excess H_2O_2 was destroyed with platinum black. Most of the methanol and water in the reaction mixture was removed on a rotary evaporator. The residue was then dried under vacuum to give a white solid (the amine oxide).

The flask containing the dry white solid was connected to a Dry Ice–acetone trap by means of a stopcock adapter. The system was evacuated to <0.3 mm. The flask containing the solid was then heated slowly to 150° and kept at this temperature until no further material distilled from the flask. The distillate in the trap was transferred to a separatory funnel with 120 ml of ether. The ether solution was extracted three times with 30-ml portions of 1 *N* HCl. The aqueous acid extracts were combined and extracted once with 50 ml of ether. The ether solutions were combined, extracted twice with 20-ml portions of saturated aqueous $NaHCO_3$ solution, and dried over $MgSO_4$. The solution was filtered and stripped of solvent. The reaction mixture was purified by column chromatography with silica gel as the solid phase and 15% ether–85% hexane (by volume) as the eluent. A mass spectrum of the purified product had the correct parent at *m/e* 124. *Anal.* Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.19; H, 9.52.

That the product possessed the correct structure was shown by the following chemical tests. Approximately 75 mg of the product was stirred with 0.5 g of MnO_2 in 5 ml of $CHCl_3$ for 48 hr at room temperature. The mixture was filtered and the solvent removed under aspirator vacuum distillation. The infrared spectrum of this product had a strong absorption at 1660 cm^{-1}, indicating than an α,β-unsaturated ketone was present and consequently that the starting material was an allylic alcohol. The position and stereochemistry of the hydroxyl group was proved by hydrogenation over platinum and subsequent Jones oxidation[8] of the purified pyrolysis product. The hydrogenation product was *cis*-7 and not *trans*-7, as indicated by comparison with an authentic sample (ir spectrum and vpc retention time with 20 ft × 1/8 in. 12% Carbowax on Chromosorb G column). The ketone obtained after Jones oxidation was **4** (verified by vpc retention time and ir analysis). Prominent infrared absorptions (cm^{-1}) of *cis*-**1** are as follows: 3350 (s), 3010 (m), 2870 (m), 2720 (w), 1650 (w), 1465 (m), 1040 (s), and 990 (s). The nmr spectrum ($CDCl_3$) consisted of δ 0.1 (m, 2, cyclopropane ring), 1.5 (m, 6, cyclopropane and cycloheptane ring), 3.2 (s, 1, OH), 4.2 (m, 1, CHO), and 5.7 (m, 2, alkenic protons).

cis*-Bicyclo[5.1.0]oct-4-en-3-yl tosylate** (cis*-1-OTs**) was prepared by Tipson's method.[13] Though not crystalline, the material was pure by nmr spectroscopy. The tosylate was subjected to buffered acetolysis for 14 hr at 45°[3] and analyzed by the procedures previously described (acetates → unsaturated alcohols → saturated alcohols → ketone). The products from this solvolysis were identified as the *cis*- and *trans*-bicyclo[5.1.0]-oct-2-en-4-yl acetates.

Bicyclo[5.1.0]octan-2-one (**6**) was obtained by the method of Scheme II. Since the material is not related to any described in this study, the details have been recorded elsewhere.[11]

***cis*-Bicyclo[5.1.0]octan-3-ol** (*cis*-**7**) was obtained by hydrogenation of *cis*-bicyclo[5.1.0]oct-5-en-3-ol[2] over the Adams catalyst (hydrogenated PtO_2). This catalyst was found not to open the three-membered ring, whereas palladium on charcoal gave considerable ring opening. Cope, *et al.*,[4] prepared the identical material by a different route.

Bicyclo[5.1.0]octan-3-one (**4**) was prepared by the Jones oxidation[8] of *cis*-**7**. This material was identical with that prepared by Cope, *et al.*[4]

Registry No.—*cis*-**1**, 32675-19-7; *cis*-**1** tosylate, 31026-60-5; **4**, 32675-20-0; 4-pyrrolidinobicyclo-[5.1.0]octan-3-ol, 32675-21-1.

The Persistence of the 1-Axial Preference in Thianes

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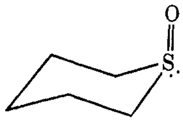
The axial preference of the oxide in thiane 1-oxide and of the imide in thiane 1-(*N*-tosyl)imide is reversed in the presence of a 3,3-dimethyl group, because of the syn-axial interaction. In protonated 3,3-dimethylthiane, however, the 1 proton persists in the axial position, despite the syn-axial interaction. The 4,4-dimethyl derivatives of the 1-oxide, the 1-(*N*-tosyl)imide, and the protonated form all have the normal 1-axial preference. 4,4-Dimethylthiane 1-oxide 1-imide and its *N*-tosyl derivative have also been examined and found to exist as two conformers.

A curious property of the thiane system is the preference of certain 1 substituents for the axial position. Thus in thiane 1-oxide (**1**),[2] thiane 1-(*N*-tosyl)imide (**2**),[3] and protonated thiane (**3**),[4] the 1-axial conformation is favored, respectively, by 175 cal/mol (−90°), 145 cal/mol (−89°), and >1500 cal/mol (−30°). An attractive interaction between the 1 substituent and the 3,5-axial protons has been invoked to explain this unusual preference for the case of the 1-oxide.[5] The preference must be unrelated to similar observations recently reviewed in terms of the "gauche effect,"[6] of which the anomeric effect is one example, since interactions between two polar bonds are the determining factor in these systems.



