mL) gave the mesylate as a dark oil (0.9 g); $^1\text{H NMR}$ (CDCl_3 , T-60) δ 7.3 (4 H, s), 5.4 (2 H, s), 3.8 (2 H, s), 2.9 (3 H, s), 2.5 (2 H, q), 1.3 (3 H, t) (plus solvent signals). The crude mesylate on treatment with NaSCN in methanol at room temperature for 15 min gave the thiocyanate (**10**); recrystallization from ether yielded white crystals, mp 43–45 °C; IR (CHCl_3) 3000 (m), 2970 (m), 2930 (m), 2150 (s), 1450 (m), 1225 (br m), 690 (m), 640 (m); $^1\text{H NMR}$ (CD_3CN) δ 7.35 (4 H, s), 4.41 (2 H, s), 3.85 (2 H, s), 2.47 (2 H, q), 1.21 (3 H, t); MS, *m/e* calcd for $\text{C}_{11}\text{H}_{13}\text{NS}_2$ 223.0489, found 223.0490. Reaction of the crude mesylate with thiourea in ethanol for $1/2$ h at room temperature gave the thiuronium mesylate as a dark oil; ion extraction of a CHCl_3 solution with aqueous NaClO_4 (8 eq) yielded **12** as a yellowish liquid; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) δ 9.1 (4 H, br s), 7.34 (4 H, br "s"), 4.58 (2 H, s), 3.87 (2 H, s), \sim 2.5 (obscured by $\text{Me}_2\text{SO}-d_6$), 1.18 (3 H, t). Ion extraction of **12** with CHCl_3 -aqueous picric acid gave the picrate as yellow crystals (from ethanol), mp 176–177 °C; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) δ 9.1 (4 H, br s), 8.60 (2 H, s), 7.34 (4 H, br s), 4.58 (2 H, s), 3.88 (2 H, s), \sim 2.5 (obscured by $\text{Me}_2\text{SO}-d_6$), 1.18 (3 H, t). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_7\text{S}$: C, 43.49; H, 4.08; N, 14.92; S, 13.66. Found: C, 43.61; H, 4.13; N, 14.80; S, 13.59.

S-[2-[(2-Methylpropylthio)methyl]phenyl]methylthiuronium Perchlorate (16) and Picrate. A mixture of [*o*-(hydroxymethyl)phenyl]methanethiol³⁹ (1 g, 6.5 mmol), sodium methoxide (from 0.5 g of Na, 22 mmol), and isobutyl bromide (1.4 mL, 12.9 mmol) in methanol (45 mL) was stirred at room temperature for 48 h; workup gave the crude isobutyl thioether (1.4 g, 100%) which was purified by chromatography on silica gel and distillation in a short-path cold-finger apparatus, yielding a colorless oil; $^1\text{H NMR}$ (CD_3CN) δ 7.5–7.2 (4 H, m), 4.71 (2 H, d), 3.78 (2 H, s), 3.23 (1 H, t), 2.35 (2 H, d), 2.76 (2 H, m, partly obscured by CHD_3CN), 0.93 (6 H, d). The thioether-alcohol was converted via the mesylate to the thiuronium mesylate and then to the amorphous thiuronium perchlorate (**16**) as for **12**, above; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) 9.1 (4 H, br s), 7.5–7.3 (4 H, m), 4.60 (2 H, s), 3.86 (2 H, s), 2.37 (2 H, d), 1.74 (1 H, m), 0.92 (6 H, d); ion exchange to the picrate, as above, gave yellow crystals (from methanol), mp 175–176 °C; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) δ 9.1 (4 H, br s), 7.36 (4 H, br "s"), 4.59 (2 H, s), 3.85 (2 H, s), 2.36 (2 H, d), 1.73 (1 H, m), 0.91 (6 H, d). Anal. Calcd for

$\text{C}_{19}\text{H}_{23}\text{O}_7\text{N}_3\text{S}_2$: C, 45.87; H, 4.66; N, 14.08; S, 12.89. Found: C, 45.63; H, 4.76; N, 14.19; S, 12.71.

2-Ethyl-3,4-dihydro-1H-2-benzothiopyranium Perchlorate (7). A mixture of **19** (0.93 g, 4.9 mmol) and triethyloxonium tetrafluoroborate (1.1 g), as in the conversion **8** \rightarrow **4b**, gave **7** as off-white crystals (0.4 g, 30%), mp 64.5–65.5 °C; IR 2980 (m), 1455 (m), 1415 (m), 1080 (vs), 765 (s), 625 (s); $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) δ 7.44 (4 H, s), 4.58 (2 H, s), 3.9–3.6 (1 H, m), 3.4–2.7 (5 H, m), 1.36 (3 H, t). Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}_4\text{S}$: C, 47.42; H, 5.38; Cl, 12.74; S, 11.49. Found: C, 47.51; H, 5.43; Cl, 12.81; S, 11.38.

