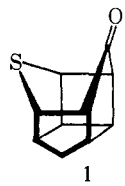
# Analysis of the Stereochemical and Proximity Requirements for $R_2S$-4 Participation in Carbonium Ion Reactions. Solvolysis of Stereoisomeric Caged Thia Alcohol Derivatives

**Leo A. Paquette, George V. Meehan,[1] and Lawrence D. Wise**

*Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.* *Received January 15, 1969*

**Abstract:** The kinetics of acetolysis of the epimeric octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*c,d*]pentalen-7-yl and octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*c,d*][2]benzothiophen-7-yl tosylates have been measured. In buffered acetic acid, the *endo* tosylates solvolyze at a rate comparable to that of *anti*-pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]-decan-6-yl tosylate (**10**) thus indicating that the sulfur atom exerts no neighboring group participation effects. Strikingly, however, the *exo* tosylate in the ethano-bridged series solvolyzes 5564 times faster than **10** and the acetate of retained configuration is produced in quantitative yield. In the case of the *exo*-methano-bridged tosylate, only a 32-fold rate enhancement is observed and product analysis indicates that approximately 20% of the reaction occurs *via* a heterolytic fragmentation. A connection is drawn between the stereochemistry of the leaving group and the internuclear distance between the sulfur atom and the incipient carbonium ion center. The bearing of these results on precise proximity requirements for anchimeric assistance by an heteroatomic neighboring group is discussed. Further consideration is given to the various cations which are produced in these caged systems upon ionization.

Caged keto sulfides **1** and **2** were recently prepared in an initial attempt to evaluate nonbonded interactions of divalent sulfur in a quantitative manner.[2]



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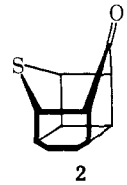

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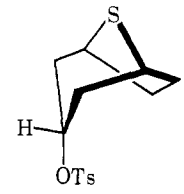
The inflexible boat conformations necessarily adopted by the six-membered heterocyclic rings in **1** and **2** were seen to permit reasonably accurate assessment of S–$C_{CO}$ interactions in these structures. On a comparative basis, the lesser interatomic distance between the sulfur atom and carbonyl group in **2** relative to **1**[3] resulted in more effective interaction of the sulfur orbitals with the $\pi$ orbitals of the ketone function. These data suggested that substantial quantitative information concerning the stereochemical and proximity requirements for divalent sulfur participation in carbonium ion reactions could be gained by an examination of the solvolysis of the epimeric tosylates derivable from **1** and **2**.

Additionally, any neighboring group assistance which sulfur might convey to the developing electron-deficient center in these caged systems must be of the $R_2S$-4 variety.[4] Although comparative kinetic information on the relative ease of sulfide groups to undergo ring closure by intramolecular nucleophilic substitution is limited, examples of $R_2S$-4 participation are even more conspicuous by their scarcity.[5,6] In perhaps the most pertinent study bearing on this point, Ireland and Smith[6d] found that the rates of solvolysis of **3** and **4** in aqueous ethanol were slower ($k_{rel}^{77°}$ = 0.46 and 0.21, respectively) than the rate for *trans*-4-*t*-butyl-



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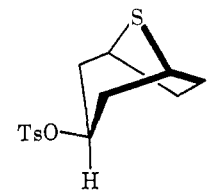

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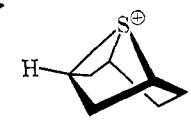

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cyclohexyl tosylate ($k_{rel}^{77°}$ = 1.00). These workers concluded that direct participation by sulfur was not operative during the rate-determining step since facilitation of ionization was not encountered. On the other hand, the clean stereospecificity of these solvolyses (only *endo* alcohol from either tosylate) was interpreted to mean that sulfonium ion **5** probably intervened after ionization had taken place. These results, although interesting, are obviously nonrepresentative of sulfur's capability for electronic interaction because of the conformational mobility available to both **3** and **4** and the expected heavy bias away from the strained boat conformation needed for participation. Within this frame of reference, therefore, the present study was undertaken.

## Results

The *endo* alcohols **6a** and **8a** were available from our earlier study.[2] Their derived tosylates gave infrared and nmr spectra which were consistent with the assigned structures. In particular, all isomers of the *endo* series, *i.e.*, **6** and **8**, are characterized by a doublet of doublets

(1) Ohio State University Postdoctoral Fellow, 1967–1969.

(2) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **89**, 6659 (1967).

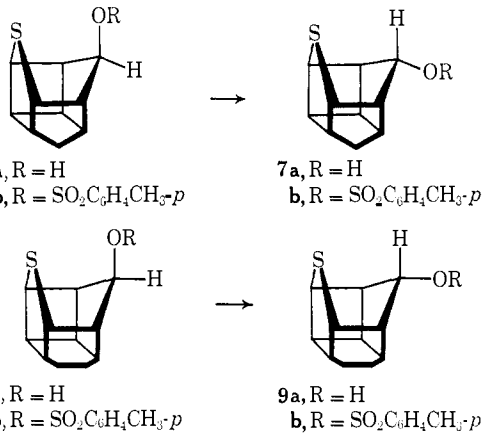
(3) Systematic addition of methylene units to the carbon bridge in question results in a compensating compression of the sulfide and carbonyl groups.

(4) The symbolism $R_2S$-*n* is herein employed to denote the size of the heterocyclic ring (*n* members) ultimately realizable if cyclization were to occur, as suggested earlier for neighboring methoxyl participation [S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958)].

(5) For a recent review of neighboring group participation, see B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

(6) (a) G. M. Bennett, F. Heathcoat, and A. N. Mosses, *J. Chem. Soc.*, 2567 (1929); (b) G. M. Bennett and E. G. Turner, *ibid.*, 813 (1938); (c) H. Böhme and K. Sell, *Chem. Ber.*, **81**, 123 (1948); (d) R. E. Ireland and H. A. Smith, *Chem. Ind.* (London), 1252 (1959); (e) C. J. M. Stirling, *Angew. Chem. Intern. Ed. Engl.*, **7**, 648 (1968); (f) A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc., B*, 1218 (1968).

pattern (sometimes appearing as a triplet) in the $\delta$ 4.0–4.5 region, which absorption is assignable to the *exo* proton attached to carbon bearing the oxygenated



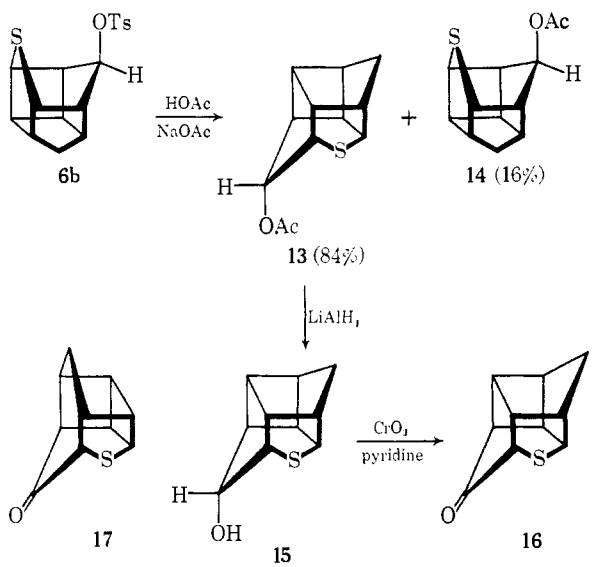

substituent. The observed coupling constants (approximately 4 Hz) are in good agreement with the magnitude of the vicinal coupling predicted by the Karplus correlation[7] on the basis of a 58° dihedral angle (measurement made on Dreiding models).