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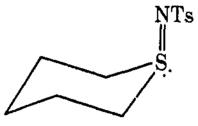

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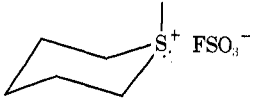

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If the 1-axial preference is caused by an attractive 1,3 interaction, replacement of a 3-axial proton by a methyl group should make the interaction repulsive (or less attractive) and decrease the proportion of the 1-axial isomer. We have previously used this technique to explore the NH axial preference in piperidine[7] and the methyl–halogen syn-axial interaction in the 1-halo-

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[1] (a) This work was supported by the National Science Foundation (Grants GP-9257 and GP-22942) and the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4,5). (b) National Science Foundation Trainee, 1968–1969.

[2] J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).

[3] J. B. Lambert, C. E. Mixan, and D. S. Bailey, *Chem. Commun.*, 316 (1971).

[4] J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Amer. Chem. Soc.*, **89**, 5921 (1967).

[5] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, **91**, 337 (1969).

[6] S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971).

[7] J. B. Lambert, D. S. Bailey, and B. F. Michel, *Tetrahedron Lett.*, 691 (1970).

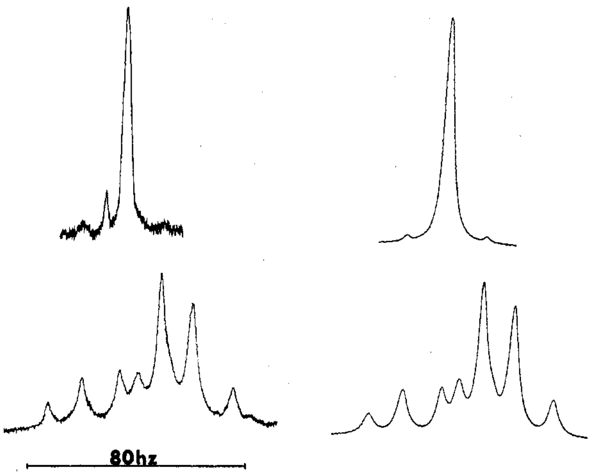
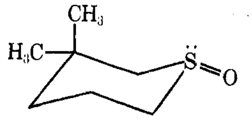


Figure 1.—The observed (left) and calculated 90-MHz spectra of the 6α protons of 4,4-dimethylthiane-*2,2,5,5*-d_4 1-oxide (**7**-d_4) in $CHClF_2$ at 30° (upper) and −90°. The small impurity peak visible to the left of the 30° spectrum is due to the sulfone.

3,3-dimethylcyclohexanes.[8] In piperidine, the proportion of the NH-equatorial isomer is increased, and in the halocyclohexanes the proportion of equatorial halogen is raised in an increasing fashion in the order F < Cl < Br < I.

To explore the reasons for the axial preferences in the thiane series, we have prepared the 3,3-dimethyl derivatives of thiane 1-oxide (**4**), thiane 1-(*N*-tosyl)imide (**5**), and protonated thiane (**6**). We find that the oxide and imide become all (>95%) equatorial, but that the protonated compound remains in the axial conformation. As models for assessing the effect of a geminal dimethyl grouping, the 4,4-dimethyl derivatives **7–9** have also been prepared. These compounds maintain a predominance of the 1-axial isomer. We have also examined the sulfoximides **10** and **11** to determine whether oxide or imide has the greater preference for the axial position.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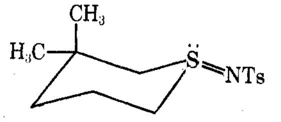
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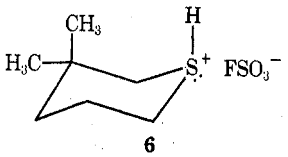
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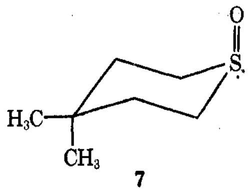
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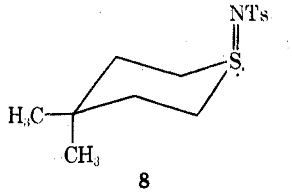
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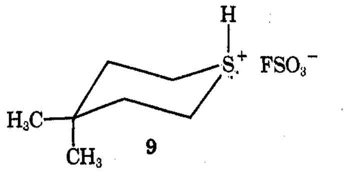
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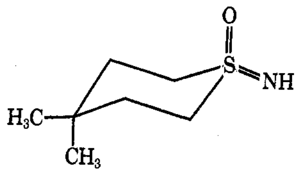
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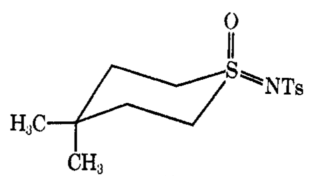
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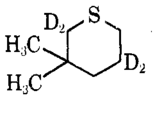
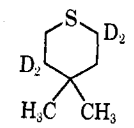
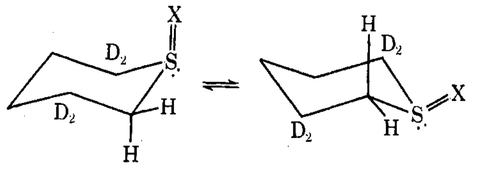
Synthesis.—3,3-Dimethylthiane (**12**) and 4,4-dimethylthiane (**13**) are the sources of all eight compounds under study (**4–11**). To assign the configuration of the 1 substituent, chemical-shift and coupling-constant data must be obtained for the α protons[2-4] (*vide infra*). There are two different sets of α protons (2 and 6) in the 3,3-dimethyl case. Only the unperturbed set on the side opposite the methyl groups (the 6 protons) gives unambiguous shielding information. To isolate the α protons from coupling to the β protons and to remove the 2α protons for the 3,3-dimethyl case, the deuterated derivatives **12**-d_4 and **13**-d_4 are required. Both compounds come from the same synthetic route, outlined in Scheme I. The 3,3-dimethyl- and 4,4-dimethylthianes were separated by preparative gas chromatography. The alterations of the functionality at sulfur are illustrated for the 4,4-dimethyl series in Scheme II.