Reaction of the Sulfonium Salts with Nucleophiles. The reactions of **4**, **5**, and **6** with thiourea in $\text{Me}_2\text{SO}-d_6$ or KSCN in CD_3CN saturated with 18-crown-6 were monitored by spectrometry, the signals due to the starting material being replaced as the reaction proceeded by those known from authentic spectra to be characteristic of the products. For example, in the reaction of a solution of **4c** (0.09 M) and thiourea-*d*₄ (0.82 M) in $\text{Me}_2\text{SO}-d_6$ at 106.5 °C, the signals (XL-100) due to **4c** (those given above except for a shift of the doublet at δ 3.08 to δ 3.18) rapidly shrank ($t_{1/2}$ 8–10 min) and were replaced by peaks at 7.5–7.2, 4.60, 3.87, 2.42, 1.78, and 0.94 ppm clearly due to **16**, along with smaller peaks (a singlet at 4.21 ppm and doublets at 3.10 and 1.00 ppm, the latter partly obscured) due to **8** and **17** in equal amounts; after 60 min the signals from **4c** had completely disappeared, and further heating at this temperature had no effect; upon raising the temperature to \sim 135 °C, a slow further reaction, characterized by growth of the peak at 4.2 ppm (assigned to **8**) and gradual disappearance of the singlets at 4.6 and 3.86 ppm due to **16** together with signs of more general decomposition, was observed.

A solution of **7** (0.094 M) was prepared by dissolving **7** (13.5 mg) in a preheated (83 °C) solution of thiourea (34 mg, 0.81 M) in $\text{Me}_2\text{SO}-d_6$ (570 mg) and a series of $^1\text{H NMR}$ spectra (XL-100, at 83.0 ± 0.2 °C) started immediately. The signals due to **7** (at 7.44, 4.58, 3.9–3.6, 3.4–2.7, and 1.36 ppm) shrank while those assigned to **18** (7.33, 4.54, \sim 3, 1.21 ppm) and to the small amount of **19** (7.15 and 3.73 ppm) grew ($t_{1/2} \sim 7$ min, essentially complete reaction after 60 min, with the spectrum unchanged after a further 190 min). Extended heating of the reaction product at 110 °C ($t_{1/2} \sim 2$ h) replaced these signals by those of an equimolar mixture of **19** (NMR as above plus the multiplet centered at 2.9 ppm) and **11** (peaks at 3.16 and 1.28 ppm); this spectrum was unaffected by further heating of the mixture at \sim 85 °C for 90 h.

In a control experiment a mixture of dibenzyl sulfide and ethyl thiocyanate was unaffected (T-60 NMR) after standing for 2 h in KSCN and 18-crown-6 in CD_3CN at 25 °C.

Kinetic Measurements. Rates were determined by following the disappearance of starting material as determined by comparing the NMR integral of a (set of) peak(s) characteristic of the substrate with that of both starting material and product(s); e.g., the fraction of unreacted **4c** was obtained from (integral of the AB quartet of **4c**)/[(integral of the AB quartet of **4c**) + 2 (integral of the δ 4.6 singlet of **16**) + (integral of the δ 4.2 singlet of **8**)]. In a typical kinetic run a stock solution of the sulfonium salt (0.10–0.20 M) in CD_3CN or $\text{Me}_2\text{SO}-d_6$ and of the nucleophile (0.10–1.0 M) in the same solvent (in the case of CD_3CN , previously saturated with 18-crown-6) was transferred with a syringe to an NMR tube to make up the required concentrations; the minimum amount of Me_4Si was added and the mixture shaken immediately. With those reactions fast enough to be followed directly in the spectrometer, the NMR tube was then quickly placed in the probe of the T-60 or XL-100 instrument which had been set at the desired temperature. For the slower reactions the NMR tube was placed in ice bath, flame-sealed, and then maintained at the specified temperature in a previously equilibrated constant temperature bath, with the tube being withdrawn and the NMR integrations run at appropriate intervals.

Collection and Reduction and X-ray Data. White crystals of **4c** were obtained by slow recrystallization of **4c** from absolute ethanol. A photographic examination using Weissenberg and precession photography showed that the crystals were monoclinic, and preliminary cell constants were obtained. Systematic absences of $h0l$, $h + l$ odd, and $0k0$, k odd, led to an unambiguous assignment of the space group as $P2_1/n$, equivalent positions $\pm(x,y,z)$ and $\pm(1/2 + x, 1/2 - y, 1/2 + z)$, an alternative setting of $P2_1/c$, No. 14.^{40a} The density was determined by flotation in a mixture of 1,2-dibromoethane and hexane and corresponds to four formula units per cell, requiring no crystallographic site symmetry.

