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Conformational Analysis. 35. *S*-Alkylthianium Salts[1,2]

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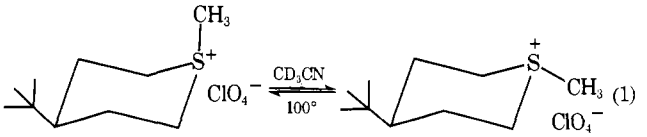
Abstract: *S*-Methylthianium hexafluorophosphates or perchlorates (34) were synthesized by methylation of thiane, 2-, 3-, and 4-methylthiane, *cis*- and *trans*-2,6-, -3,5-, -2,5-, -2,4-, and -3,4-dimethylthiane, 3,3- and 4,4-dimethylthiane, 3,3,5-, 2,4,4-, and 2,2,4-trimethylthiane, and 4-*tert*-butylthiane. Of these 20 thianes, 15 gave diastereomeric pairs of thianium salts and all but one (*trans*-*S*,3,3,5-tetramethylthianium) were obtained though not always in pure form. Also obtained were *S*-phenyl- and *S*-benzylthianium fluoroborate, the diastereomeric 4-*tert*-butyl- and 2,6-dimethyl-*S*-benzylthianium fluoroborates, 4-*tert*-butyl-*S*-ethylthianium perchlorates and the four *S*-methyl-*cis*- and -*trans*-1-thiadecalinium hexafluorophosphates or perchlorates. The position of equilibrium, attained thermally, of a number of diastereomeric *S*-methyl, *S*-ethyl, and *S*-benzylthianium salts was studied as a function of ring substitution. $-\Delta G^\circ$ for ^+S-Me is 0.0–0.3 kcal/mol (apparently depending on temperature, suggesting $\Delta S^\circ \approx 1.5$ Gibbs), for ^+S-Et 0.66 ± 0.06, for ^+S-CH_2Ph 0.82 ± 0.08 kcal/mol. Buttressing by one equatorial methyl group at C(2) boosts $-\Delta G^\circ$ for ^+S-Me to 0.6, two such groups [at C(2) and C(6)] enhance it to 1.0 kcal/mol; the ^+S-CH_2Ph value is enhanced to 1.5 kcal/mol by two such methyl groups. Substantial buttressing of axial Me(2) by equatorial ^+S-Me was also observed, and an earlier reported enhancement of the proportion of axial ^+S-Me by geminal 4,4-dimethyl was confirmed, though its origin may be different from that postulated. Conformational equilibria of several of the above *S*-methylthianium salts were also measured by low-temperature NMR and/or averaged chemical shifts employing model compounds.

The conformational energy ($\Delta G^\circ_{\text{axial} \rightleftharpoons \text{equatorial}}$) of the methyl group in methylcyclohexane, −1.7 kcal/mol, is one of the longest known[3] and most thoroughly studied[4,5] parameters in conformational analysis which still commands interest.[6,7] Much less is known about corresponding conformational energies in 1-methylheterocyclohexanes, although the values for 1-methylsilacyclohexane (0.0[8a] or 0.2[8b] kcal/mol), *P*-methylphosphacyclohexane (−0.68 kcal/mol[9]), and *N*-methylpiperidine[10,11] (−3.0 kcal/mol[11]) have recently been determined. Compounds of this type are of particular interest in connection with the recent postulate of Wertz and Allinger[12,13] that the large preference for the equatorial conformation in methylcyclohexane is due not so much to axial methyl/syn-axial hydrogen repulsion, but to the interaction of four vicinal gauche hydrogen atoms with the methine hydrogen of the axial conformer as compared to only two such interactions in the equatorial.

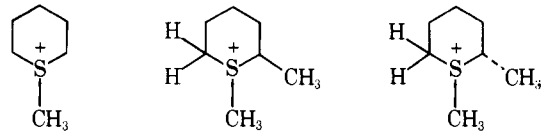
In this connection we have reported, in a preliminary com-

munication,[14] the conformational equilibrium of the *S*-methyl group in an anancomeric[15] (conformationally biased) *S*-methylthianium salt (eq 1). For this compound, $-\Delta G°$ is less



cis-1 *trans*-2

than 0.3 kcal/mol presumably because, as was shown by x-ray crystallographic study,[14] the axial *S*-methyl group is able to escape strong repulsion by the syn-axial hydrogen atom through a large (and obviously facile) flattening of the ring at the otherwise puckered sulfur vertex of the chair. Thus $\tau_{C(3)-C(2)-S-C(6)} = 46°$ in the cis (**1**) isomer vs. 64° in the trans (**2**). The resulting outward motion of the *S*-methyl group is further aided by the leverage effect of the long S–C bond. This finding[14] was of particular interest in view of an earlier assertion,[16] based on the magnitude of the geminal proton coupling constants at C(2) and C(6) in the parent *S*-methylthianium salt (**3**), that the ^{+}S-CH_3 group was largely equatorial. However, this assertion is clearly incorrect in the light of a more recent study of thianium salts[17] which agrees with our preliminary result.[14]



3 **4** **5**

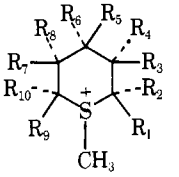
Further interest in this problem was occasioned by the report[18,19] that exchange of the two diastereotopic protons at C(2) or C(6) in **3** proceeds at nearly the same rate, in contrast to the situation in the five-membered analogue where substantial differences were found.[18,19] The question arose as to whether this lack of discrimination in **3** as well as its diastereomeric 2-methyl derivatives **4** and **5**[18] was intrinsic or was due to the presence of two rapidly interconverting conformations contributing in nearly equal amount.