12-d_4


13-d_4

Results and Discussion

The Oxides and the Imides.—The two possible conformers, with methyl substitution omitted, are given by the structures in eq 1. In the 4,4-dimethyl series, both forms are present at equilibrium for both the oxide **7**-d_4 and the imide **8**-d_4, since the α-proton resonance consists of two AB spectra at −90° (Figure 1). The AB quartet from the isomer with the oxide or imide group equatorial (lone pair axial) has been found always to have the larger chemical-shift difference [$\delta_{ae}(\alpha)$], the smaller coupling constant [$J_{ae}(\alpha)$], and the lower field centerpoint.[2,3,9]


(1)

In the spectrum (Figure 1) for 4,4-dimethylthiane 1-oxide (**7**) at −90°, peaks 1, 2, 4, and a shoulder on the right side of peak 5 correspond to the equatorial-oxide isomer, whereas peaks 3, 5, 6, and 7 correspond to the axial-oxide isomer. Configuration was assigned by the

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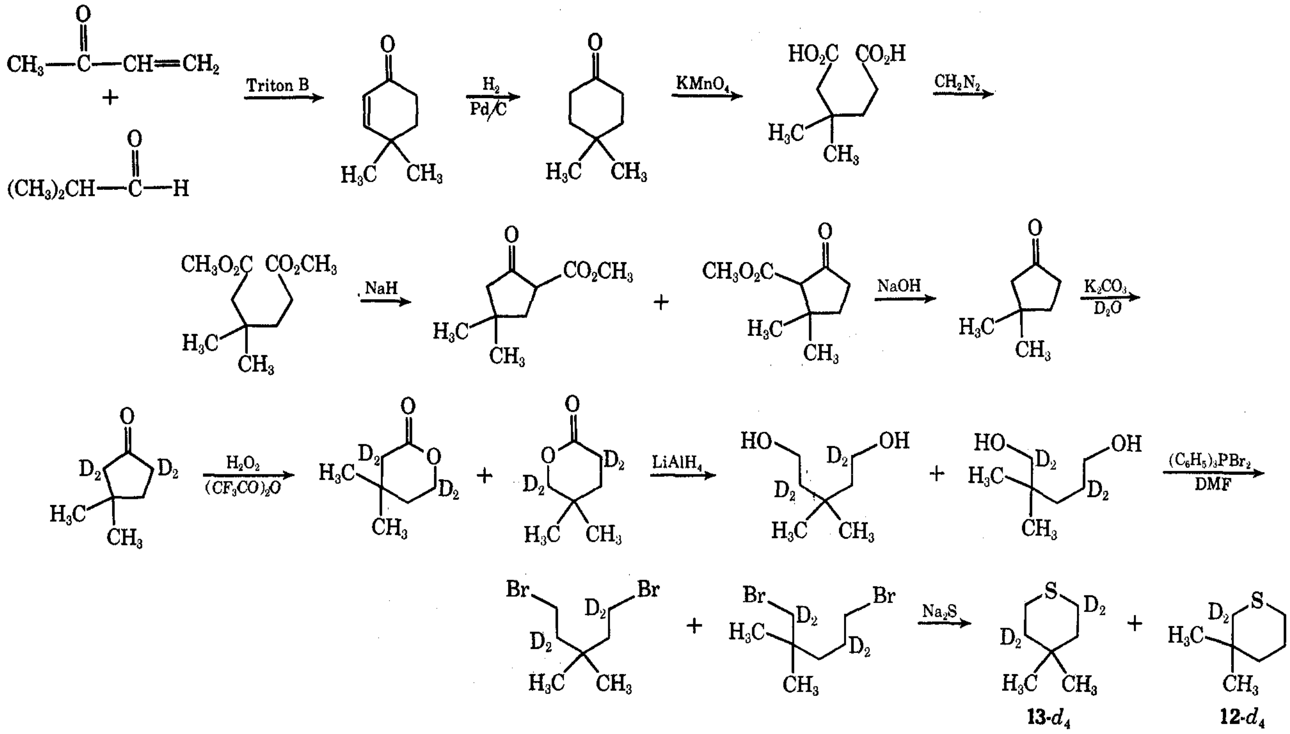
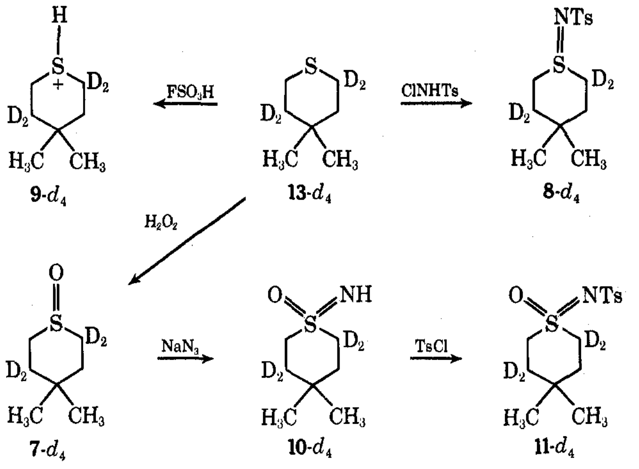
[8] D. S. Bailey, J. A. Walder, and J. B. Lambert, *J. Amer. Chem. Soc.*, **94**, 177 (1972).