A crystal of equant habit, with approximate dimensions $0.24 \times 0.21 \times 0.20$ mm, was chosen and an orientation matrix determined by using the search and index routines on an Enraf-Nonius CAD4F diffractometer.⁴¹ All measurements were made with Cu $K\alpha$ radiation. ω -Scans

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Table V. Crystal Data and Experimental Conditions

compound	C ₁₂ H ₁₇ ClO ₄ S
formula weight	292.78
temperature	20 °C
unit cell dimensions	$a = 17.382 (1) \text{ \AA}$ $b = 9.1731 (6) \text{ \AA}$ $c = 8.7828 (3) \text{ \AA}$ $\beta = 91.7 (2)^\circ$
cell volume	1399.8 Å ³
Z	4
density (obsd)	1.394 (1) g cm ⁻³
density (calcd)	1.391 g cm ⁻³
space group	<i>P</i> 2 ₁ / <i>n</i>
radiation	Cu Kα, λ = 1.54184 Å
filter	Ni foil, prefilter, 0.015 mm
crystal faces	{100} {001} {101} {110}
crystal volume	7.89 × 10 ⁻³ mm ³
absorption coefficient	38.76 cm ⁻¹
detector aperture (vert)	4 mm
detector aperture (horiz)	4.00 + 0.5 tan θ mm
crystal detector dist	205 mm
scan	θ-2θ, at 1.4-3.4 deg min ⁻¹
scan range	1.00 + 0.14 tan θ
data collected	0 < θ < 76°, 0 ≤ h ≤ 19 -1 ≤ k ≤ 10, -9 ≤ l ≤ 9
standard reflections	10 1 -1, 5 4 1, 0 3 3

of several intense, low-angle reflections with a wide open counter had an average width at base of 0.15°, a satisfactory value.⁴² A summary of the crystal data is given in Table V.

Intensity data were recorded at variable scan speeds so as to optimize counting statistics within a maximum time per datum of 100 s. Background estimations were made by extending the scan by 25% on each side. Standard reflections were monitored every 120 min of X-ray exposure time and showed a 4.3% decrease over the total experimental time of 120 h. A linear decay correction was therefore applied.⁴³

The crystal orientation was checked every 500 observations recorded, but no significant change was observed. A total of 3340 reflections was measured, and these were corrected for background, Lorentz, and polarization effects, and monochromator polarization, by using the SDP package running on a PDP-11/23+ computer.⁴³ Standard deviations were assigned on the basis of counting statistics, and a starting value of 0.04 chosen for *p*.⁴⁴ The 10 crystal faces were identified by optical goniometry and the crystal measured by using a microscope fitted with a filar eyepiece. The data were corrected for absorption by the Gaussian method.⁴⁵ After the equivalent forms (*R* = 0.012 on *F*) were averaged, a total of 2819 unique data with *F* > 0.0 remained. Experimental details are given in Table V.

Structure Solution and Refinement. The structure was solved by direct methods using the program MULTAN,⁴⁶ through which all but one of the 17 non-hydrogen atoms were located. Scattering factors for neutral, non-hydrogen atoms were taken from ref 40b, while those for H were from Stewart et al.⁴⁷ Real and imaginary corrections for anomalous dispersion were included for all nonhydrogen atoms.^{40b} Refinement was by full-matrix least squares on *F*, minimizing the function $\sum w(|F_o - F_c|)^2$, where the weight *w* is given by $4F_o^2/\sigma^2(F_o)$. With all non-hydrogen atoms assigned anisotropic thermal parameters, refinement converged at $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.095$, and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2)^{1/2} = 0.127$.

All 17 hydrogen atoms were readily located in a difference Fourier synthesis and included in the refinements with isotropic thermal parameters. An inspection of *F*_o and *F*_c showed that an extinction parameter should be refined, and two reflections were given zero weights due to asymmetric background. The final cycles of refinement included 232 variables and a *p* value of 0.08, used 2054 independent reflections with *F* > 2σ, and converged at agreement factors of *R*₁ = 0.044 and *R*₂ = 0.066. The largest parameter shift in the final cycle was 0.16 σ, in the *z* coordinate of the methyl H atom H1C13. A final difference Fourier