Results

Methylation of 20 thianes[1] with either methyl iodide followed by exchange of the iodide for perchlorate or with trimethyloxonium hexafluorophosphate gave the 34 *S*-methylthianium perchlorates or hexafluorophosphates shown in Scheme I. The conformationally mobile parent, 3,3-, 4,4-, *trans*-2,6-, and *trans*-3,5-dimethylthianes can give only a single thianium salt and the thiane having an axial methyl group at C(3) (the 3,3,5-trimethyl compound) gave only one of the two possible products. In all other cases two diastereomeric thianium salts were formed from a given thiane and were separated or partially separated in a number of cases.

Except for diastereoisomerism at sulfur, the structure of the thianium salts follows from that of their thiane precursors.[1] The diastereomeric structures were, in all cases, unequivocally assigned on the basis of ^{13}C NMR spectra.[20] No ambiguity arises in those cases where the *S*-methyl groups are axial and equatorial, respectively, in the two diastereomers, since the axial *S*-methyl group resonates substantially upfield of the equatorial one[14] as do the C(3,5) carbons when *S*-Me is axial. Thus the only pairs where assignment was not immediately obvious were **18/19, 22/23,** and **26/27.** The **18/19** assignment is based on the fact[1,21,22] that the α_e effect of a methyl substituent is more deshielding than the α_a effect [this criterion can be applied at both C(2) and C(5)]. The **22/23** assignment similarly rests on the fact that the β_e effect is greater than β_a [criterion applied at C(5)] and the **26/27** assignment is based on the upfield shift of C(6) in **26** caused by the γ_a effect of Me(4).

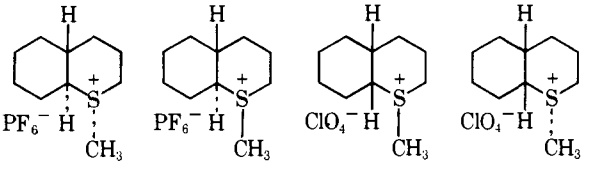
Scheme I



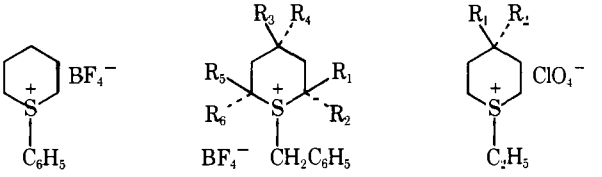
Ligands not indicated are H

6, R_4 = Me
7, R_3 = Me
8, R_5 = Me
9, R_6 = Me
10, $R_1 = R_9$ = Me
11, $R_2 = R_{10}$ = Me
12, $R_1 = R_{10}$ = Me
13, $R_4 = R_8$ = Me
14, $R_3 = R_7$ = Me
15, $R_3 = R_8$ = Me
16, $R_1 = R_8$ = Me
17, $R_2 = R_7$ = Me
18, $R_1 = R_7$ = Me
19, $R_2 = R_8$ = Me
20, $R_1 = R_5$ = Me
21, $R_2 = R_6$ = Me
22, $R_2 = R_5$ = Me
23, $R_1 = R_6$ = Me
24, $R_4 = R_5$ = Me
25, $R_3 = R_6$ = Me
26, $R_3 = R_5$ = Me
27, $R_4 = R_6$ = Me
28, $R_3 = R_4$ = Me
29, $R_5 = R_6$ = Me
30, $R_3 = R_4 = R_7$ = Me
31, $R_1 = R_5 = R_6$ = Me
32, $R_2 = R_5 = R_6$ = Me
33, $R_1 = R_2 = R_6$ = Me
34, $R_1 = R_2 = R_5$ = Me

Scheme II



35 **36** **37** **38**



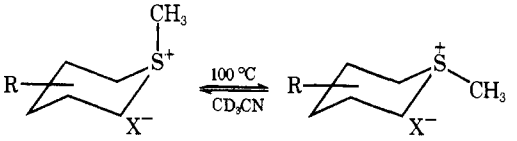
39 **40–45** **46, 47**

40, all R's = H
41, $R_3 = C(CH_3)_3$
42, $R_4 = C(CH_3)_3$
43, $R_1 = R_5 = CH_3$
44, $R_2 = R_6 = CH_3$
45, $R_1 = R_6 = CH_3$
46, $R_1 = C(CH_3)_3$
47, $R_2 = C(CH_3)_3$
all other R's = H

In addition to the above methylthianium salts, the 1-thiadecalinium salts **35–38** (Scheme II) were synthesized by methylation of *trans*- and *cis*-1-thiadecalin.[23] Configurational assignment was straightforward (vide supra) for the *trans*-1-thiadecalin derivatives **35** and **36** on the basis that **36** has axial *S*-methyl. A similar distinction can be made between **38,** which has purely equatorial *S*-Me, and **37** in which both conformers contribute; as a result, the *S*-Me, C(3), and C(10) signals in **37** are upfield of those in **38.** The *S*-phenyl, *S*-benzyl, and *S*-ethyl derivatives **39–47** (Scheme II) were obtained as described in the Experimental Section and their configurations, where uncertain, were determined by ^{13}C NMR spectroscopy as outlined earlier.[20]

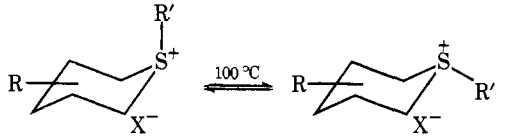
S-Methylthianium epimers (11 pairs), two pairs of *S*-methyl-1-thiadecalinium salts, two pairs of *S*-benzyl, and one pair of S-ethyl derivatives were subjected to thermal equilibration at sulfur[24] by heating at 100 °C in CD_3CN for several

Table I. Configurational Equilibria of Alkyl-Substituted *S*-Methylthianium Salts