[9] (a) J. B. Lambert, C. E. Mixan, and D. S. Bailey, *ibid.*, **94**, 208 (1972); (b) A. B. Foster, T. D. Inch, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 1086 (1968); (c) R. R. Fraser and F. J. Schuber, *Can. J. Chem.*, **48**, 633 (1970); (d) B. J. Hutchinson, K. K. Andersen, and A. R. Katritzky, *J. Amer. Chem. Soc.*, **91**, 3839 (1969); (e) D. H. R. Barton, F. Comer, and P. G. Sammes, *ibid.*, **91**, 1529 (1969); (f) Y. Allingham, R. C. Cookson, and T. A. Crabb, *Tetrahedron*, **24**, 1989 (1968); (g) P. J. Chivers and T. A. Crabb, *ibid.*, **26**, 3389 (1970).

SCHEME I



SCHEME II



above criteria, and the populations were determined during the process of spectral fitting. The chemical-shift, coupling-constant,and population data are listed in Table I. The axial-oxide isomer predominates by a 70:30 ratio at −90°, compared to 62:38 in the unmethylated compound.[2]

4,4-Dimethylthiane 1-(*N*-tosyl)imide (**8**) gives a very similar spectrum, and the axial-imide isomer was found to predominate by 73:27 ratio (Table I), compared to 60:40 in the unmethylated compound.[3] One anomaly is noted in the spectrum, since $\delta_{ae}(\alpha)$ is smaller for the equatorial than for the axial isomer. The 4-axial methyl group is expected to have this kind of shielding effect on the α protons.[10] Thus, $\delta_{ae}(\alpha)$ is sensitive not only to the configuration at sulfur but also to substitution elsewhere in the molecule. The criterion is quite reliable in molecules unsubstituted except at the 1 position, but introduction of substituents elsewhere can lead to extraneous effects on $\delta_{ae}(\alpha)$. The coupling-constant criterion is not subject to this limitation; so it is reliable for any kind of substitution. Henceforward in this paper we will use the coupling-constant criterion exclusively.

As the temperature is raised, the axial and equatorial forms of **7** and **8** interconvert more rapidly (eq 1), so that the spectrum at room temperature represents an average for the two conformers (Figure 1).

The β-proton resonances of **7** and **8** have also been analyzed (Table II). The only important points to note are that the proportions agree with those from the α resonances (Table I) and that $J_{ae}(\beta)$ is normal (~14 Hz). For the α protons, J_{ae} is normal when the lone pair is equatorial, but small (~12 Hz) when the lone pair is axial (oxide or imide equatorial). The fact that $J_{ae}(\beta)$ for both isomers in eq 1 is the same as $J_{ae}(\alpha)$ for the axial-oxide or -imide isomer demonstrates that a vicinal axial lone pair is required for observation of the "abnormal" 12-Hz coupling.[2,3,9]

In contrast to the 4,4-dimethyl cases, the low-temperature spectra of 3,3-dimethylthiane 1-oxide (**4**) and 3,3-dimethylthiane 1-(*N*-tosyl)imide (**5**) show only a single AB quartet for the α protons, indicative of the presence of only one isomer. A second AB quartet could not be found even at high gain. For the oxide, $J_{ae}(\alpha)$ is 12.0 Hz from room temperature to −110°; for the imide, $J_{ae}(\alpha)$ is 12.4 Hz from room temperature to −80° (Table I). Since these coupling constants are "abnormal," the AB spectrum is attributed to the equatorial isomer (axial lone pair) for both the oxide and the imide. The AB quartet does not collapse to an A_2 spectrum at higher temperatures because only one form is present. The constancy of $J_{ae}(\alpha)$ with temperature is a further indication that the equatorial isomer is present exclusively (>95%). The spectra of the γ protons have also been analyzed for both compounds (Table II).

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[10] H. Booth, *Tetrahedron*, **22**, 615 (1966).