Treatment of **6a** and **8a** with aluminum isopropoxide and acetone in refluxing toluene for 48 hr[8] afforded the epimeric *exo* alcohols **7a** and **9a**, respectively, in high yield. Convincing proof that skeletal rearrangement had not occurred during the equilibrations was derived not only from the spectral data, but also from the observation that mild oxidation of **7a** and **9a** led exclusively to the corresponding thia ketones of known structure.[2] The preparation of tosylate **7b** proceeded without difficulty, but the corresponding ethano-bridged tosylate (**9b**) proved more elusive. Tosylation of **9a** with *p*-toluenesulfonyl chloride in pyridine at 0–5° using a slightly acidic work-up or in tetrahydrofuran with *n*-butyllithium as the base led to the recovery of appreciable amounts of unchanged alcohol. However, this difficulty was overcome by the use of a nonacidic work-up of the pyridine reaction. The nmr spectra of **7** and **9** show a somewhat broadened singlet at $\delta$ 4.5–5.5 (depending on substitution) corresponding to the >CHO– proton. This observation is again entirely congruent with the Karplus correlation[7] since the geometry of the proton in the *exo* series is such (dihedral angle of approximately 90°) that vicinal coupling should not be operative.

The rates of acetolysis of the four tosylates in buffered acetic acid, as well as that of three related compounds, are summarized in Table I. If *anti*-pentacyclo[5.3.0.0$^{2,5}$.0$^{3,9}$.0$^{4,8}$]decan-6-ol (**10**) is used as the model to which a relative acetolysis rate of 1 at 25° is assigned,[9] it is seen that the *exo* isomer (**11**) is five times as reactive.[11] The added strain embodied in 9-homocubyl tosylate (**12**)[12,13] gives rise to a rate enhancement of approximately 15. No significant differences are seen in the rates of acetolysis of *endo* tosylates **6b** and **8b**. This was not unexpected since the geometrical features of these particular isomers are not conducive to $R_2S$-4 neighboring group participation. It is equally significant to note that $k_{exo}/k_{endo}$ (4.9) for the hydrocarbon series (**10** and **11**) is quite comparable to the relative reactivity ratio of the *exo* and *endo* tosylates in the methano-bridged series (3.8), suggesting that very little assistance to cation formation has resulted from the introduction of the sulfur atom.[14] In marked contrast, the *exo* isomer in the ethano-bridged series (**9b**) is $3 \times 10^3$ times more reactive than its *endo* counterpart **8b**. The substantially increased acceleration exhibited by *exo* isomer **9b** is the reflection of anchimerically assisted ionization by the neighboring sulfur atom. The widely divergent kinetic behavior of **7b** and **9b** will be discussed below.

The products of the solvolysis of **6b** in buffered acetic acid (100°, ten half-lives) are shown in Scheme I. The

**Scheme I**




mixture of acetates **13** and **14** could be readily separated by column chromatography on silica gel. The minor solvolysis product was readily identified as *endo* acetate **14**. This assignment was based on comparison of its vpc retention times and nmr and infrared spectra with those of an authentic sample of **14**, independently synthesized by treatment of **6a** with acetic anhydride in pyridine. The major component could be shown by its nmr spectrum to be a product of skeletal rearrangement. Elemental analysis demonstrated that compositional integrity of the substrate had been maintained in the conversion to **13**. Reduction of **13** with lithium aluminum hydride and oxidation of the resulting alcohol (**15**) with chromium trioxide–pyridine afforded ketone **16**. The nonidentity of this substance with **1** was confirmatory for the occurrence of a rearrangement. Since two concerted 1,2-alkyl shifts of a carbon–carbon bond

(7) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); *J. Am. Chem. Soc.*, 85, 2870 (1963).

(8) This procedure represents an adaptation of the method of C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, 28, 1079 (1963).

(9) As a consequence of the conventions established in the pioneering efforts of Winstein and coworkers,[10] acetolysis rates of tosylates are ordinarily compared at 25°. The availability of such data for **10**–**12** has dictated our choice of this parameter in this work.

(10) S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, 70, 812 (1948); S. Winstein, E. Grunwald, and L. Ingraham, *ibid.*, 70, 821 (1948).

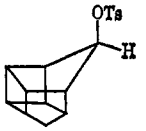
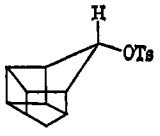
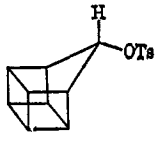
(11) W. L. Dilling and C. E. Reinecke, *Tetrahedron Letters*, 2547 (1967).

(12) P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, 89, 698 (1967).

(13) In view of the plane of symmetry in **12**, the *exo*/*endo* or *syn*/*anti* designations are, of course, not applicable.

(14) This type of internal standardization eliminates the small inequities that can be caused by the inductive effect of sulfur when direct comparison with the hydrocarbon series is made.