Entry	R		X^-	K_{eq}	$-\Delta G°_{373}$, kcal/mol
1	4-*tert*-Butyl-	(**1**, **2**)	ClO_4^-	1.43 ± 0.05	0.27 ± 0.03
2	*cis*-3,5-Dimethyl-	(13, 14)	ClO_4^-	1.54 ± 0.06	0.32 ± 0.03
3	4-Methyl-	(8, 9)	PF_6^-	1.31 ± 0.04	0.20 ± 0.03
4	3-Methyl-	(6, 7)	PF_6^-	1.11 ± 0.02	0.08 ± 0.01
5	2-Methyl-	(4, 5)	PF_6^-	1.96 ± 0.06	0.50 ± 0.03
6	*trans*-2,5-Dimethyl-	(16, 17)	PF_6^-	2.25 ± 0.10	0.60 ± 0.03
7	*cis*-2,4-Dimethyl-	(20, 21)	PF_6^-	2.22 ± 0.10	0.59 ± 0.03
8	*cis*-2,6-Dimethyl-	(10, 11)	PF_6^-	3.85 ± 0.20	1.00 ± 0.04
9	*trans*-1-Thiadecalin	(36, 36)	PF_6^-	2.94 ± 0.12	0.80 ± 0.04
10	2,4,4-Trimethyl-	(31, 32)	PF_6^-	1.91 ± 0.06	0.48 ± 0.08
11	3,3,5-Trimethyl-	(30)	PF_6^-	>30	>2.5
12	2,2,4-Trimethyl-	(33, 34)	PF_6^-	0.88 ± 0.04	−0.10 ± 0.04
13	*cis*-1-Thiadecalin	(37, 38)	ClO_4^-	0.11 ± 0.01	−1.67 ± 0.06

Table II. Configurational Equilibria in Alkyl-Substituted *S*-Alkylthianium Salts



Entry	R		R'	Solvent	K_{eq}	$-\Delta G°_{373}$, kcal/mol
1	4-*tert*-Butyl-[a]	(41, 42)	$-CH_2Ph$	CD_3CN	3.01 ± 0.10	0.82 ± 0.08
2	*cis*-2,6-Dimethyl-[a]	(43, 44)	$-CH_2Ph$	CD_3CN	7.50 ± 0.50	1.50 ± 0.10
3	4-*tert*-Butyl-[b]	(46, 47)	−Et	$CDCl_3$	2.45 ± 0.08	0.66 ± 0.06

[a] Tetrafluoroborate. [b] Perchlorate.

hours. The results are shown in Tables I and II. In several instances (**3**, **12**, **27**, **29**, and **37**) equilibrium was also studied by direct observation of the two conformers by ^{13}C NMR spectroscopy at low temperature in hexadeuterioacetone, with the results shown in Table III. The difference between the low-temperature value, $\Delta G = 0.0$ kcal/mol, for the parent compound **3** and that shown in Table I for the 4-*tert*-butyl (entry 1) and *cis*-3,5-dimethyl (entry 2) derivatives is not necessarily caused by the holding group; the difference in solvent may be responsible or there may be a small entropy difference between the conformers;[25] a difference of 1.5 Gibbs (see also below) would be required to explain the difference in $\Delta G°$ of about 0.3 kcal/mol over a 190 °C temperature range.

An alternative way of assessing conformational equilibria is based on the fact that NMR signals in conformationally mobile systems are weighted averages of the corresponding signals of the contributing conformers: $\nu = n_e\nu_e + n_a\nu_a$ or $K = n_e/n_a = (\nu_a - \nu)/(\nu - \nu_e)$. The required shifts ν_e and ν_a of the two pure conformers may be determined in models.[26] The method is not, in general, as accurate as low-temperature NMR in determination of conformational equilibria,[27] but we have recently found good agreement in data obtained by the two procedures employing ^{13}C NMR.[28] Results of the application of this method are summarized in Table IV; the accord, in the present case, is fair at best, probably because of the difficulty in picking good reference shifts (ν_e and ν_a). (Details are given in Table V in the Appendix.)[29]

Discussion

Entries 1 and 2 in Table I indicate the comparatively small value of $-\Delta G°$ for the *S*-methyl group to which we already drew attention in our preliminary communication[14] and which has recently been confirmed by Fava and co-workers.[17] The difference between 4-*tert*-butyl and *cis*-3,5-dimethyl holding groups is minor and in the same direction as in other series.[30] An explanation for this difference in terms of buttressing of the syn-axial hydrogens at C(3,5) by the methyl substituents has been provided.[31]

Although $-\Delta G°$ is small for a single *S*-Me, entry 11 indicates a substantial impediment for such a group to become syn-axial with a *C*-methyl group.[32] Entries 3 and 4 support the usual additivity principle for conformational energies of remote groups. Thus the complete equilibrium for entry 3 is depicted in Scheme III and the equilibrium constant K is given by

$$K = \frac{T_1 + T_2}{C_1 + C_2} = \frac{T_1}{C_1 + C_2} + \frac{T_2}{C_1 + C_2} = \left(\frac{C_1 + C_2}{T_1}\right)^{-1} + \left(\frac{C_1 + C_2}{T_2}\right)^{-1}$$

and since $C_1/T_1 = 1/K_{SMe}$, $C_2/T_1 = 1/K_{CMe}$, $C_1/T_2 = K_{CMe}$, and $C_2/T_2 = K_{SMe}$,

$$K = \left(\frac{1}{K_{SMe}} + \frac{1}{K_{CMe}}\right)^{-1} + (K_{CMe} + K_{SMe})^{-1} \quad \text{(i)}$$

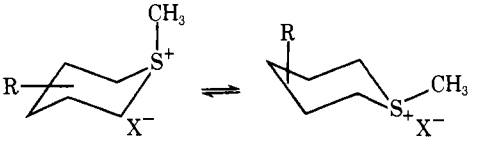
$$= \frac{K_{SMe}K_{CMe}}{K_{SMe} + K_{CMe}} + \frac{1}{K_{SMe} + K_{CMe}} = \frac{1 + K_{SMe}K_{CMe}}{K_{SMe} + K_{CMe}} \quad \text{(ii)}$$