TABLE I

SPECTRAL PARAMETERS FOR THE α PROTONS OF THE *gem*-DIMETHYL DERIVATIVES OF THIANE 1-OXIDE AND THIANE 1-(*N*-TOSYL)IMIDE[a]

	7	**8**	**4**	**5**	**1**[b]	**2**[b]
$\delta_{ae}(\alpha)$	30.8	6.0	94.0[c]	46.0	78.3[d]	33.2
$\lvert J_{ae}(\alpha)\rvert$	12.4	12.5	12.0	12.4	11.7	12.0
Pop.	0.30	0.27	>0.95	>0.95	0.38	0.40
$\delta_{ae}'(\alpha)$	21.0	15.4	*e*	*e*	43.2[d]	2.0
$\lvert J_{ae}'(\alpha)\rvert$	14.9	14.8			13.7	14.4
Pop.′	0.70	0.73			0.62	0.60
Solvent	$CHClF_2$	CH_2Cl_2–$CHClF_2$	$CHClF_2$	CH_2Cl_2–$CHClF_2$	CH_2Cl_2	$CHClF_2$
Temp, °C	−90	−90	−90	−80	−90	−89
$\Delta G°$, kcal/mol[f]	−305	−360	>+1300	>+1300	−175	−145

[a] All chemical-shift differences are in hertz at 90 MHz, and coupling constants are in hertz; δ, J, and Pop. (population) refer to the lower field (equatorial) isomer; δ', J', and Pop.′ refer to the higher field (axial) isomer. [b] Data from ref 2 and 3. [c] The magnitude of $\delta_{ae}(\alpha)$ for **4** is temperature dependent (73.5 Hz at 35°), but $J_{ae}(\alpha)$ is constant. [d] Data from 60 MHz converted to 90 MHz. [e] The axial isomer was not observed. [f] A positive sign for $\Delta G°$ denotes an excess of equatorial oxide or imide.

TABLE II

SPECTRAL PARAMETERS FOR THE β AND γ PROTONS OF THIANE 1-OXIDE, THIANE 1-(*N*-TOSYL)IMIDE, AND THEIR *gem*-DIMETHYL DERIVATIVE[a]

	7	**8**	**4**	**5**	**1**[b]	**2**[b]
$\delta_{ae}(\beta)$	62.0	73.0	*c*	*c*	*c*	*c*
$\lvert J_{ae}(\beta)\rvert$	14.3	14.4				
Pop.	0.70	0.73				
$\delta_{ae}'(\beta)$	3.6	7.0				
$\lvert J_{ae}'(\beta)\rvert$	14.0	14.4				
Pop.′	0.30	0.27				
$\delta_{ae}(\gamma)$	*d*	*d*	8.35	11.0	30.6[e]	40.0
$\lvert J_{ae}(\gamma)\rvert$			14.8	13.6	14.0	14.4
Pop.			>0.97	>0.97	0.62	0.60
$\delta_{ae}'(\gamma)$			*f*	*f*	36.2[e]	41.6
$\lvert J_{ae}'(\gamma)\rvert$					14.3	14.2
Pop.′					0.38	0.40

[a] All chemical-shift differences are in hertz at 90 MHz, and coupling constants are in hertz; δ, J, and Pop. refer to the lower field isomer; δ', J', and Pop.′ refer to the higher field isomer; the solvents and temperatures are given in Table I. [b] Data from ref 2 and 3. [c] No data on the β protons are available. [d] No data on the γ protons are available. [e] Data from 60 MHz converted to 90 MHz. [f] Only one isomer is observable.

Again, in both cases only one AB quartet is found over the entire temperature range and $J_{ae}(\gamma)$ is normal.

From the data in Table I, it is seen that the 4,4-dimethyl oxide and imide have an even greater proportion of the axial isomer than do the unmethylated compounds. The quaternary carbon at position 4 is puckered from the normal position because the C(3)–C(4)–C(5) angle is reduced. As a result, the 3- and 5-axial protons are bent away from the 1 position, thereby permitting a larger proportion of axial oxide or imide. This effect has also been observed in the 1-halo-4,4-dimethylcyclohexanes.[8] The increase in the proportion of the 1-axial conformer thus seems to be general for molecules with the 4,4-dimethyl grouping.

Introduction of the *gem*-dimethyl grouping at the 3 position, on the other hand, completely obliterates any axial isomer. The syn-axial interaction between the methyl group and the oxide or imide must be greater than 2 kcal/mol to reverse the preference so drastically.

Protonated Thianes.—Thiane is readily protonated in FSO_3H–SO_2.[4] The solution is indefinitely stable at room temperature, but spectra must be taken below −20° in order to slow down exchange of the proton on sulfur. For the parent, unmethylated compound (β deuterated), the resonance for the S proton is a triplet of triplets, with the 1,2-vicinal couplings analyzed to be $J_{H_{ax}CSH}$ = 14.1 Hz and $J_{H_{eq}CSH}$ = 2.3 Hz. A considerable volume of data is available that attests to the fact that H–X–C–H couplings follow a Karplus-like curve.[11] The 14.1-Hz vicinal coupling therefore requires that the proton on sulfur be axial. No resonances were observed for the equatorial isomer.