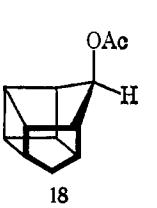
**Table I.** Rates of Acetolysis

| Compound | $T$, °C | $k$, sec$^{-1}$ | Rel $k_1$ (25°) | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu |
|---|---|---|---|---|---|
| **6b** | 115.0 | $3.38 \pm 0.06 \times 10^{-4}$ | 8.4 | 27.89 ± 0.13 | −3.09 ± 0.35 |
| | 100.0 | $7.69 \pm 0.04 \times 10^{-5}$ | | | |
| | 85.0 | $1.51 \pm 0.02 \times 10^{-5}$ | | | |
| | 50.0[a] | $1.94 \times 10^{-7}$ | | | |
| | 25.0[a] | $4.63 \times 10^{-9}$ | | | |
| **7b** | 100.0 | $2.75 \pm 0.04 \times 10^{-4}$ | 32.2 | 27.75 ± 0.12 | −0.93 ± 0.34 |
| | 85.0 | $5.54 \pm 0.05 \times 10^{-5}$ | | | |
| | 70.0 | $9.63 \pm 0.09 \times 10^{-6}$ | | | |
| | 50.0[a] | $7.27 \times 10^{-7}$ | | | |
| | 25.0[a] | $1.77 \times 10^{-8}$ | | | |
| **8b** | 115.0 | $1.47 \pm 0.02 \times 10^{-4}$ | 1.8 | 29.72 ± 0.13 | −0.04 ± 0.35 |
| | 100.0 | $3.09 \pm 0.02 \times 10^{-5}$ | | | |
| | 85.0 | $5.39 \pm 0.07 \times 10^{-6}$ | | | |
| | 50.0[a] | $5.28 \times 10^{-8}$ | | | |
| | 25.0[a] | $9.92 \times 10^{-10}$ | | | |
| **9b** | 65.0 | $5.60 \pm 0.04 \times 10^{-4}$ | 5564 | 25.41 ± 0.10 | +1.42 ± 0.30 |
| | 50.0 | $9.07 \pm 0.03 \times 10^{-5}$ | | | |
| | 35.0 | $1.29 \pm 0.02 \times 10^{-5}$ | | | |
| | 25.0[a] | $3.06 \times 10^{-6}$ | | | |
|  **10** | 130.0[b,c] | $1.19 \pm 0.01 \times 10^{-4}$ | 1 | 27.2 ± 2.3 | −9.7 ± 5.8 |
| | 120.0 | $4.90 \pm 0.22 \times 10^{-5}$ | | | |
| | 25.0[a] | $5.5 \times 10^{-10}$ | | | |
|  **11** | 120.0[b,c] | $2.84 \pm 0.12 \times 10^{-4}$ | 4.9 | 27.6 ± 3.0 | −5.1 ± 7.6 |
| | 110.0 | $1.10 \pm 0.04 \times 10^{-4}$ | | | |
| | 25.0[a] | $2.7 \times 10^{-9}$ | | | |
|  **12** | 125.0[c,d] | $4.75 \pm 0.03 \times 10^{-3}$ | 15.5 | 31.2 | −0.4 |
| | 100.0 | $3.38 \pm 0.09 \times 10^{-4}$ | | | |
| | 25.0[a] | $8.53 \times 10^{-9}$ | | | |

[a] Extrapolated values. [b] W. L. Dilling and C. E. Reinecke, *Tetrahedron Letters*, 2547 (1967). [c] Performed in unbuffered acetic acid. [d] P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, **89**, 698 (1967).

may take place in the ionization of **6b** (see Discussion section), it became necessary to differentiate between **16** and **17**. Since the carbonyl group in **17** is situated in a six–six fused ring system whereas that in **16** forms part of a more strained five–six bicyclic moiety (as in **1**), the carbonyl stretching bands of the two ketones would be expected to differ perceptibly, with that of **16** appearing at higher wave number. Because the pertinent infrared absorption of this thia ketone (1735 cm$^{-1}$) compared favorably with the carbonyl bands observed for **1** (1740 cm$^{-1}$) and 2-phenylthiocyclopentanone (1730 cm$^{-1}$),[15] a definitive choice in favor of **16** could be made. Additional confirmation of this structural assignment was derived from the acetolysis of the related carbocyclic tosylate **10**.[11] Acetates **18** (15%) and **19** (85%) were obtained, the latter product arising *via* a 1,2 migration of the *trans*-disposed cyclobutyl (and not cyclopentyl) carbon–carbon bond during ionization.

(15) In contrast, the carbonyl stretching frequency of 2-phenylthiocyclohexanone is seen at 1710 cm$^{-1}$. We thank Mary L. Wise for the preparation of these model compounds.



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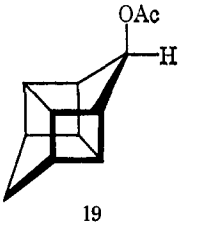
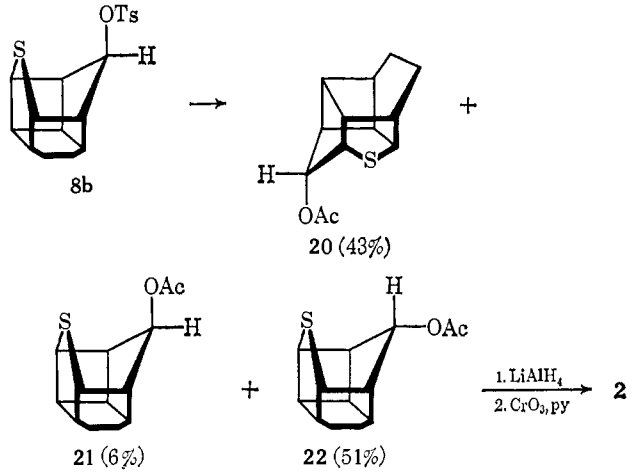


**19**

The acetolysis of **8b** led almost quantitatively to the formation of a three-component mixture, vpc analysis of which indicated the percentage composition which appears in Scheme II (order of elution from the gas chromatograph). For preparative purposes, the minor acetate (**21**) was conveniently separated from **20** and **22** by silica gel chromatography after which the remaining two acetates were separated by vapor phase chromatography. Again in this instance, the least predominant product (**21**) was shown to have retained the gross structure and stereochemistry of its precursor by direct comparison with an authentic sample. The spectral characteristics of **20** were very similar to those

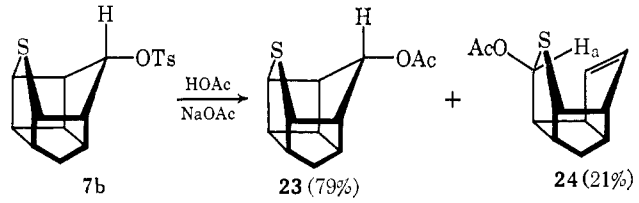
**Scheme II**




displayed by **13**. On the basis of a parallel argument and in view of the fact that a significant portion of the reaction was expected to proceed by a like mechanism, this acetate was assigned the structure resulting from migration of the more strained cyclobutyl bond. Independent acetylation of **9a** confirmed that the major product was *exo* acetate **22**. Added proof for this assignment was provided by conversion of **22** to the previously characterized keto sulfide **2**.[2]

Of the two products obtained in 95.5% yield from the preparative acetolysis of **7b**, that which predominated proved to be unrearranged *exo* acetate **23** (Scheme III).

