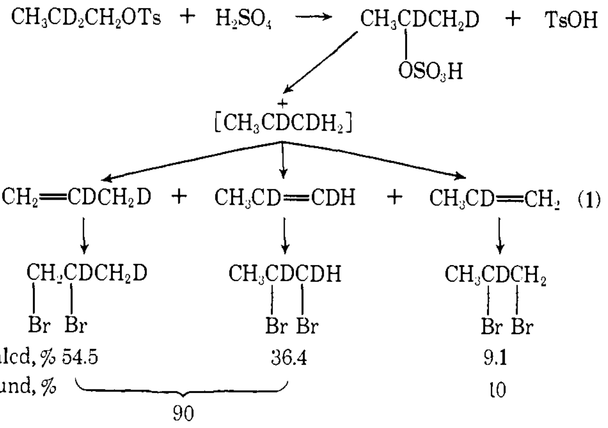
tetrachloride. When $D_2SO_4$ was used, the dibromopropane isolated contained less than 1 atom % deuterium (mass spectrum). Solvolytic rearrangement of propyl-2,2-$d_2$ tosylate in 96% $H_2SO_4$ with bromine trapping of products yielded a mixture of dideuterio- and monodeuterio-1,2-dibromopropanes, consistent with the scheme shown in eq 1, where an isotope effect in elimination to form propene $(k_H/k_D)_{elim}$ of 2.0 is assumed,[15] and secondary isotope effects in elimination are neglected in the calculation of the product distribution. Mass spectral fragmentation patterns and the nmr spectrum (Figure 1) of the dibromide product are consistent with the distribution predicted.



Sulfuric acid solvolysis of propyl-2-$d_1$ tosylate and product trapping with bromine yielded mainly monodeuterio-1,2-dibromopropane. By integration of the methyl singlet with respect to the methyl doublet (Figure 2) and making appropriate corrections for deuterium affixed to the methyl carbon, an intramolecular (product) isotope effect $(k_H/k_D)_{intra}$ of 2.1 ± 0.3 was obtained. This value may be compared with the intermolecular (kinetic) isotope effect $(k_H/k_{\beta\text{-}d_2})$ of 1.85 ± 0.10 determined by both direct measurements of rates of solvolysis of propyl and propyl-2,2-$d_2$ tosylates and by competitive intermolecular rate studies.[16]

Application of bromine-trapping procedures to the 96% $H_2SO_4$ solvolysis of isobutyl tosylate at 0° led to the isolation and identification of a mixture of di- and tribromobutanes: 1,2-dibromo-2-methylpropane (**1**), 35%; *meso*- and *dl*-2,3-dibromobutane (**2**), 38%; 1,2,3-tribromo-2-methylpropane (**3**), 22%; other tribromobutanes (**4**), *ca.* 5%.[17] Parallel solvolysis of isobutyl-2-$d_1$ tosylate in 96% $H_2SO_4$ with bromine trapping yielded **1** (90% $d_1$), 21%; **2** (82% $d_1$), 55%; **3**, 13%; **4**, 11%. A product-distribution isotope effect $(k_H/k_D)_{prod}$ of 2.4 is estimated by assuming that products **1** and **3** represent hydrogen migration and **2** and **4** represent methyl migration. Competitive solvolysis of mixtures of isobutyl and isobutyl-$d_1$ tosylate yield a kinetic isotope effect $(k_H/k_{\beta\text{-}d_1})$ of 1.9 ± 0.1. Upon correction for the hydrogen:methyl migration ratio a value of 2.4 is obtained, in accord with the observed product-distribution isotope effect.

The treatment of solvolysis reactions of alkyl derivatives in terms of two competing pathways, anchimerically assisted $(k_\Delta)$ and anchimerically unassisted $(k_s)$, has long been advocated and repeatedly explored by Winstein and coworkers.[19] Inherent in this treatment is the expectation that assistance by a neighboring group should become increasingly important as the nucleophilicity of the ionizing solvent decreases.[20] The 96% $H_2SO_4$ as well as the $CF_3COOH$[3a] solvolysis studies of primary alkyl tosylates appear as striking realizations of this expectation. The rate-limiting character of hydrogen transfer in $H_2SO_4$ solvolysis of propyl and isobutyl tosylates is substantiated by the near congruence of the intermolecular (kinetic) and intramolecular (product) isotope effects. Bromine trapping permits estimates of hydrogen:methyl migration rates under solvolytic conditions that do not permit direct detection of first-formed products.