Inserting values $K_{SMe} = 1.43$ (from entry 1) and $K_{CMe(4)}$[373] $= 11.3$[1] one calculates $K = 1.35$ compared to the observed 1.31.[33]

In the case of the 3-methyl compound (entry 4, Table I) the simpler equation[34]

$$1/K = 1/K_{SMe} + 1/K_{CMe} \quad \text{(iii)}$$

Table III. Conformational Equilibria in *S*-Methylthianium Salts Determined by Low-Temperature ^{13}C NMR



Entry	Compd	Solvent	T, °C[a]	K_{eq}	ΔG, kcal/mol
1	1-Methylthianium hexafluorophosphate (**3**)	$(CD_3)_2CO$	−90	1.00 ± 0.10	0.00 ± 0.02
2	*rac*-1,*cis*-2,*trans*-6-Trimethylthianium hexafluorophosphate (**12**)	$(CD_3)_2CO$	−90	0.58 ± 0.04	0.20 ± 0.03
3	*rac*-1,*trans*-3,*trans*-4-Trimethylthianium hexafluorophosphate (**27**)	$(CD_3)_2CO$	−90	2.01 ± 0.27	−0.25 ± 0.05
4	1,4,4-Trimethylthianium hexafluorophosphate (**29**)	$(CD_3)_2CO$	−90	0.40 ± 0.03	0.32 ± 0.03
5	1-β-Methyl-*cis*-1-thiadecalinium perchlorate (**37**)	CD_3CN	−65	1.77 ± 0.07	−0.24 ± 0.04

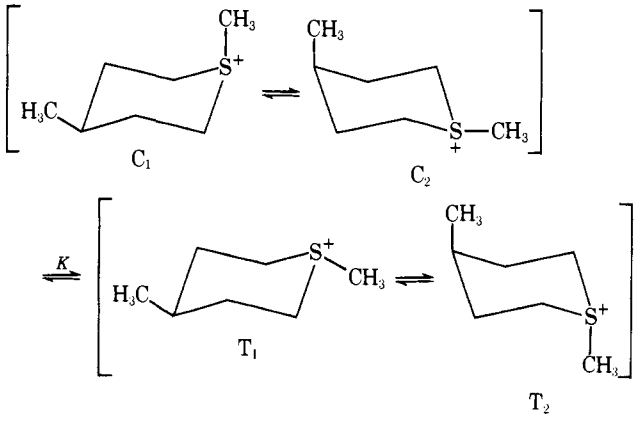
[a] ±5 °C.

Table IV. Accord of Conformational Free Energies[a] Determined by Chemical Shift Method[26]

Compd	**3**	**4**	**5**	**6**	**12**	**19**	**22**	**23**	**27**	**29**
$\Delta G°$, computed[b]	−0.18	1.64	−1.44	1.28	0.34	0.15	0.76	−0.11	−0.32	0.2
$\Delta G°$, expected[c]	(−0.17)[d]	1.5	−1.6	1.1	0.1	−0.2	0.2	−0.3	−0.8	−0.2

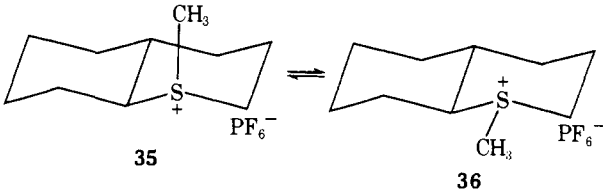
[a] In kcal/mol for $S\text{-Me}_a \rightleftharpoons S\text{-Me}_e$. [b] From above[26] equation. [c] Using data in Table 1 and in ref 1 (for $\Delta G°$ of ring methyl groups) and assuming additivity of $\Delta G°$'s: −0.2 kcal/mol for *S*-Me, −1.4 for Me(2) and Me(3),[1] −1.8 for Me(4),[1] −0.6 for *cis*-*S*,2-dimethyl (axial *S*-Me, vide supra), and −2.1 kcal/mol for *cis*-*S*,2-dimethyl (axial 2-Me—see ref 1 and discussion below). [d] Interpolated between value for **3** at 183 K (Table III, entry 1) and value for **1** ⇌ **2** at 373 K (eq 1 and Table I, entry 1).

Scheme III



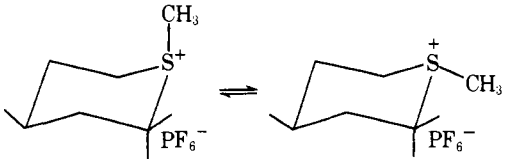
may be used since the diaxial conformer of the cis compound may be disregarded; with $K_{CMe(3)}^{373} = 6.79$[1] this yields K = 1.18 calculated vs. 1.11 observed. In both instances, the $\Delta G°$'s for the *S*- and 3- (or 4-) methyl groups are thus additive.

We now turn to the 2-methyl substituted thianium salts, initially to entry 7, which relates to the anancomeric[15] compounds **20** and **21.** The enhanced (relative to entry 1) $-\Delta G°$ of 0.59 kcal/mol reflects a buttressing of the axial *S*-methyl group in the sense that this group is inhibited, by the adjacent equatorial 2-methyl, from bending outward to the extent it does in **1.** The flattening of the ring known to occur in **1**[14] and responsible for most of the outward bending of the axial *S*-methyl in **1** as well as in **13** is opposed in **20** by the incipient eclipsing of *S*-Me and *C*(2)-Me. The nearly anancomeric[35] *trans*-2,5-dimethyl compounds **16, 17** (entry 6, Table I) have virtually the same $-\Delta G°_{SMe}$. From these results (entries 6, 7) the buttressing effect of the equatorial 2-methyl group may be assessed as 0.6–0.3 or 0.3 kcal/mol. An additional buttressing of about the same magnitude (0.4 kcal/mol) seems to be caused by the second vicinal equatorial methyl group in the *cis*-2,6-dimethyl compounds **10** and **11** (entry 8, Table I).