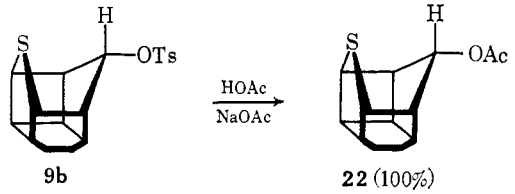
**Scheme III**




Although **23** could be separated by careful chromatography on silica gel, the minor component could not be completely freed of **23** by this technique. Attempts to purify **24** by chromatography on neutral alumina and by preparative scale vpc resulted in substantial decomposition. However, a sample of **24** which was partially purified by this last method showed a strong infrared band at 1740 $cm^{-1}$ and an nmr spectrum compatible with the assigned structure (see Experimental Section). Of particular significance in this spectrum are the well-defined olefinic and acetyl absorptions and the low-field ($\delta$ 5.45) singlet assignable to $H_a$.

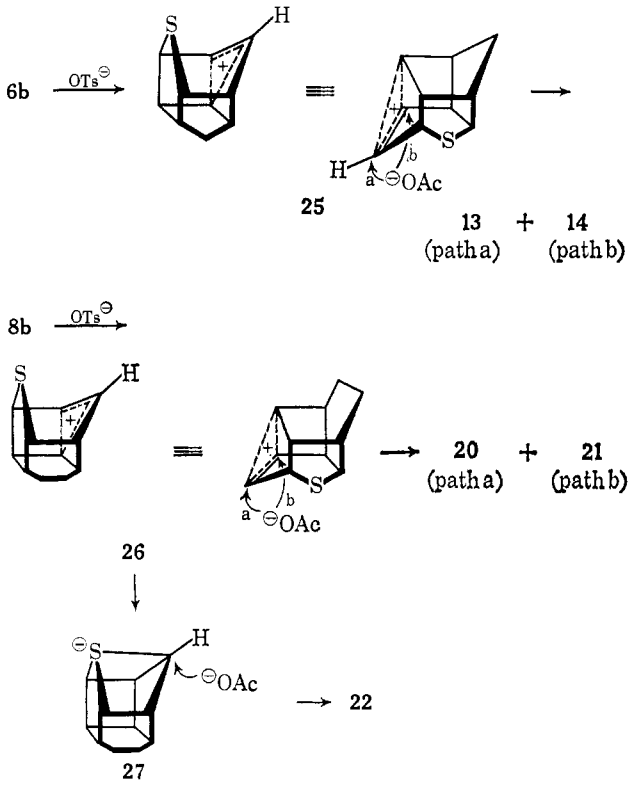
Solvolysis of **9b** afforded a quantitative yield of a crystalline acetate identified as *exo* acetate **22** (Scheme IV). Evidence for the formation of even trace amounts of other products could not be found in this instance.

**Scheme IV**




## Discussion

An important feature of the rate sequence found in Table I is the comparable reactivities of *endo* tosylates **6b** and **8b** and the corresponding *endo* tosylate in the hydrocarbon series (**10**). It is apparent from these results that the sulfur atom in **6b** and **8b** exerts no substantial driving force during the ionization of the C–OTs bond. The data are not unreasonable, since in these epimers the sulfur atom is positioned at the frontside of the leaving group and is unable to affect the bond heterolysis. Interestingly, however, rate retardation caused by the inductive effect of the proximate sulfur atom is not seen perhaps because the solvolysis rates of caged molecules of this type are already significantly enhanced. Dilling and Reinecke, for example, have noted that comparison of the experimental solvolysis rates for **10** and **11** with the values for unassisted solvolysis calculated by Schleyer's equation[16] indicate rate accelerations of $3 \times 10^3$ and $1 \times 10^4$, respectively.[11,17] The roughly equal ionization rates of **6b**, **8b**, and **10** are best explained by postulating bridged (or rapidly equilibrating[18]) carbonium ions **25** and **26** since the geometry for anchimeric assistance by the *trans*-disposed cyclobutyl C–C bond is uniquely favorable for stabilization of the developing cationic center at C-7 in all three cases. Clearly, this picture agrees with the experimental facts in that it indicates retention




(16) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964).

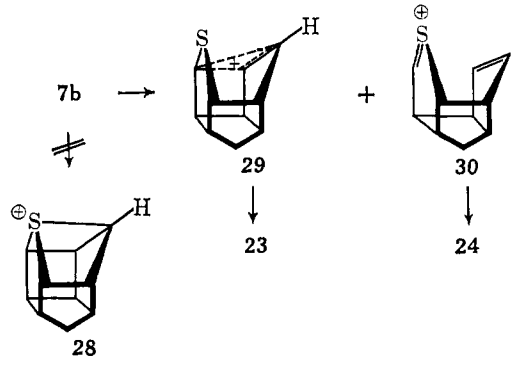
(17) Correlations of this type for **6b** and **8b** which must necessarily be founded on the carbonyl stretching frequencies of the corresponding ketones (**1** and **2**, respectively) would very likely not be meaningful since we have already shown[2] that the orbitals on sulfur in these caged thia ketones are not in a position to overlap with the nonbonding electrons on oxygen but can overlap with the $\pi$ orbital of the carbonyl group and thereby abnormally affect its stretching mode.

(18) Bridged ions are employed herein because they lend themselves better to economy of space. In no way, do we wish to discriminate against the concept of rapidly equilibrating carbonium ions. However, see ref 11.

of configuration at C-7 in **14** and **21** and *syn* stereochemistry in **13** and **20**. The *syn* orientation of the acetoxyl function in **13** and **20** is congruent with the absence of significant vicinal coupling of the *anti* proton in the nmr spectra of these molecules (dihedral angle relationship of approximately 75°—Prentice-Hall Models).[7] This scheme is likewise compatible with the observation that once **26** is formed the sulfur electrons are sufficiently close to interact with the reaction center and give sulfonium ion **27** which subsequently reacts with solvent to produce *exo* acetate **22**. A striking aspect of this comparison is seen in the absence of $R_2S$-4 participation in **25**, despite the fact that the sulfur atom is firmly held only a small additional distance from C-7 of the cation relative to **26**.[19]

A quite different situation prevails in the solvolysis of *exo* tosylates **7b** and **9b**. It is apparent from our results that the sulfide group in these epimers exerts a substantial driving force during the ionization of the C–OTs bond, although to quite different degrees. The acetolysis of **9b** can be formulated as involving direct interaction of a lone-pair orbital on sulfur with the developing cationic center at C-7 to stabilize the transition state and thereby lead directly to sulfonium ion **27**. It is clear that the geometry of this system must be uniquely favorable for sulfur neighboring group participation of the $R_2S$-4 variety. The full extent of anchimeric assistance to ionization may be appreciated only after noting that the rate of acetolysis of **11**, to which the solvolytic behavior of **9b** may be compared, is itself estimated to be accelerated by a factor of $10^4$.[11] Consequently, on this basis the observed rate for **9b** is about $10^7$ faster than it would be if the transition state resembled a simple localized cation.[20] The control of stereochemistry at C-7 would naturally follow directly from intermediate **27**.