The apparent enhancements of $k_\Delta$ processes observed in weakly nucleophilic solvents such as $CF_3COOH$ and $H_2SO_4$ are indeed instructive. They lead one to reconsider the question: can solvolytic conditions be found which force neighboring hydrogen participation of simple ethyl derivatives? Experiments directed toward an answer are the subject of the next communication.[21]

**Acknowledgment.** We thank Professor S. Winstein and Dr. A. Diaz for a number of helpful discussions and information prior to publication concerning solvolysis of alkyl tosylates in $CF_3COOH$ and $HSO_3F$.

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[15] S. Ehrenson, S. Seltzer, and R. Diffenbach, *J. Amer. Chem. Soc.*, **87**, 563 (1965).

[16] Competitive rate studies were conducted by solvolyzing equimolar mixtures of labeled and unlabeled alkyl tosylates and isolating the unconsumed alkyl tosylates from measured aliquots. The extent of over-all reaction was determined by uv analysis,[10] and the H/D ratio in the unconsumed reactant was determined by mass spectrometry.

[17] Substitution accompanying addition is well documented.[18] We presume that the tribromobutanes isolated are formed by substitution followed by addition.

[18] P. B. D. de la Mare and R. Bolton, "Electrophilic Addition to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966.

[19] S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **75**, 148 (1953).

[20] A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968), and references cited therein.

[21] P. C. Myhre and E. Evans, *ibid.*, **91**, 5641 (1969).

[22] National Science Foundation Undergraduate Research Participant, 1965–1966.

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## Solvolysis of Ethyl Tosylate in $HSO_3F$

*Sir:*

Accumulating data provide important support for the view that neighboring group participation in solvolysis reactions is strongly enhanced in weakly nucleophilic ionizing solvents.[1] Correlations of the effect of these solvents on the $k_\Delta$ and $k_s$ modes of solvolysis of simple primary alkyl tosylates have been discussed in the accompanying communications.[1g,h] Propyl tosylate exhibits a striking change in solvolytic behavior upon variation of solvent: <1% rearrangement in HCOOH,[2] 89% rearrangement in $CF_3COOH$,[1g] and essentially

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[1] (a) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956); (b) P. E. Peterson, *et al.*, *ibid.*, **89**, 5902 (1967), and references therein; (c) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968); (d) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); (e) W. G. Dauben and J. L. Chitwood, *ibid.*, **90**, 6876 (1968); (f) P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969); (g) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969); (h) A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, 5637 (1969).

[2] C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966).