35 **36**

For the *trans*-thiadecalin derivatives **35** and **36** (entry 9), $-\Delta G°_{SMe}$ is slightly larger, suggesting either that the syn-axial $CH_3H(8)_a$ interaction in the cis isomer **35** is slightly greater than the $CH_3/H(8)_e$ peri interaction in the trans isomer **36,** or that the syn-axial interactions in **35** are greater than in the monocyclic analogues **16** and **20.**[36] In the *S*,2-dimethyl compounds **4** and **5** (entry 5, Table I) $-\Delta G°$ is slightly smaller than for entries 6, 7, and 9 because of conformational heterogeneity; the calculated value of 0.58 kcal/mol (see Appendix[29]) is close to the experimental (0.50 kcal/mol).



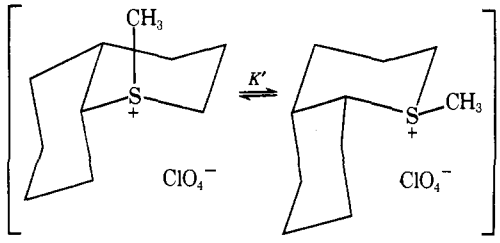
33 **34**

$\Delta G°$ = 0.1 kcal/mol

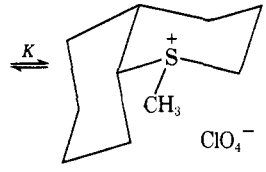
Equilibrium of compounds **33** and **34** (both anancomeric because of syn-axial Me/Me interactions in the alternate conformations) differs by 0.7 kcal/mol in $\Delta G°$ from that in **20** and **21** (compare entries 12 and 7 in Table I). Apart from possible minor deformations of the ring caused by the geminal dimethyl groups, the difference is in a $Me(2)_a/S\text{-}Me_e$ interaction in **34** which is absent in **33;** this interaction is evidently quite large. In the accompanying paper[1] it was pointed out that the conformational energy of a Me(2) group in thiane is appreciably less (by 0.4 kcal/mol) than that of a Me(4) group; an even larger difference was anticipated on the basis of force

field calculations.[37] Evidently the axial Me(2) in the thiane (and, presumably, in the corresponding thianium salt) leans outward in much the same way as *S*-methyl does (vide supra) and it is therefore not surprising that it should suffer a similar buttressing effect from a vicinal equatorial methyl group (*S*-Me).

An even larger buttressing effect is computed from the equilibration of the *S*-methyl-*cis*-1-thiadecalinium salts **37** and **38**. Here K = **38**/(**37a** + **37e**) = 0.105 (entry 13, Table



37a **37e**



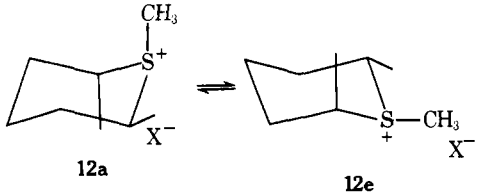
38

I). The equilibrium **37a** ⇌ **37e** (Table III) corresponds to $\Delta G°$ = −0.24 kcal/mol[38] and if one assumes $\Delta S°$ = 0 (but see above) K' = **37e**/**37a** = 1.38 at 373 K. If one inserts **37e** = 1.38 × **37a** in the value for K one obtains **38**/**37a** = 0.25, i.e., ΔG_{373} (**37a** ⇌ **38**) = 1.38 × **37a**. If one adds to this figure the 0.27 kcal/mol gained in making the axial *S*-Me group in **37a** equatorial in **38**, one arrives at the conclusion that the buttressing of the axial methylene, $CH_2(8)$, in **38** by the equatorial *S*-Me enhances its conformational energy by 1.2 kcal/mol. The larger value in **38** as compared to **34** may be due to the conformational rigidity of the decalin system (see earlier discussion regarding **35** and **36**).

Values of $-\Delta G°$ for *S*-ethyl[39] and *S*-benzyl are larger than for *S*-methyl (Table II, entries 1 and 3) and the *S*-benzyl value is further enhanced by buttressing resulting from the presence of equatorial methyl groups at C(2) and C(6) (entry 2).

We turn, finally, to Table III. It has already been indicated that the *S*-methyl equilibrium in **3** may be subject to a relatively sizable entropy effect: $-\Delta G°$ = 0.0 kcal/mol at 208 K (Table III, entry 1) compared to 0.27 kcal/mol at 373 K (Table I, entry 1). This assumption is supported by the intermediate value at 303 K determined by the chemical shift method (Table IV) of 0.17 kcal/mol.

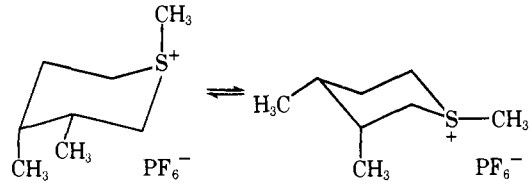
Compound **12** (entry 2) shows a preference for axial *S*-methyl despite the buttressing by an equatorial 2-methyl group in **12a**. Apparently the axial 2-methyl group in **12e** experiences



12a **12e**

an equal or even larger buttressing from the adjacent equatorial *S*-Me; in addition **12e** suffers from a (presumably small) *S*-Me/Me(6)$_e$ gauche interaction. The situation parallels that already described for **33** and **34** (vide supra).