In the case of **7b**, the kinetic and product analyses reveal that the sulfur atom in this system is not disposed structurally for conversion to sulfonium ion **28**. The




slower rate for **7b** argues again for the presence of added geometric constraint in the methano-bridged series. Although relatively small in magnitude,[19] the increased sulfur–C-7 internuclear distance in **7b** relative to **9b** is sufficient to cause not only a 170-fold decrease in rate of ionization but also the onset of a competing mechanism. The formation of **23** (79%) can be formulated most simply in terms of bridged ion **29** or its rapidly equilibrating counterpart.[18] The stereochemical control in this instance is totally analogous to that observed with **11**.[11] Another possibility, explicable in terms of **28** affording **23**, is much less attractive because of the kinetic behavior of this tosylate (only a sixfold rate increase over **11**). Also, to invoke the intervention of **28** after the generation of **29** does not seem plausible for reasons of geometry and because such an event is not observed with **25**.

The sixfold increase in solvolytic rate brought about by the sulfur atom in **7b**, which occurs despite inductive effects which are expected to produce significant retardation, may perhaps arise from that portion of the total reaction which constitutes a heterolytic fragmentation.[21] In proceeding from **7b** to intermediate **30**, the sulfur atom functions as an electrofugal group[22] which promotes the release of the nucleofugal tosylate ion through the developing olefinic linkage. There is accordingly a new driving force for ionization arising from this alternative pathway which, because it competes effectively with the production of **29**, is perhaps concerted. That is to say, we consider it plausible that some incipient stabilization of the cation may occur at the transition state not only from bridged or rapidly equilibrating cation **29** but also from fragmentation with development of positive charge on sulfur as in **30**.

So far, no clear analysis of precise proximity requirements for heteroatomic neighboring group participation has appeared, although much work in this area has been reported.[5] In this study, a critical relationship is seen to exist between the capability of divalent sulfur for $R_2S$-4 interaction and the internuclear distance to the developing electron-deficient center. We hope to study the matter further.

## Experimental Section[23]

***endo*-Octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*c*,*d*]pentalen-7-ol *p*-Toluenesulfonate (6b).** A solution of 1.00 g (5.55 mmol) of **6a** in 20 ml of dry pyridine was prepared, cooled to 0°, and 1.06 g (5.55 mmol) of *p*-toluenesulfonyl chloride was added. The mixture was allowed to stand in a refrigerator for 2 days after which it was poured into 25 ml of ice-cold dilute hydrochloric acid. The aqueous suspension was extracted several times with methylene chloride and the combined organic extracts were dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* to afford a light colored oil which was taken up in a minimum amount of ether and allowed to crystallize. The material was recrystallized from benzene–hexane to give 0.90 g (48.5%) of **6b**, mp 98–99°; $\nu_{max}^{CHCl_3}$ 1340 and 1175 $cm^{-1}$ (–$SO_2$–); $\delta_{TMS}^{CDCl_3}$ 1.50 (AB quartet, $J_{AB}$ = 11.5 Hz, 2 H, –$CH_2$–), 2.42 (singlet, 3 H, aryl-$CH_3$), 2.00–3.10 (multiplet, 6 H, methine protons), 3.28 (multiplet, 1 H, >C*H*S–), 3.77 (multiplet, 1 H, >C*H*S–), 4.46 (triplet, $J$ = 4.5 Hz, 1 H, >C*H*O–), and 7.50 (AB quartet, aryl protons).

*Anal.* Calcd for $C_{17}H_{18}O_3S_2$: C, 61.05; H, 5.42; S, 19.18. Found: C, 61.00; H, 5.49; S, 19.23.

***endo*-Octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*c*,*d*][2]benzothiophen-7-ol *p*-Toluenesulfonate (8b).** A solution of 3.00 g (15.4

(19) Dreiding models indicate a distance between sulfur and C-7 of 2.75 Å in **25** and 2.6 Å in **26**. However, the rigidity of such models may not be entirely suitable for this analysis. As already discussed,[2] the dipole moments of **1** and **2** clearly indicate that the heterocyclic ring of **2** is more folded than that of **1**. In the final analysis, however, only X-ray data will provide sufficiently accurate information on these distances. Such a study is presently being initiated.

(20) The accuracy of this analysis is, of course, ultimately dependent on the validity of Schleyer's equation and the suitability of **11** as a model. At the present time, **11** is in fact the best model system available.

(21) For a recent review of this class of organic reactions, see C. A. Grob and P. W. Schiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1 (1967).

(22) To our knowledge, no previous example of electrofugal behavior by divalent sulfur has been reported.

(23) Melting points are corrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer and nmr spectra were recorded with a Varian A-60 spectrometer.

mmol) of **8a** and 2.95 g (15.4 mmol) of *p*-toluenesulfonyl chloride in 40 ml of dry pyridine was allowed to stand for 5 days at 0–5°. The reaction mixture was worked up in the above fashion to give 2.65 g (49.5%) of **8b** as white needles, mp 115–116° (from benzene–hexane); $\nu_{max}^{CHCl_3}$ 1340 and 1165 cm$^{-1}$ (–$SO_2$–); $\delta_{TMS}^{CDCl_3}$ 1.25–3.00 (multiplet, 10 H, aliphatic protons), 2.45 (singlet, 3 H, aryl-$CH_3$), 3.20 (multiplet, 1 H, >C*H*S–), 4.00 (multiplet, 1 H, >C*H*S–), 4.45 (doublet of doublets, $J$ = 5.0 and 5.6 Hz, 1 H, >C*H*O–), and 7.59 (AB quartet, aryl protons).

*Anal.* Calcd for $C_{18}H_{20}O_3S_2$: C, 62.04; H, 5.79; S, 18.40. Found: C, 61.84; H, 5.74; S, 18.16.

***exo*-Octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*c,d*]pentalen-7-ol (7a).** A mixture of 1.80 g (10.0 mmol) of **6a**, 4.08 g (20.0 mmol) of aluminum isopropoxide, and 0.24 ml of purified acetone in 50 ml of dry toluene was heated under reflux for 48 hr. The reaction mixture was poured into 100 ml of 2 *N* hydrochloric acid, and the product was extracted with chloroform. The chloroform solution was washed with saturated aqueous sodium bicarbonate (one 50-ml portion) and water (two 50-ml portions), dried, and evaporated *in vacuo* to give 1.65 g (92%) of **7a**, mp 264–265° (sealed capillary) after recrystallization from hexane; $\nu_{max}^{CHCl_3}$ 3535 and 3365 cm$^{-1}$ (–OH); $\delta_{TMS}^{CDCl_3}$ 1.54 (AB quartet, $J_{AB}$ = 11 Hz, 2 H, –$CH_2$–), 2.0–3.35 (multiplet, 7 H, aliphatic and hydroxyl protons), 3.55 (multiplet, 1 H, >C*H*S–), 4.00 (multiplet, 1 H, >C*H*S–), and 4.20 (slightly broadened singlet, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{10}H_{12}OS$: C, 66.62; H, 6.71; S, 17.79. Found: C, 66.67; H, 6.69; S, 17.68.