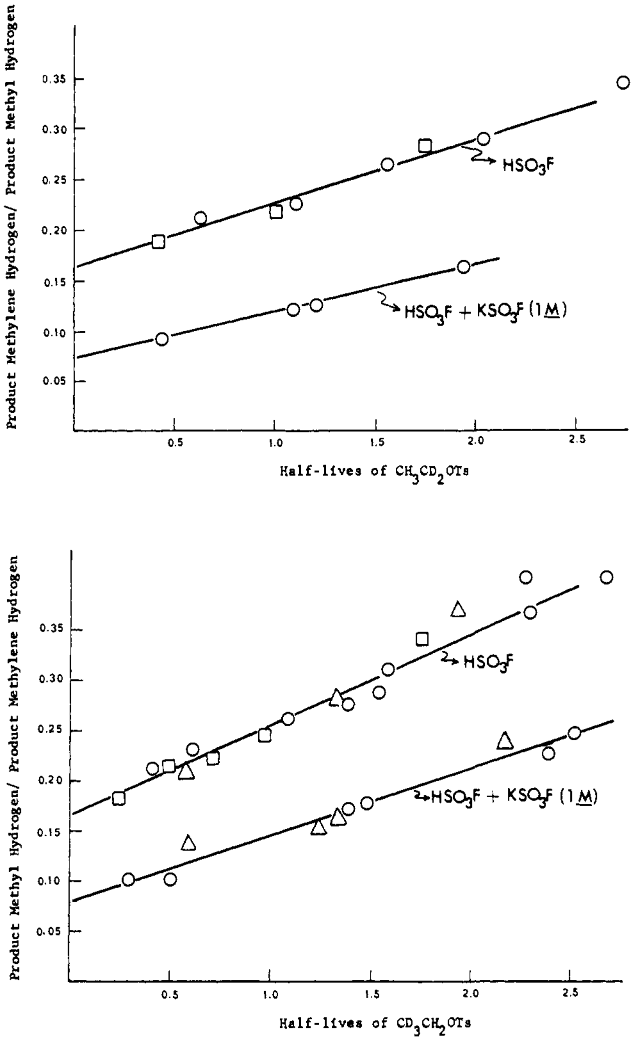


Figure 1. Ratio of hydrogen on methylene and methyl carbon atoms of the $EtOSO_2F$ product derived from the solvolysis of $CH_3CD_2OTs$ (upper) and $CH_3CD_2OTs$ (lower) in $HSO_3F$ and $HSO_3F + KSO_3F$ (1 *M*) at 0° as a function of reactant half-life; □, 0.2 *M* ROTs; △, 0.8 *M* ROTs; 0, 1.2 *M* ROTs.

complete rearrangement in $H_2SO_4$ and $HSO_3F$.[1f,h] The inter- and intramolecular isotope effects observed for propyl tosylate in $CF_3COOH$, $H_2SO_4$, and $HSO_3F$ provide evidence of the rate-limiting character of the 1,2-hydride shift.[1f-h]

By contrast, $H_2SO_4$ solvolyses of labeled ethyl tosylates yield unrearranged products. The *β-d* isotope effect in $H_2SO_4$, while large for solvolysis of an ethyl derivative, does not indicate important involvement of neighboring hydrogens in the rate-limiting step. Can an ionizing solvent be found that forces hydrogen participation in solvolysis of ethyl derivatives? In an effort to press this issue one step farther, we have investigated the products and isotope effects of $HSO_3F$ solvolysis of ethyl tosylate and report results of these studies here.

Hydrogen migration accompanies solvolysis of ethyl tosylate in $HSO_3F$. Solvolyses of $CH_3CD_2OTs$ in $HSO_3F$ at 0° yield measurable amounts of $CD_2HCH_2OSO_2F$ (broad doublet, $\delta$ 4.7, $J$ = 7.5 Hz). Similar solvolyses of $CD_3CH_2OTs$ yield $CDH_2CD_2OSO_2F$ (broad singlet, $\delta$ 1.3). Small but measurable amounts of rearranged reactant are also observed. Thus, recovery of unconsumed $CH_3CD_2OTs$ after 40% reaction indicates *ca.* 2% $CHD_2CH_2OTs$ (nmr). First-formed solvolysis products are not indefinitely stable. Scrambling of hydrogen within the alkyl products proceeds, increasing the amount of apparent rearrangement product with time. Almost statistical distribution of the deuterium labels is achieved before exchange of deuterium with solvent acid can be detected. Extrapolation of the rearrangement data to zero time provides a measure of the rearrangement during ethyl tosylate solvolysis (Figure 1).[3,4] The degree of rearrangement is approximately halved and the rate of solvolysis is decreased by a factor of about 15–20 by addition of $KSO_3F$ (1 *M*) to the solvent acid.

The *β-d* and the *α-d* isotope effects on solvolysis in $HSO_3F$ differ significantly from the largest reported values for solvolysis of an ethyl derivative.[5] Measurements were made by solvolyzing the reactant pairs, $CD_3CH_2OTs + CH_3CH_2OTs$ and $CH_3CD_2OTs + CH_3CH_2OTs$. Aliquots were carefully quenched in aqueous methanol at −60° and the unconsumed ethyl tosylates plus *p*-toluenesulfonyl fluoride isolated.[6] The extent of total reaction (nmr integration and/or glpc analysis of the product–reactant mixtures) and the D/H ratio (mass spectra of recovered tosylates) permitted evaluation of the kinetic isotope effects. A summary of these data is presented in Table I.