4,4-Dimethylthiane-*2,2,6,6*-d_4 was dissolved in FSO_3H–SO_2 and the proton spectrum of **9**-d_4 was examined at −40° and 90 MHz. The 3β proton was a closely coupled AB quartet, $\delta_{ae}(\beta)$ = 21 Hz, $J_{ae}(\beta)$ = 15.3 Hz. The 6α resonance consisted of an AB quartet distorted to ABX by coupling with the proton on sulfur (Figure 2). Analysis of the three-spin system gave $\delta_{ae}(\alpha)$ = 9 Hz, $J_{ae}(\alpha)$ = 15.0 Hz. The 4-axial methyl group, as noted before, decreases $\delta_{ae}(\alpha)$.[10] The S–H resonance was a second-order quartet (the X part of the ABX spectrum), from which were obtained $J_{H_{ax}CSH}$ = 12.7 Hz and $J_{H_{eq}CSH}$ = 5.2 Hz. The value of 12.7 Hz for the vicinal coupling requires that the proton on sulfur be in the axial position. The normal value of the geminal coupling, $J_{ae}(\alpha)$ = 15.0 Hz, further indicates that the lone pair is equatorial. No resonances were discernible for an equatorial isomer. Since a 4,4-dimethyl grouping is known to enhance the proportion of a 1-axial substituent, this result is fully expected.

The spectrum of 3,3-dimethylthiane-*2,2,5,5*-d_4 in FSO_3H–SO_2 (**6**-d_4) at −40° resembled very closely that of **9**-d_4. The γ resonance was an AB quartet, $\delta_{ae}(\gamma)$ = 9.5 Hz, $J_{ae}(\gamma)$ = 14.8 Hz, and the α resonance (Figure 3) was the AB part of an ABX spectrum, $\delta_{ae}(\alpha)$ = 29 Hz, $J_{ae}(\alpha)$ = 14.5 Hz. The S-proton resonance again was a quartet, from which were obtained $J_{H_{ax}CSH}$ = 13.7 Hz and $J_{H_{eq}CSH}$ = 2.5 Hz. The 13.7-Hz coupling again requires that the proton on sulfur be axial. The normal value of $J_{ae}(\alpha)$, 14.5 Hz, reinforces this assignment. The axial preference (**6**) therefore persists even in the presence of a 3-axial methyl group. The syn–axial CH_3–H interaction must not force the proton into the equatorial position, as occurred for the oxide **4** and the imide **5**. According to the currently accepted interpretation,[4,5] the interaction between the S proton and the 3-axial methyl group must in fact be attractive to maintain the axial preference. The longer

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[11] See, *inter alia*, H. Booth and R. U. Lemieux, *Can. J. Chem.*, **49**, 777 (1971); R. R. Fraser, M. Kaufman, P. Morand, and G. Govil, *ibid.*, **47**, 403 (1969); J. B. Lambert, W. L. Oliver, Jr., and G. F. Jackson, III, *Tetrahedron Lett.*, 2027 (1969).

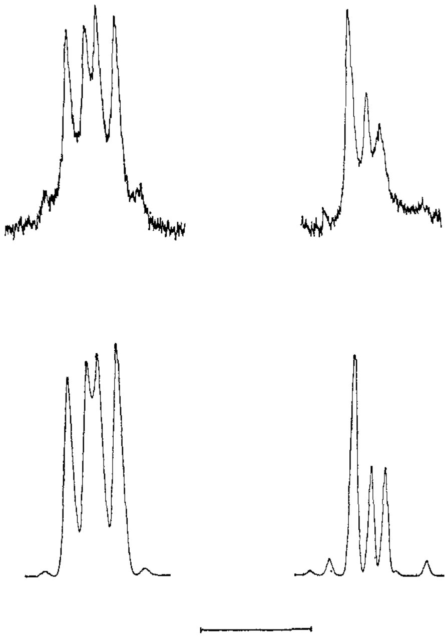

Figure 2.—The observed (upper) and calculated 90-MHz spectra for the 6α protons (right) and the S proton of 4,4-dimethylthiane-*2,2,5,5*-d_4 (9-d_4) in FSO_3H-SO_2 at −40°. The gain is different for the two resonances; so the 2:1 ratio is not reproduced. The calibration bar represents 40 Hz.

C–S bond permits such a diaxial arrangement without the onset of a repulsive interaction. Classical calculations[8] show that the CH_3–H syn–axial interaction is attractive almost to the distances of carbocyclic systems. Replacement of H by a larger and more electronegative atom such as F, O, or N makes the interaction much more repulsive.[8] Thus the CH_3-oxide and CH_3-imide interactions in **4** and **5** must be sufficiently repulsive to give the equatorial preference. These experiments demonstrate the rather impressive preference that the 1 proton has for the axial position.