**Oxidation of 7a.** Dicyclohexylcarbodiimide (930 mg, 4.52 mmol) was added to a solution of 200 mg (1.11 mmol) of **7a** in 3 ml of anhydrous dimethyl sulfoxide and 3 ml of benzene containing 0.12 ml of pyridine and 0.06 ml of trifluoroacetic acid. The resulting suspension was stirred at room temperature for 48 hr. Benzene (15 ml) was added, the precipitate was removed by filtration, and the filtrate was washed thoroughly with water and dried. The solvent was removed *in vacuo* to give an oily solid which was chromatographed on Florisil. Elution with hexane–ether (5:1) afforded 190 ml (95%) of a white solid, mp 240.5–242.5° dec, the infrared spectrum of which was identical with that of authentic octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*cd*]pentalen-7-one (**1**).[2]

***exo*-Octahydro-1,3,5-ethanylylidene-2H-thiacyclobuta[*c,d*]pentalen-7-ol *p*-Toluenesulfonate (7b).** A solution of 0.90 g (5.0 mmol) of **7a** and 0.95 g (5.0 mmol) of *p*-toluenesulfonyl chloride in 20 ml of pyridine was allowed to stand in a refrigerator for 48 hr. The reaction mixture was worked up in the above fashion to give 1.34 g (80%) of a viscous oil which crystallized on standing. Recrystallization from ether–pentane afforded pure **7b**, mp 99.5–101°; $\nu_{max}^{CHCl_3}$ 1355 and 1172 cm$^{-1}$ (–$SO_2$–); $\delta_{TMS}^{CDCl_3}$ 1.53 (AB quartet, $J_{AB}$ = 11 Hz, 2 H, –$CH_2$–), 2.43 (singlet, 3 H, aryl-$CH_3$), 2.5–3.25, (multiplet, 6 H, methine protons), 3.52 (multiplet, 1 H, >C*H*S–), 3.93 (multiplet, 1 H, >C*H*S–), 4.88 (slightly broadened singlet, 1 H, >C*H*O–), and 7.51 (AB quartet, aryl protons).

*Anal.* Calcd for $C_{17}H_{18}O_3S_2$: C, 61.05; H, 5.42; S, 19.18. Found: C, 61.32; H, 5.44; S, 18.89.

***exo*-Octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*c,d*][2]benzothiophen-7-ol (9a).** A mixture of 1.94 g (10.0 mmol) of **8a**, 4.08 g (20.0 mmol) of aluminum isopropoxide, and 0.24 ml of purified acetone in 50 ml of toluene was refluxed for 48 hr. The reaction mixture was worked up as above to give 1.90 g (98%) of **9a**, mp 217–219°. Recrystallization from chloroform–hexane gave pure **9a**, mp 219–221°; $\nu_{max}^{CHCl_3}$ 3570 and 3450 cm$^{-1}$ (–OH); $\delta_{TMS}^{CDCl_3}$ 1.10–3.16 (multiplet, 11 H, aliphatic and hydroxyl protons), 3.16–3.60 (multiplet, 1 H, >C*H*S–), 3.80–4.30 (multiplet, 1 H, >C*H*S–), and 4.55 (somewhat broadened singlet, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C, 67.85; H, 7.50; S, 16.34.

**Oxidation of 9a.** To a cold (0°) mixture of 100 mg (1.0 mmol) of chromium trioxide in 5 ml of pyridine was added 50 mg (0.26 mmol) of **9a**. The reaction mixture was stirred for 8 hr during which time the temperature was allowed to warm to 25°. After dilution of the mixture with 10 ml of ether, the inorganic salts were removed by filtration. The filtrate was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, water, dried, and evaporated to give 30 mg (60%) of a somewhat gummy solid which was purified by preparative vapor phase chromatography (0.25 in. × 10 ft aluminum column packed with 2% XF-1150 on 60–80 mesh Chromosorb W). The vpc retention time and the infrared spectrum of this material were identical with those of octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*cd*][2]benzothiophen-7-one (**2**).[2]

***exo*-Octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*c,d*][2]benzothiophen-7-ol *p*-Toluenesulfonate (9b).** A mixture of 870 mg (4.5 mmol) of **9a** and 950 mg (5.0 mmol) of *p*-toluenesulfonyl chloride in 20 ml of pyridine was allowed to stand at 0–5° for 6 days. The reaction mixture was poured into ice water (150 ml) and stirred for 20 min. The resulting solid was filtered, washed thoroughly with water, and dried to give 1.34 g (87%) of the crude tosylate. Recrystallization of this material from benzene–pentane afforded pure **9b**, mp 133.5–134.5°; $\nu_{max}^{Nujol}$ 1360, 1190, and 1175 cm$^{-1}$ (–$SO_2$–); $\delta_{TMS}^{CDCl_3}$ 1.4–3.1 (multiplet, 10 H, aliphatic protons), 2.43 (singlet, 3 H, aryl-$CH_3$), 3.46 (multiplet, 1 H, >C*H*S–), 4.09 (multiplet, 1 H, >CHS–), 5.32 (slightly broadened singlet, 1 H, >C*H*O–), and 7.50 (AB quartet, aryl protons).

*Anal.* Calcd for $C_{18}H_{20}O_3S_2$: C, 62.03; H, 5.79; S, 18.40. Found: C, 62.25; H, 5.77; S, 18.10.

**Solvolysis of 6b.** A solution of 1.00 g (3.00 mmol) of **6b** and 287 mg (3.50 mmol) of anhydrous sodium acetate in 35 ml of glacial acetic acid was heated at 100° for 15 hr. The reaction mixture was cooled to room temperature and diluted with 50 ml of water. The resulting suspension was extracted several times with pentane and the combined organic extracts were washed with 2.5% sodium bicarbonate solution and water. The pentane solution was dried and evaporated to give 670 mg (100%) of light yellow oil. Vapor phase chromatography on the above column showed the presence of two components which were separable by column chromatography on silica gel. Elution with hexane–ether (19:1) afforded 590 mg (84.4%) of **13** as a colorless oil. Molecular distillation of this material yielded a white solid which was subsequently recrystallized from hexane solution at −70°, mp 33–35°; $\nu_{max}^{CHCl_3}$ 1730 cm$^{-1}$ (>C=O); $\delta_{TMS}^{CDCl_3}$ 1.50 (AB quartet, $J_{AB}$ = 11 Hz, 2 H, –$CH_2$–), 2.00 (singlet, 3 H, –OCOC*H*$_3$), 2.23–3.34 (multiplet, 6 H, methine protons), 3,50 (multiplet, 2 H, >C*H*S–), and 5.25 (slightly broadened singlet, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; S, 14.43. Found: C, 64.94; H, 6.53; S, 14.46.