Rates of solvolysis of some alkyl tosylates in concentrated $H_2SO_4$ can be directly related to the $h_0$ function. Presumably, conjugated acids of these alkyl tosylates are the reactive species, and solvolysis involves the departure of a neutral leaving group (*p*-toluenesulfonic acid), not an anion. Consistently, the rate of solvolysis of ethyl tosylate increases by a factor of *ca.* $10^3$ on going from 96% $H_2SO_4$ to $HSO_3F$.[7] Rate retardation due to addition of $KSO_3F$ is most simply associated with a mass law effect that represses conjugate acid formation.

The rearrangements observed, both during and subsequent to solvolysis of the tosylate, must be intramolecular. Integrations of the nmr spectra show that the number of alkyl protons (three or two with respect to the three aromatic methyl protons) remains constant over more than five reactant half-lives. Thus, rearrangement during solvolysis as well as the subsequent scrambling of hydrogens in the product cannot be attributed to an elimination–addition sequence.

It is attractive to explain the observed rearrangements and the kinetic isotope-effect data, particularly the changes in isotope effect that occur upon variation of

(3) Rearrangement data were collected by allowing reaction mixtures to solvolyze at 0° with periodic quenching to *ca.* −40° to record and integrate the spectrum. A Varian A-60 was used for ROTs concentrations of about 1 *M*, and a Varian HR-220 was used for runs made with ROTs at 0.2 *M*.

(4) A considerable amount of information is derivable from the hydrogen-scrambling data as a function of reactant half-life, if it is assumed that the scrambling subsequent to solvolysis of the reactant merely represents continuing solvolysis of the product.

(5) (a) A. Streitwieser, Jr., C. L. Wilkens, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968): (b) compare values of the *α-d* isotope effects reported here with recent studies and predictions made by V. J. Shiner, Jr., M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *ibid.*, **90**, 7171 (1968).

(6) Control studies demonstrate the rapid conversion of *p*-toluenesulfonic acid to *p*-toluenesulfonyl fluoride in $HSO_3F$. Thus, the sulfonyl fluoride was used as the measure of consumed ROTs. Ultraviolet spectra of the aqueous portions of the aliquots (after extraction) showed less than 2% *p*-toluenesulfonic acid.

(7) See R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968), and references therein for discussions of relative acidity.

Table I. Kinetic Isotope Effects in Solvolysis of $CD_3CH_2OTs$ and $CH_3CD_2OTs$ in $HSO_3F$ and 96% $H_2SO_4$[a]

| Conditions | $k_H/k_{\beta\text{-}d_3}$ | $k_H/k_{\alpha\text{-}d_2}$ | $10^3k_H$,[d] sec$^{-1}$ |
|---|---|---|---|
| 96% $H_2SO_4$ at 30° (0.2 *M* ROTs) | 1.20 ± 0.03[b] | 1.18 ± 0.02[b] | 0.0155 |
| $HSO_3F + KSO_3F$ (1 *M*) at 0° (0.2 *M* ROTs) | 1.44 ± 0.05 | 1.27 ± 0.03 | 0.051 ± 0.005[e] |
| $HSO_3F$ at 0° (0.2 *M* ROTs) | 1.58 ± 0.04 | 1.30 ± 0.05 | 0.92 ± 0.06 |
| $HSO_3F$ at 0° (0.05 *M* ROTs) | 1.53 ± 0.06[c] | | 1.4 ± 0.2 |

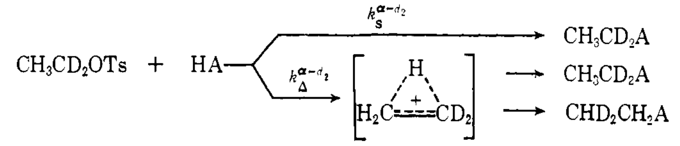
[a] Data were obtained from two or more independent runs. In each run, three to five aliquots were withdrawn at total conversions ranging from 25 to 90%. Error limits represent maximum experimental deviations. [b] Data from ref 1f. [c] Controls of the extraction procedure indicate that this value may be low due to incomplete extraction of unconsumed ROTs. [d] Rate constants reported were extracted from the competitive intermolecular isotope-effect studies; the period of time required for aliquot withdrawal represents a major source of experimental error. [e] At 25°, $k_H = 1.1 \times 10^3$ sec$^{-1}$.