Sulfoximides.—Because sulfoximides are readily prepared from sulfoxides (Scheme I), we have also examined 4,4-dimethylthiane-*2,2,5,5*-d_4 1-oxide 1-imide (**10**) and its *N*-tosyl derivative (**11**). Insufficient material was available for examination of the 3,3-dimethyl series. The spectrum of the α protons of **10** at −105° consists of two AB spectra (Figure 4). The AB quartets average to a single AB at room temperature by rapid ring reversal. The β protons exhibit only a single AB quartet at −105°, presumably by accidental superposition. The spectral data are collected in Table III. The population ratio is 55:45 at −105°. No comparison can be made with the unmethylated sulfoximide, because the parent compound gave no equilibrium data.[9a] The ratio is therefore the first measured for a simple sulfoximide. We hypothesize that the favored conformation has an axial oxide and an equatorial imide, because thiane 1-oxide is 62% axial oxide and thiane 1-imide is 55% equatorial imide.

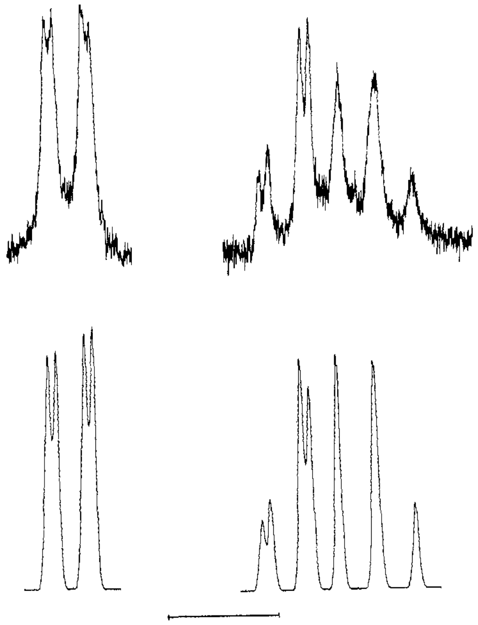

Figure 3.—The observed (upper) and calculated 90-MHz spectra for the 6α protons (right) and the S proton of 3,3-dimethylthiane-*2,2,5,5*-d_4 (6-d_4) in FSO_3H-SO_2 at −40°. The calibration bar represents 40 Hz.

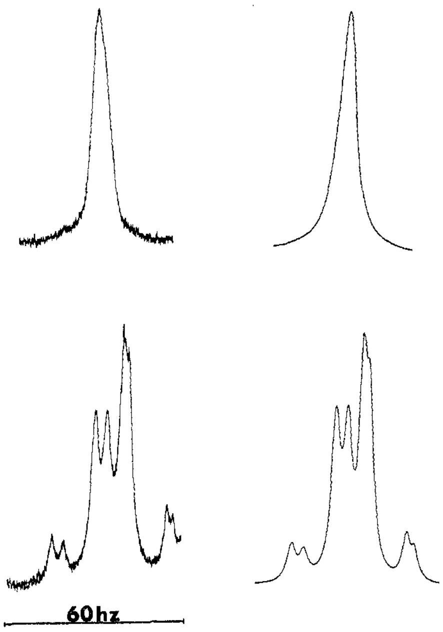

Figure 4.—The observed (left) and calculated 90-MHz spectra of the 6α protons of 4,4-dimethylthiane-*2,2,5,5*-d_4 1-oxide 1-imide (10-d_4) in $CHClF_2$ at 30 (upper) and −90°.

4,4-Dimethylthiane-*2,2,5,5*-d_4 1-oxide 1-(*N*-tosyl)-imide (**11**) exhibits a low-temperature α resonance similar to that of **10**. The data for the two AB quartets are given in Table III. It is noted that all the values of $J_{ae}(\alpha)$ for **10** and **11** are normal, *i.e.*, close to 14 Hz. Sulfoximides have no sulfur lone pair, and it is an axial lone pair that is the cause of the abnormally low values observed for sulfoxides and sulfimides.[3,9] For the *N*-tosylimide **11**, the β protons also give two AB quartets at −85° (Table III). The populations corroborate those determined from the α resonances. The isomer ratio of 62:38 compares to 67:33 for the unmethylated case.[9a] We believe that the *N*-tosylimide group in **11** is equatorial and oxide axial, because the imide group generally has a lower axial preference than the oxide. This point is by no means certain.

Conclusions

We have found that a 3,3-dimethyl grouping on thiane 1-oxide and thiane 1-(*N*-tosyl)imide reverses a slight preference of the 1 substituent for the axial position in the unmethylated compounds to a complete

TABLE III

SPECTRAL PARAMETERS FOR THE α, β, AND γ PROTONS IN SULFOXIMIDES[a]

	10	**11**	**14**[b]	**15**[b]
$\delta_{ae}(\alpha)$	18.6	45.4	*c*	74.8
$J_{ae}(\alpha)$	14.6	14.4		13.7
Pop.	0.55	0.62		0.67
$\delta_{ae}'(\alpha)$	16.4	19.8		47.6
$J_{ae}'(\alpha)$	14.8	13.5 ± 1[d]		14.8
Pop.′	0.45	0.38		0.33
$\delta_{ae}(\beta,\gamma)$	27.0[e,f]	26.4[f]	40.5[e,g]	40.2[g]
$J_{ae}(\beta,\gamma)$	14.6	14.4	14.1	14.8
Pop.		0.62		0.33
$\delta_{ae}'(\beta,\gamma)$	27.0[e]	15.4	40.5[e]	45.2
$J_{ae}'(\beta,\gamma)$	14.6	14.0	14.1	14.4
Pop.′		0.38		0.67
Solvent	$CHClF_2$	CH_2Cl_2–$CHClF_2$	CH_2Cl_2	$CHClF_2$
Temp, °C	−85	−85	−85	−89
$\Delta G°$, kcal/mol	±75	±180	*h*	±250