Comparison of entry 4 with entry 1 is of particular interest: the (geminal) 4-methyl groups apparently deform the ring in such a way as to favor the axial *S*-methyl conformation, a fact which has already been noted by Fava et al.[17] These investigators explained their observations in terms earlier suggested by Lambert and co-workers:[40] introduction of the geminal dimethyl group at C(4) reduces the endocyclic C(3)–C(4)–C(5) bond angle and thus splays the syn-axial hydrogens at C(3) and C(5) away from the *S*-Me group. This explanation, though reasonable, has never been confirmed by direct structural studies and we should like to point out an alternative possibility which is supported by the finding (entry 3 in Table III) that even in a compound having only a single axial methyl group at C(4), the *S*-Me axial conformation **27a** is more



27a **27e**

$\Delta G°$(found) = −0.25 kcal/mol
$\Delta G°$(calcd) = −0.60 kcal/mol

prevalent than expected on the basis of additivity of conformational energies. (The calculated $\Delta G°$ is derived from that for *S*-Me, 0.0 kcal/mol, and that for *cis*-3,4-dimethylthiane, −0.60 kcal/mol.[1])

Our explanation is in terms of a "reflex effect":[41] the flattening of the ring near the axially substituted sulfur atom [C(6)–S–C(2)] splays H(2)$_a$ and H(6)$_a$ outward, thus relieving the interactions of the syn-axial hydrogens with Me(4)$_a$. There is, as a result, a synergistic effect between an axial *S*-Me and an axial Me(4) in both **27a** and **29a**.

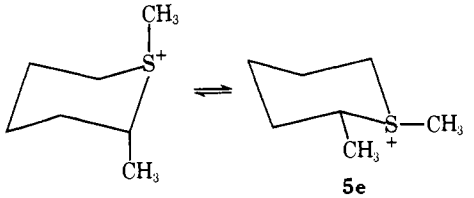
Returning to Table I we note that the increased tendency for an axial *S*-methyl group engendered by geminal methyl groups at C(4) is also seen in the comparison of the 2,4,4-trimethyl system (entry 10) with the 2,4-dimethyl system (entry 7), although the increased tendency for *S*-Me to be axial (or decreased tendency to be equatorial) is less in this system (0.1 kcal/mol) than in the systems lacking the 2-methyl group described above.

Summary

The most salient findings of the conformational analysis of thianium salts are the following: (1) $-\Delta G°$ for *S*-Me in *S*-methylthianium salts is small (0.0–0.3 kcal/mol) because of facile flattening of the six-membered ring at the sulfur end. (2) Accordingly, equatorial substituents at C(2) and C(6) enhance the conformational energy of *S*-Me by inhibiting the flattening. (3) A corresponding reciprocal buttressing effect is seen in $-\Delta G°$ for Me(2), which is enhanced by equatorial *S*-Me. (4) Geminal dimethyl groups and (more tentatively) a single axial methyl group at C(4) stabilize the conformation of axial *S*-Me. A reflex effect is suggested to account for this result instead of the earlier postulated[40] angle deformation effect at C(4). (5) The conformational equilibria for *cis*- and *trans*-*S*,2-dimethylthianium salts are found to be as shown in eq 2 and 3 (entries 2 and 3, Table IV). Both compounds are thus largely anancomeric, with the *S*-Me being largely (>90%) equatorial in the first case and axial in the second. The earlier discussed[18] lack of stereoselectivity in the H/D exchange at C(6) is therefore not due to rapid site exchange of axial and equatorial positions.

Experimental Section

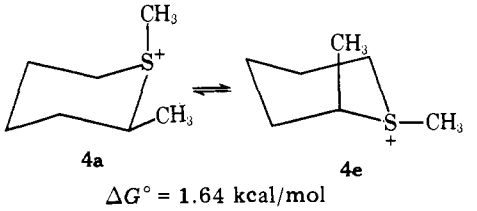
The instrumentation used has been discussed in the accompanying paper[1] as has the synthesis of the parent thianes except for 2,2,4- and 2,4,4-trimethylthiane and *trans*-1-thiadecalin, which were donated by Dr. F. W. Vierhapper (University of Vienna, Austria); the preparation of these compounds and *cis*-1-thiadecalin will be described elsewhere.[23] ^{1}H NMR signals for compounds **1–3, 5, 7, 9, 11–15, 17,**



(2)

5a ⇌ 5e

$\Delta G^\circ = -1.44$ kcal/mol



(3)

4a ⇌ 4e

$\Delta G^\circ = 1.64$ kcal/mol

21, 25, 28–30, 32, 35, 37, 39–41, 43–45, and **47** are listed in the Appendix.[29]

***rac*-1,*cis*-3,*cis*-5-Trimethylthianium Perchlorate (14).** A 100-ml Erlenmeyer flask containing 13.0 g (0.10 mol) of *cis*-3,5-dimethylthiane, 40 ml of absolute alcohol, and 42.6 g (0.30 mol) of methyl iodide was stoppered and allowed to stand for 48 h in the dark. The solvent and excess methyl iodide were removed at reduced pressure to yield 27.8 g of a slightly yellow powder. NMR analysis (*S*-Me's) indicated an isomer ratio (**14**/**13**) of approximately 90:10. This material was dissolved in 50 ml of 85:15 water/methanol and passed through an anion exchange column (Dowex 1 × 8-100) which had previously been converted to the hydroxide form. The eluate was carefully neutralized with 70% perchloric acid and the solvent removed at reduced pressure to yield 20 g of a white powder. The powder was recrystallized several times from water to yield 4 g of pure *rac*-1,*cis*-3,*cis*-5-trimethylthianium perchlorate, mp 75–76 °C.