Table VI. Atomic Positional^a and Thermal^a Parameters

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
C1	2483.7 (4)	5575.1 (7)	215.5 (7)	541 (2)
S	1998.5 (3)	5033.9 (7)	4483.6 (7)	442 (2)
O1	1775 (2)	4883 (4)	434 (4)	1200 (10)
O2	2419 (2)	6647 (3)	-953 (2)	830 (7)
O3	2702 (2)	6299 (4)	1589 (3)	962 (9)
O4	3029 (2)	4550 (3)	-216 (5)	1633 (12)
C2	1484 (2)	4501 (3)	6163 (3)	538 (7)
C3	858 (2)	5619 (3)	6342 (3)	510 (7)
C4	349 (2)	5630 (4)	7526 (4)	725 (9)
C5	-228 (2)	6654 (5)	7536 (4)	900 (11)
C6	-289 (2)	7685 (4)	6398 (5)	892 (11)
C7	220 (2)	7690 (4)	5225 (4)	694 (9)
C8	792 (1)	6643 (3)	5199 (3)	499 (7)
C9	1353 (2)	6509 (3)	3941 (3)	522 (7)
C10	2813 (2)	6017 (3)	5310 (3)	461 (6)
C11	3453 (2)	5006 (3)	5814 (3)	500 (7)
C12	4058 (2)	5902 (4)	6677 (4)	722 (10)
C13	3797 (2)	4205 (4)	4485 (4)	695 (9)
HC4	38 (2)	493 (3)	824 (3)	7.3 (9)
HC5	-57 (2)	662 (4)	828 (4)	12 (1)
HC6	-70 (2)	843 (5)	642 (4)	15 (2)
HC7	20 (2)	847 (4)	438 (4)	11 (1)
H1C2	188 (2)	448 (3)	695 (3)	9 (1)
H2C2	127 (2)	346 (4)	587 (4)	12 (1)
H1C9	114 (2)	621 (4)	290 (4)	11 (1)
H2C9	170 (2)	735 (3)	380 (3)	8 (1)
H1C10	262 (2)	658 (3)	611 (3)	8 (1)
H2C10	298 (2)	667 (4)	450 (4)	11 (1)
HC11	325 (2)	431 (3)	655 (3)	7.4 (9)
H1C12	384 (2)	630 (4)	765 (4)	11 (1)
H2C12	450 (2)	533 (4)	699 (4)	11 (1)
H3C12	418 (2)	673 (4)	600 (4)	12 (1)
H1C13	338 (2)	364 (4)	396 (4)	12 (1)
H2C13	402 (2)	489 (5)	374 (5)	17 (2)
H3C13	416 (2)	354 (4)	486 (4)	14 (1)

^a × 10⁴. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(1/6)\pi^2[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$. Hydrogen atom parameters: position (× 10³) and thermal (× 10²).

synthesis contained 11 peaks ranging from 0.45 (5) to 0.19 (5) e Å⁻³, all of which were in the region of the perchlorate anion. Apparently there is some disorder present; nevertheless it is minor, so no effort was made to include a disorder model. The error in an observation of unit weight is 1.34 e, and an analysis of *R*₂ in terms of the magnitude of *F*_o, λ⁻¹ sin θ, and various combinations of Miller indices showed no unusual trends.

Final positional parameters and *U*(equiv) or *U* thermal parameters are given in Table VI for all atoms. Thermal parameters for those atoms assigned anisotropic parameters (Table S111), root-mean-square amplitudes of vibration (Table S1V), and structure amplitudes (Table SV) have been deposited.⁴⁸

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Registry No. **4a**, 73224-89-2; **4b**, 95675-83-5; **4c**, 95675-85-7; **5a**, 21529-87-3; **5b**, 51616-78-5; **7**, 95675-86-8; **8**, 2471-92-3; **9**, 542-90-5; **10**, 73224-90-5; **11**, 95675-87-9; **12** perchlorate, 95675-89-1; **12** picrate, 95676-00-9; **13**, 6263-62-3; **14**, 3012-37-1; **15**, 95675-90-4; **16** perchlorate, 95675-92-6; **16** picrate, 95676-02-1; **17**, 95675-93-7; **18**, 95675-95-9; **19**, 4426-75-9; Et₃OBF₄, 368-39-8; (PhCH₂)₂S, 538-74-9; HOCH₂-*o*-C₆H₄CH₂SH, 26257-08-9; EtSCH₂-*o*-C₆H₄CH₂OH, 95675-98-2; EtSCH₂-*o*-C₆H₄CH₂OSO₂Me, 95675-99-3; HOCH₂-*o*-C₆H₄CH₂SCH₂CH(CH₃)₂, 95676-01-0; KSCN, 333-20-0; (NH₂)₂C=S, 62-56-6; isobutyl [2]betylate perchlorate, 95675-97-1; easy mesyl, 55791-04-3.

Supplementary Material Available: Tables of torsion angles (Table SI), weighted least-squares planes (Table SII), anisotropic thermal parameters (Table SIII), root-mean-square amplitudes of vibration (Table SIV), and structure amplitudes (Table SV), (17 pages). Ordering information is given on any current masthead page.

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