[a] See footnote *a*, Table II. [b] Data from ref 9a. [c] The α resonance of **14** remains a broad singlet down to −89°.[9a] [d] Due to peak overlap, this quantity could not be measured accurately. [e] Only one AB quartet is observed, so both isomers must have the same parameters. [f] Parameters for β protons. [g] Parameters for γ protons. [h] An equilibrium constant is not measurable.[9a]

preference for the equatorial position. In protonated thiane, however, the 3,3-dimethyl grouping has no effect on the strong preference of the proton on sulfur for the axial position. The original 1-axial preferences of the proton, the oxide, and the imide in the parent systems are due to attractive interactions with the 3,5-axial protons. Replacement of one of these protons with a methyl group gives rise to a sufficiently repulsive interaction with the 1-axial substituent to make the oxide and the imide prefer the equatorial position. For the protonated case, the syn–axial interaction between the methyl group and the S proton must still be attractive since the 1-axial preference persists. The long C–S bonds and the small size of the 1 proton makes this example unique in our studies of 3,3-dimethyl ring systems.

Experimental Section

Infrared spectra were measured on a Beckman IR-5. Routine nmr spectra were recorded on Varian T-60 and A-60 spectrometers. Low-temperature experiments were carried out on the Bruker HFX-10 at 90 MHz.[12] Computer analyses were performed on a CDC-6400 with Calcomp plotting accessories. Elemental analyses were executed by Miss H. Beck, Analytical Services Laboratory, Department of Chemistry, Northwestern University.

1,5-Dibromo-2,2-dimethylpentane-*1,1,4,4-d*$_4$ and 1,5-Dibromo-3,3-dimethylpentane-*1,1,4,4-d*$_4$.—The preparation of these compounds as a mixture has been described in a previous paper in this series.[13]

3,3-Dimethylthiane-*2,2,5,5-d*$_4$ (12) and 4,4-Dimethylthiane-*2,2,5,5-d*$_4$ (13).[2]—To a 100-ml, round-bottomed flask equipped with a heating mantle, a magnetic stirrer, and a reflux condenser and containing 3.0 g of sodium sulfide nonahydrate in 30 ml of refluxing 50% aqueous ethanol, was added (separately) 3.5 g of the dibromodimethylpentane mixture and 3.0 g of sodium sulfide nonahydrate in 30 ml of 50% ethanol. The mixture was refluxed for 3.5 hr. The thianes were distilled along with the ethanol from the reaction mixture, extracted into CH_2Cl_2, washed twice with H_2O, and dried ($MgSO_4$). The CH_2Cl_2 was removed by distillation, leaving the thianes as a residue. The isomeric thianes (in a 70:30 ratio favoring the 4,4 isomer) were preparatively separated on a 7 ft × 0.25 in. 12% Carbowax 20M on Chromasorb G-DMCS-AW 60/80 at 130° and 70 ml/min. The products were identical with known materials.[14]

Protonated Dimethylthianes (6, 9).[4]—About 100 mg of the deuterated thiane was placed in the bottom of an nmr tube. Three times this volume of freshly distilled FSO_3H and of SO_2 were placed in the tube, which was then sealed. The nmr spectra were recorded at −40°.

The oxides (4, 7), the imides (5, 8), and the sulfoximides (10, 11) were prepared as outlined in Scheme II by methods reported in detail for the unsubstituted series.[9a] The oxides (4, 7) and the sulfoximide **10** were extremely hygroscopic, so good elemental analyses and melting points were not obtained. The structures are not in doubt because of their nmr spectra and because the derivative *N*-tosylsulfoximide (**11**) gave good analytical results.

3,3-Dimethylthiane 1-(*N*-tosyl)imide (5) had mp 172–173°. *Anal.* Calcd for $C_{14}H_{21}NO_2S_2$: C, 56.18; H, 7.02; N, 4.68. Found: C, 55.72; H, 7.20; N, 4.55.

4,4-Dimethylthiane 1-(*N*-tosyl)imide (8) had mp 185–186°. *Anal.* Calcd for $C_{14}H_{21}NO_2S_2$: C, 56.18; H, 7.02; N, 4.68. Found: C, 55.81; H, 7.20; N, 4.70.

4,4-Dimethylthiane 1-oxide 1-(*N*-tosyl)imide (11) had mp 183–184°. *Anal.* Calcd for $C_{14}H_{21}NO_3S$: C, 53.33; H, 6.67; N, 4.44. Found: C, 53.26; H, 6.77; N, 4.36.

Registry No.—**4**, 31815-13-1; **5**, 31815-14-2; **7**, 31815-15-3; **8**, 31815-16-4; **10**, 31815-17-5; **11**, 31815-18-6.

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(12) We thank the National Science Foundation for an equipment grant to purchase signal-averaging accessories for the HFX-10.

(13) J. B. Lambert, D. S. Bailey, and B. F. Michel, submitted.

(14) L. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, **74**, 2885 (1952).