***rac*-1,*trans*-3,*trans*-5-Trimethylthianium Perchlorate (13).** The combined mother liquors from the isolation of the major isomer were concentrated to 150 ml and refluxed for 72 h. Analysis then showed that the isomer ratio was approximately 55:45. Several careful recrystallizations from H_2O yielded the *rac*-1,*trans*-3,*trans*-5-trimethylthianium perchlorate pure, mp 133–135 °C.

***trans*-1-Methyl-4-*tert*-butylthianium Perchlorate (2).** Following the procedure for the synthesis of **14,** 4-*tert*-butylthiane was allowed to react with 3 molar equiv of methyl iodide in absolute alcohol, and the crude iodides were converted to a mixture of the perchlorates by passing the solution through an anion exchange column (OH^-), neutralizing the eluate with perchloric acid, and removing the solvent at reduced pressure. NMR analysis of the crude mixture of perchlorates showed two isomers (**2** and **1**) present in a ratio of approximately 88:12. Repeated recrystallizations from H_2O yielded the pure trans isomer, mp 149–150 °C.

Anal. Calcd for $C_{10}H_{21}SClO_4$: C, 44.03; H, 7.76. Found: C, 44.29; H, 7.69.

***cis*-1-Methyl-4-*tert*-butylthianium Perchlorate (1).** The combined mother liquors from the synthesis of the trans isomer were concentrated to 150 ml and refluxed for 48 h; the solvent was then removed at reduced pressure. The resulting solid was recrystallized several times from water to yield the pure *cis*-1-methyl-4-*tert*-butylthianium perchlorate, mp 173–174 °C.

Anal. Calcd for $C_{10}H_{21}SClO_4$: C, 44.03; H, 7.76. Found: C, 44.04; H, 7.89.

***trans*-1-Ethyl-4-*tert*-butylthianium Perchlorate (47).** Following the procedure for the synthesis of **14,** 4-*tert*-butylthiane was allowed to react with a twofold excess of ethyl iodide in absolute alcohol for 2 weeks. The excess ethyl iodide and solvent were removed at reduced pressure. The resulting solid was dissolved in 50 ml of 60% water/methanol and passed through an anion exchange column (OH^- form) and the eluate neutralized with 10% perchloric acid. The solvent was removed at reduced pressure and the resulting solid recrystallized from 85% H_2O/15% EtOH several times to yield pure *trans*-1-ethyl-4-*tert*-butylthianium perchlorate, mp 83–84 °C.

***Cis*-Enriched 1-Ethyl-4-*tert*-butylthianium Perchlorate (46).** The combined mother liquors from the synthesis of the trans isomer were concentrated to 100 ml and refluxed for 72 h. The solvent was removed at reduced pressure and the resulting powder analyzed by ^1H NMR ($CDCl_3$). Two isomers were present in a ratio of approximately 75(trans):25(cis). The mixture resisted all attempts at separation by fractional crystallization except for a slight enrichment of the minor isomer (to ≈35%).

Table VIII. Diastereomer Distribution in the Methylation of Unsymmetrical Dimethylthianes and a Highly Hindered Thiane with Trimethyloxonium Hexafluorophosphate

Thiane	Diastereomer[a]	Percentage	Diastereomer[a]	Percentage
cis-2,5-Dimethyl	**18**	15	**19**	85
trans-2,4-Dimethyl	**22**	70	**23**	30
cis-3,4-Dimethyl	**26**	25	**27**	75
2,2,4-Trimethyl	**34**	65	**33**	35

[a] For compound structures see Scheme I.

1-β-Methyl-*cis*-1-thiadecalinium Perchlorate (37). Following the procedure for the synthesis of **14,** *cis*-1-thiadecalin was let stand with a 3 molar equiv of methyl iodide in absolute alcohol for 3 days and the solvent and excess methyl iodide were then removed at reduced pressure. The crude iodide was dissolved in 50:50 methanol/water and passed through an anion exchange column (OH^- form). The eluate was neutralized with perchloric acid, the solvent removed at reduced pressure, and the product recrystallized from water, mp 82–84 °C.

1-Methylthianium Perchlorate (3, ClO_4^-). 1-Methylthianium perchlorate was prepared from 1-methylthianium iodide by the procedure outlined for *trans*-1-methyl-4-*tert*-butylthianium perchlorate. It was recrystallized twice from water, mp >200 °C. The ^1H NMR spectrum in CD_3CN was identical with that of the corresponding hexafluorophosphate.

Synthesis of 1-Methylthianium Hexafluorophosphates. Compounds **3, 5, 7, 9, 11, 12, 15, 17, 21, 25, 28, 29, 30, 32,** and **35** were all synthesized by allowing the appropriate thiane to react with 1.05 molar equiv of trimethyloxonium hexafluorophosphate in methylene chloride (35 ml/0.01 mol thiane) for 6–24 h, removing the solvent and recrystallizing the white powder from water several times. The ^1H NMR for these compounds are reported in the Appendix.[29]

Compounds **4, 6, 8, 10, 16, 20, 24, 31,** and **36** were not isolated in pure form. They were investigated as mixtures with their corresponding equatorial *S*-methyl isomers (above) generated by thermal equilibrations. The ^1H NMR shifts of the *S*-methyls and, where possible, the *C*-methyls are reported in Table VI, Appendix.[29]

Compound pairs **18/19, 22/23, 26/27,** and **33/34** were synthesized as mixtures by methylation of the appropriate thianes with trimethyloxonium hexafluorophosphate as described earlier. No attempt was made to separate the mixtures, except in the case of **26** and **27,** where several recrystallizations from water yielded compound **27** pure. The ^1H NMR shifts of the *S*-methyls and, where possible, the *C*-methyls are reported in Table VII (Appendix[29]). In Table VIII the isomer distributions obtained in the syntheses are summarized.