Table II. Product Rearrangement Data: Derived and Estimated Rate Ratios[a]

| | $(k_\Delta/k_s)^{\alpha\text{-}d_2}$ | $(k_\Delta/k_s)^{\beta\text{-}d_3}$ | $(k_\Delta{}^H/k_\Delta{}^{\beta\text{-}d_3})^b$ |
|---|---|---|---|
| $HSO_3F$ | 0.73 | 0.42 | 2.4 |
| $HSO_3F$ + $KSO_3F$ (1 *M*) | 0.26 | 0.17 | 2.1 |

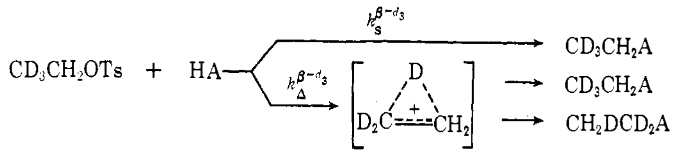
[a] Not corrected for internal return; see ref 8. [b] Reference 10.

the reaction conditions, in terms of two competing solvolysis paths, one of which involves a rate-limiting migration of a neighboring hydrogen. We represent this competition within the familiar framework that assumes an internally assisted ($k_\Delta$) and an externally (solvent) assisted ($k_s$) mode of solvolysis. The use of this scheme permits estimation of $k_\Delta/k_s$ from extrapolated rearrangement data, eq 1 and 2.[8]



(1)

$$\frac{\text{product methylene hydrogen}}{\text{product methyl hydrogen}} = \frac{k_\Delta{}^{\alpha\text{-}d_2}}{3k_s{}^{\alpha\text{-}d_2} + 2k_\Delta{}^{\alpha\text{-}d_2}} = R^{\alpha\text{-}d_2}$$



(2)

$$\frac{\text{product methyl hydrogen}}{\text{product methylene hydrogen}} = \frac{k_\Delta{}^{\beta\text{-}d_3}}{2k_s{}^{\beta\text{-}d_3} + k_\Delta{}^{\beta\text{-}d_3}} = R^{\beta\text{-}d_3}$$

The values so obtained together with estimated values of $k_\Delta{}^H/k_\Delta{}^{\beta\text{-}d_3}$ are shown in Table II. The use of this scheme leads to the conclusion that (1) $k_\Delta$ is almost as large as $k_s$ in $HSO_3F$, (2) $k_\Delta$ is markedly reduced with respect to $k_s$ upon addition of $KSO_3F$ to the solvent acid, and (3) the estimated *β-d* isotope effects for the $k_\Delta$ reaction are independent of the magnitude of the $k_\Delta/k_s$ ratio and are comparable in magnitude to related hydrogen migrations.[1g,9]

Estimated values of $k_\Delta{}^H/k_\Delta{}^{\beta\text{-}d_3}$ require the assumption of values for several rate-constant ratios. While these may well be individually in error, the errors tend to cancel in the combination used.[10] By analogous methods, the $k_\Delta{}^H/k_\Delta{}^{\beta\text{-}d_3}$ values obtained from the rearrangement data, coupled with the observed degree of rearrangement, can be used to predict the kinetic isotope effects observed (Table I). Within error limits, the agreeement is satisfactory.