Elution with hexane–ether (9:1) led to the isolation of 100 mg (15.6%) of **14** as a colorless oil which crystallized on standing. The vpc retention times and spectra of this material were identical with those of an authentic sample of **14**.

***endo*-Octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*c,d*]pentalen-7-ol Acetate (14).** A solution of 1.00 g (5.55 mmol) of **6a** in 4 ml of pyridine and 4 ml of acetic anhydride was allowed to stand at room temperature for 1 week. The reaction mixture was poured into a mixture of ice and dilute hydrochloric acid and the aqueous mixture was extracted several times with methylene chloride. The combined organic extracts were dried and evaporated to give 1.15 g (93.5%) of an oil which slowly crystallized. Repeated recrystallization from aqueous methanol afforded pure **14**, mp 57–58°; $\nu_{max}^{CHCl_3}$ 1725 cm$^{-1}$ (>C=O); $\delta_{TMS}^{CDCl_3}$ 1.58 (AB quartet, $J_{AB}$ = 10.5 Hz, 2 H, –$CH_2$–), 2.07 (singlet, 3 H, –OCOC$H_3$), 2.22–3.32 (multiplet, 6 H, methine protons), 3.57 (multiplet, 1 H, >C*H*S–), 3.98 (multiplet, 1 H, >C*H*S–), and 4.64 (triplet, $J$ = 4.2 Hz, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; S, 14.43. Found: C, 64.74; H, 6.26; S, 14.50.

**Lithium Aluminum Hydride Reduction of 13.** A solution of 900 mg (4.04 mmol) of **13** in 15 ml of anhydrous ether was treated with 154 mg (4.04 mmol) of lithium aluminum hydride. The suspension was allowed to stir overnight at room temperature. Work-up of the reaction mixture under the usual alkaline conditions afforded 700 mg (96%) of **15** as an oily semisolid. Recrystallization of this material from benzene and sublimation gave hard white crystals, mp 223–225°; $\nu_{max}^{CHCl_3}$ 3500 and 3340 cm$^{-1}$ (–OH); $\delta_{TMS}^{CDCl_3}$ 1.47 (AB quartet, $J_{AB}$ = 11 Hz, 2 H, –$CH_2$–), 2.24–3.52 (complex pattern, 8 H, methine protons and both –C*H*S–), 2.87 (singlet, 1 H, –OH), and 4.31 (singlet, 1 H, >C*H*OH).

*Anal.* Calcd for $C_{10}H_{12}OS$: C, 66.62; H, 6.71; S, 17.79. Found: C, 66.81; H, 6.80; S, 18.03.

**Oxidation of 15.** To the chromium trioxide–pyridine complex prepared by addition of 500 mg (5.0 mmol) of chromium trioxide to 25 ml of pyridine at 0° was added 500 mg (2.77 mmol) of **15**. The suspension was stirred under nitrogen for 12 hr during which time the contents were gradually allowed to warm to room temperature. At this point, ether (25 ml) was added, and the inorganic salts were removed by filtration. The filtrate was washed with dilute hydrochloric acid, aqueous sodium bicarbonate solution, and water and dried. Evaporation of the solvent afforded 280 mg (56%) of crude **16** which was purified by chromatography on silica gel and recrystallization from hexane, mp 207–210°; $\nu_{max}^{CHCl_3}$ 1735

$cm^{-1}$; $\delta_{TMS}^{CDCl_3}$ 1.55 (AB quartet, $J_{AB}$ = 11 Hz, 2 H, $-CH_2-$) and 2.40–3.65 (complex series of peaks, 8 H, methine protons).

*Anal.* Calcd for $C_{10}H_{10}OS$: C, 67.38; H, 5.65; S, 17.99. Found: C, 67.55; H, 5.58; S, 17.86.

**Acetolysis of 8b.** A solution of 1.00 g (2.87 mmol) of **8b** and 262 mg (3.20 mmol) of anhydrous sodium acetate in 32 ml of glacial acetic acid was refluxed for 8 hr. The reaction mixture was cooled, diluted with 50 ml of water, and worked up as above. There was obtained 680 mg (100%) of brown oil which was found by vpc analysis to contain three components in the ratio 43.3:5.6:51.1. This product was subjected to column chromatography on silica gel. Elution with hexane–ether (19:1) afforded a mixture of **20** and **22** which was then separated by preparative vpc on the above column. The more rapidly eluted component (**20**) was obtained as a white solid which when recrystallized from cold hexane melted at 45–46°; $\nu_{max}^{CHCl_3}$ 1730 $cm^{-1}$ (>C=O); $\delta_{TMS}^{CDCl_3}$ 1.64–2.18 (multiplet, 4 H, $-CH_2CH_2-$), 1.97 (singlet, 3 H, $-OCOCH_3$), 2.38–3.35 (multiplet, 6 H, methine protons), 3.58 (multiplet, 1 H, >C*H*S–), 4.23 (multiplet, 1 H, >C*H*S–), and 5.58 (slightly broadened singlet, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{13}H_{16}O_2S$: C, 66.06; H, 6.83; S, 13.57. Found: C, 66.03; H, 6.99; S, 13.56.

The second component was also a white solid, mp 85–86° (from hexane), which proved to be identical in all respects with an authentic sample of **22**.

Elution of the column with hexane–ether (9:1) yielded a colorless oil which subsequently crystallized, mp 76–76.5° (from aqueous methanol). This product was found to be identical with the acetylation product of **8a**, *i.e.*, **21**.

***endo*-Octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*c*,*d*][2]benzothiophen-7-ol Acetate (21).** Acetylation of 1.00 g (5.14 mmol) of **8a** with 4 ml each of pyridine and acetic anhydride for 1 week at room temperature afforded 1.12 g (91.8%) of crude acetate, mp 70–75°. Recrystallization from aqueous methanol gave white crystals, mp 76–76.5°; $\nu_{max}^{CHCl_3}$ 1725 $cm^{-1}$ (>C=O); $\delta_{TMS}^{CDCl_3}$ 1.25–3.24 (multiplet, 10 H, $-CH_2-$ and methine protons), 2.10 (singlet, 3 H, $-OCOCH_3$), 3.40 (multiplet, 1 H, >C*H*S–), 4.15 (multiplet, 1 H, >C*H*S–), and 4.55 (doublet of doublets, $J$ = 5.0 and 5.5 Hz, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{13}H_{16}O_2S$: C, 66.06; H, 6.83; S, 13.57. Found: C, 65.86; H, 6.63; S, 13.30.