1-Phenylthianium Tetrafluoroborate (39). This compound was prepared by the procedure of Oae et al. for the corresponding perchlorate, substituting silver tetrafluoroborate for silver perchlorate.[42]

***trans*- and *cis*-1-Benzyl-4-*tert*-butylthianium Tetrafluoroborate (40 and 41).** In a 50-ml round-bottom flask covered with aluminum foil was placed 4-*tert*-butylthiane (3.16 g, 0.02 mol), benzyl bromide (3.39 g, 0.02 mol), 30 ml of methylene chloride, and a small magnetic stirring bar. Silver tetrafluoroborate/acetonitrile complex [$AgBF_4 \cdot (CH_3CN)_4$, 6.36 g, 0.02 mol] was added, the flask stoppered, and stirred for 3 days. Then 20 ml of acetonitrile was added, the solution filtered, and the solvent removed at reduced pressure. The resulting solid was recrystallized several times from 75:25 v/v water/ethanol. ^1H NMR analysis (*tert*-butyl signals) showed two isomers present in an 88:12 ratio.

***rac*-1-Benzyl-*trans*-2,*trans*-6-Dimethylthianium Tetrafluoroborate (44).** Following the above procedure, 0.01 mol of *cis*-2,6-dimethylthiane was allowed to react with 0.01 mol of benzyl bromide and 0.01 mol of silver tetrafluoroborate/acetonitrile complex for 7 days in the dark. The solution was diluted with approximately 25 ml of acetonitrile and filtered. The solvent was removed and the solid recrystallized from acetonitrile twice. ^1H NMR analysis showed only one isomer (presumably the trans), mp 157–159 °C.

***rac*-1-Benzyl-*cis*-2,*trans*-6-dimethylthianium tetrafluoroborate (45)** was similarly synthesized from *trans*-2,6-dimethylthiane.

1-Benzylthianium Tetrafluoroborate (40). In a manner similar to that described for the synthesis of the *cis*- and *trans*-1-benzyl-4-*tert*-butylthianium tetrafluoroborates, thiane was treated with 1 molar equiv of both benzyl bromide and the silver tetrafluoroborate/acetonitrile complex, the solution was filtered after 24 h, and the product was recrystallized twice from water, mp 150–152 °C dec.

Equilibrations. A 20% w/v solution of the appropriate thianium salt in acetonitrile-d_3 was prepared. This was filtered into a 5-mm or 10-mm NMR tube to which a 10/30 ₹ outer joint had been attached. The NMR tube was attached to a high vacuum line and frozen with liquid nitrogen. The sample was evacuated for 2 min, the vacuum turned off, and the sample allowed to thaw. This cycle was repeated three times, and the tube was sealed. The tube was then placed in an oil bath maintained at 100 ± 2 °C for 72 h. The isomeric distribution was checked by ^{1}H NMR, and if it was unchanged, the sample was assumed to be equilibrated. In those cases where both diastereomers were available equilibrium was approached from both sides. After equilibrium had been established, the samples were analyzed by both ^{1}H and ^{13}C NMR. In the ^{13}C analysis either long pulse delay times or small flip angles were used in conjunction with homospoil to avoid effects of differences in the T_1's and NOE's of the different carbon atoms on their respective signal areas. Analyses by ^{1}H and ^{13}C NMR always agreed to within 2–3%.

Note Added in Proof. After this paper had been submitted, a publication[43] appeared in which compounds **2, 4, 5,** and **28** in addition to the previously mentioned[17] **6–9, 13,** and **14** were described. Equilibrium constants for **6** ⇌ **7** (1.33), **8** ⇌ **9** (1.44), and **13** ⇌ **14** (1.27) were reported;[43] that these constants are in only modestly good agreement with those in Table I above may be a consequence of the difference in solvent (D_2O[43] vs. CD_3CN). The conformational equilibrium of **4** was judged,[43] on the basis of chemical shift considerations, to lie very largely on the side of **4a,** in accord with eq 3.

Acknowledgment. This work was supported by NSF National Science Foundation Grant GP-35669X and by a grant-in-aid of Allied Chemical Corp. Dr. George Furst kindly provided compound **45.**

Supplementary Material Available: The calculation of the conformational distribution of compounds **4** and **5** is given in the Appendix, which also contains Tables V–VII and the ^{1}H NMR signals of the compounds indicated at the beginning of the Experimental Section (8 pages). Ordering information is given on any current masthead page.

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(25) (a) Cf. J. Reisse in ref 15, pp 219ff; (b) see also the 1-alkylphosphorinane case (ref 9) in which, however, ΔS° favors the axial conformer.
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(28) Cf. E. L. Eliel and D. Kandasamy, *J. Org. Chem.*, **41,** 3899 (1976).
(29) See paragraph at end of paper concerning supplementary material.
(30) E. L. Eliel, J. R. Powers, Jr., and F. W. Nader, *Tetrahedron*, **30,** 515 (1974).
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(32) Cf. ref 4, p 52.
(33) The assumption of additivity of ΔG°'s is not strictly correct in the case of isomer T_2, see below. If one takes into account that the free energy for the $(C_1 + C_2) \rightleftharpoons T_2$ equilibrium is 320 cal/mol more on the side of T_2, as a result of the effect of the axial Me(4) group, than calculated on the basis of additivity, the second term in eq i is changed from 0.08 to 0.12 and the calculated K is changed from 1.35 to 1.39.
(34) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79,** 5992 (1957). See also ref 4, p 67.
(35) The sum of the conformational energies of the 2- and 5-methyl groups, taken from the corresponding thianes,[1] is 2.8 kcal/mol. Even in isomer **16** in which the 2(e), 5(e)-dimethyl conformation is opposed by an axial *S*-methyl group ($\Delta G^\circ = -0.6$ kcal/mol), the preference for this conformation is 2.3 kcal/mol, corresponding to 95% of the corresponding conformer.
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