Alternative explanations can be devised. Many of these cannot be rigorously excluded by the preliminary data presented here. This study does identify conditions that result in rearrangement *during* solvolysis of ethyl tosylate.[11] The kinetic isotope effects necessarily imply that appreciable force-constant changes involving both $\alpha$ and $\beta$ hydrogens occur in the rate-limiting step of this solvolysis. We assume that the large *β-d* kinetic isotope effects serve to correlate the timing of hydrogen migration with the rate-limiting step and present a scheme based on that assumption. This scheme appears internally consistent and finds support in studies of related systems.[1] If this scheme bears scrutiny, questions concerning the proper structural formulation of $C_2H_5^+$(g) assume renewed relevance.[12]

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(8) Some internal return is observed. Thus, the $k_\Delta/k_s$ ratios are more properly $Fk_\Delta/k_s$ values where *F* represents the fraction of "bridged-ion" yielding products. The available data indicate that *F* is *ca.* 0.9 or slightly larger.

(9) (a) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958); (b) V. J. Shiner, Jr., and J. G. Jewett, *J. Amer. Chem. Soc.*, **87**, 1382, 1383 (1965).

(10) We assume that $k_s{}^{\alpha\text{-}d_2}/k_s{}^{\beta\text{-}d_3}$ is very close to unity and that $k_\Delta{}^H/k_\Delta{}^{\alpha\text{-}d_2}$ is approximately 1.4; see ref 5b and 9b. Thus, $k_\Delta{}^H/k_\Delta{}^{\beta\text{-}d_3}$ may be equated to $1.4(k_s{}^{\beta\text{-}d_3}/k_\Delta{}^{\beta\text{-}d_3})(k_\Delta{}^{\alpha\text{-}d_2}/k_s{}^{\alpha\text{-}d_2})$.

(11) Compare with the rearrangement observed (1.5%) in the reaction of ethylamine-1-$^{14}C$ with nitrous acid in aqueous solution: J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952).

(12) T. Yonezawa, H. Nakatsuji, and H. Kato, *ibid.*, **90**, 1239 (1968).

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The National Science Foundation is acknowledged for their support of the HR-220 facility located at the California Institute of Technology. We thank Professor S. Winstein and Dr. A. Diaz for a number of helpful discussions and suggestions concerning this work.

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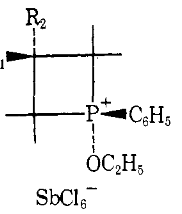
## A Test for Pseudorotation in "Pentacoordinate" Sulfur Compounds[1]

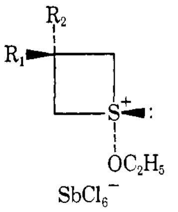
*Sir:*

That base-catalyzed hydrolysis of *cis*- and *trans*-1-ethoxy-1-phenyl-2,2,3,4,4-pentamethylphosphetanium hexachloroantimonates (**1**) proceeds with P–O cleavage and essentially complete *retention* of configuration,[2] whereas analogous acyclic ethoxyphosphonium salts undergo inversion of configuration under the same reaction conditions,[3] has been attributed[4] to pseudorotation in the intermediate cyclic phosphoranes. We wish to report our observation that *cis*- and *trans*-1-ethoxy-3-methylthietanium hexachloroantimonates (**2**) undergo base-catalyzed hydrolysis with essentially complete *inversion* of configuration, as do the acyclic, five- and six-membered ring analogs,[5] and that the contrast in behavior between the phosphorus (**1**) and sulfur (**2**) systems may be taken as evidence *against* pseudorotation in "pentacoordinate" sulfur intermediates.[6]

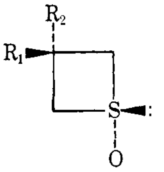
Oxidation[8] of 3-methylthietane[9] gave a mixture of *cis*- and *trans*-3-methylthietane 1-oxides (**3**) which were separated by chromatography on silica gel. The isomers, **3A** and **3B**, respectively identified as *cis* and *trans* by their characteristic[10] nmr absorption in the methylene region, had the following nmr signals: **3A**, $CH_3$, d, $\tau$ 8.75; $CH_2$, m, $\tau$ 7.35–6.85 and 6.50–6.00; CH, m, $\tau$ *ca.* 7.60; **3B**, $CH_3$, m, $\tau$ 8.72; $CH_2$, m, $\tau$ 6.70; CH, m, $\tau$ *ca.* 6.78. Since **3B** has no measurable signal downfield of $\tau$ 6.50, and since the downfield half of the methylene multiplet due to **3A** is unencumbered by interfering signals, integration of that portion of the multiplet (corresponding to two out of the total of five ring protons in **3A**) provides a convenient measure of the **3A** content of the mixture. A mixture consisting of 99% of **3A** and 1% of **3B** was O-ethylated with triethyloxonium hexachloroantimonate in dichloromethane. Base-catalyzed hydrolysis of the resulting salt (**2**) with 0.5 *M* NaOH in 50% (v/v) aqueous dioxane at room temperature afforded a mixture consisting of *ca.* 7% of **3A** and *ca.* 93% of **3B**. Ethylation of this mixture, followed by base-catalyzed hydrolysis of **2**, as described above, led to a mixture consisting of 94% of **3A** and 6% of **3B**. These experiments proved that hydroxide displaces ethoxide in **2** with ≥95% inversion of configuration at sulfur.