***exo*-Octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*c*,*d*][2]benzothiophen-7-ol Acetate (22).** Acetylation of 250 mg (1.28 mmol) of **9a** with 2 ml each of pyridine and acetic anhydride in 15 ml of chloroform (reflux, 12 hr) yielded 230 mg (76%) of oily solid which was recrystallized from hexane, mp 85–86°; $\nu_{max}^{CHCl_3}$ 1730 $cm^{-1}$; $\delta_{TMS}^{CDCl_3}$ 1.50–1.96 (multiplet, 6 H, aliphatic protons), 2.00 (singlet, 3 H, $-OCOCH_3$), 2.35–3.12 (multiplet, 4 H, aliphatic protons), 3.48 (multiplet, 1 H, >C*H*S–), 4.14 (multiplet, 1 H, >C*H*S–), and 5.50 (slightly broadened singlet, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{13}H_{16}O_2S$: C, 66.06; H, 6.83; S, 13.57. Found: C, 66.03; H, 6.99; S, 13.56.

**Reduction and Oxidation of 22.** A solution of 75 mg (0.32 mmol) of **22** in 10 ml of anhydrous tetrahydrofuran was treated with 100 mg (2.63 mmol) of lithium aluminum hydride and the suspension was refluxed with stirring overnight. The usual alkaline work-up afforded 50 mg (81%) of the thia alcohol which was directly oxidized with the complex prepared from 100 mg (1.0 mmol) of chromium trioxide and 5 ml of pyridine. Isolation of the thia ketone in the predescribed fashion afforded 30 mg (60%) of an oily solid which was purified by preparative vpc. The vpc retention time and infrared spectrum of this sample were identical with those exhibited by authentic **2**.[2]

**Solvolysis of 7b.** A solution of 1.53 g (4.57 mmol) of **7b** and 432 mg (5.34 mmol) of anhydrous sodium acetate in 53 ml of glacial acetic acid was heated at 100° for 7 hr. The reaction mixture was cooled, diluted with 70 ml of water, and worked up in the predescribed fashion to afford 693 mg (95.5%) of a light yellow oil. Vpc analysis of this product showed the presence of two components in the ratio 79:21. Chromatography of the mixture on silica gel (elution with 1% ether in pentane) served to separate partially the two components. The more slowly eluted product (major fraction) was a crystalline solid, mp 46–47°, identical in all respects with *exo* acetate **23**.

In the earlier fractions, there was obtained a viscous oil which remained contaminated with **23** (tlc analysis). A small amount of somewhat more purified **24** was isolated as a viscous oil by preparative vpc;[24] $\nu_{max}^{CCl_4}$ 1740 $cm^{-1}$; $\delta_{TMS}^{CCl_4}$ 1.1–2.8 (multiplet, 6 H, aliphatic protons), 1.99 (singlet, 3 H, $-OCOCH_3$), 3.36 (multiplet, 1 H, >C*H*S–), 5.45 (singlet, 1 H, $H_a$), 5.87 (multiplet, 1 H, vinyl proton), and 6.18 (doublet of doublets, $J$ = 6 and 3 Hz, 1 H, vinyl proton).

***exo*-Octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*c*,*d*]pentalen-7-ol Acetate (23).** Acetylation of 300 mg (1.65 mmol) of **7a** with 3 ml each of pyridine and acetic anhydride for 3.5 days at room temperature afforded 365 mg (98.5%) of a viscous oil which crystallized on standing. Recrystallization from aqueous methanol yielded pure **23**, mp 46–47°; $\nu_{max}^{CCl_4}$ 1735 $cm^{-1}$ (>C=O); $\delta_{TMS}^{CCl_4}$ 1.56 (AB quartet, $J_{AB}$ = 12.5 Hz, 2 H, $-CH_2-$), 1.92 (singlet, 3 H, $-OCOCH_3$), 2.3–3.3 (multiplet, 6 H, methine protons), 3.55 (multiplet, 1 H, >C*H*S–), 3.99 (multiplet, 1 H, >C*H*S–), and 5.07 (slightly broadened singlet, 1 H, >C*H*O–).

*Anal.* Calcd for $C_{12}H_{14}O_2S$: C, 64.81; H, 6.35; S, 14.42. Found: C, 64.96; H, 6.42; S, 14.34.

**Acetolysis of 9b.** A solution of 1.00 g (2.87 mmol) of **9b** and 262 mg (3.20 mmol) of anhydrous sodium acetate in 32 ml of glacial acetic acid was heated at 100° for 8 hr. After work-up there was obtained 680 mg (100%) of a crystalline solid, mp 84–86°, the infrared and nmr spectra of which were identical with those of authentic *exo* acetate **22**.

**Kinetic Procedure.** Anhydrous acetic acid was prepared by refluxing a solution of acetic anhydride in glacial acetic acid for 24 hr and subsequent fractional distillation in a dry atmosphere. Standard sodium acetate in acetic acid (approximately 0.10 *M*) was prepared by the addition of anhydrous acetic acid to anhydrous sodium carbonate which had been heated over an open flame and allowed to cool in a desiccator. The water of neutralization was not removed from the solution.

For each run the tosylate (accurately weighed) was about 0.06 *M* in acetic acid–sodium acetate except in the case of **9b** where solubility factors dictated the use of a low (*ca.* 0.02 *M*) concentration of sulfonate ester. Aliquots of these solutions slightly in excess of 1 ml were sealed in glass ampoules which were subsequently placed at a constant temperature bath at the desired temperature maintained to ±0.04°. After 10 min, the first ampoule was removed and quenched in ice water at which point an accurate timer was started. The remaining ampoules were removed at appropriate intervals and accurately measured aliquots (0.923 ml at 25°) were removed and titrated with standard perchloric acid in acetic acid to a brom phenol blue end point. In the case of **9b**, titration end points were determined potentiometrically with a Fisher Accumet pH meter and microprobe combination electrode.

All rates of solvolysis were determined utilizing an infinity titer (at least ten half-lives). Good first-order kinetics were observed over three half-lives except in the case of **7b** where serious deviations from linearity were noted after one half-life. For each tosylate, at least two determinations were made and the average is reported in Table I. The average deviation was generally ±2% or less. The experimental rate constants were calculated manually by means of the least-squares method whereas the activation parameters and extrapolated rate constants were computed with the aid of the ACTENG computer program developed by Professor D. F. DeTar, Florida State University, and adapted to Fortran IV by D. H. Slater, The Ohio State University.

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(24) This sample did not contain **23**; however, the presence of small amounts of thermal decomposition products was indicated by tlc and vpc analyses.