**1**



**2**



**3**

**A**, $R_1 = H; R_2 = CH_3$ **B**, $R_1 = CH_3; R_2 = H$

If the reaction proceeds by a direct SN2 displacement at sulfur, with the O–S–O angle near 180°, considerable angle strain is introduced by the presence of a four-membered ring. The equatorial (e) positions in the transition state, normally near 120° in the unstrained cases, are now forced to subtend an angle near 90°. However, if we assume the intermediacy of a "pentacoordinate" sulfur compound[7,11] (hemisulfoxal[12] **4**) of approximately trigonal-bipyramidal geometry,[7,13] the thietane ring comfortably spans the 90° angle subtended by the apical (a) and e positions. Starting from *cis*-**2** (**2A**), and disregarding isomers in which the thietane ring spans other than ae positions, three diastereomers of **4** (**A–C**), and their enantiomers, may be formed. Of these, **4C** represents a high-energy form since both electronegative groups occupy the unfavorable[13,14] e positions while the lone pair, whose position in $SF_4$ is equatorial,[7,13] now occupies the a position. If **4A** is first formed, only pseudorotation[15] (one step) to **4B**

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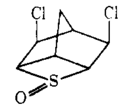
[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

[2] K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, in press.

[3] G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *ibid.*, in press; R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *Chem. Commun.*, in press.

[4] K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, in press.

[5] (a) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965); H. Hogeveen, G. Maccagagni, and F. Montanari, *J. Chem. Soc., C*, 1585 (1966). (b) It has been shown by F. Lautenschlaeger, *J. Org. Chem.*, **31**, 1679 (1966), that sulfoxide i is converted to the epimer by O-ethylation, followed by base-catalyzed hydrolysis.



i

[6] Reference is made to tetracoordinate sulfur compounds of the type $:SR_4$, and the term "pentacoordinate" is thus a misnomer. However, deliberate use of this term is nevertheless justified as a reminder of the presence of the lone pair, a phantom ligand, and to emphasize the distinction between $:SR_4$ and other compounds in which sulfur also exhibits a coordination number of four, *e.g.*, sulfones. Ligand definition thus includes a nonbonding electron pair residing in a valence orbital.[7]

[7] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[8] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

[9] F. G. Bordwell and W. A. Hewett, *ibid.*, **23**, 636 (1958).

[10] C. R. Johnson and W. O. Siegl, *Tetrahedron Lett.*, 1879 (1969).

[11] Aryl and perfluoroalkyl derivatives of $SF_4$ have been isolated and characterized: W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3058 (1962); R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962). "Pentacoordinate" sulfur compounds have been invoked as intermediates in organic reactions with less electronegative groups than fluorine as ligands: B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969), and references cited therein; *cf.* also J. Jacobus and K. Mislow, *ibid.*, **89**, 5228 (1967); W. A. Pryor and U. Tonellato, *ibid.*, **89**, 3379 (1967); G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968).

[12] The term "sulfoxal" was coined by N. J. Leonard and C. R. Johnson, *J. Amer. Chem. Soc.*, **84**, 3701 (1962), to describe "pentacoordinate" sulfur compounds of the structure $R_2S(OR)_2$.

[13] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

[14] P. C. Van der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966).

[15] F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968), and references cited therein.