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Sulfur Inversion in and Molecular Structure of *meso*-3,4-Diethyl-3,4-dimethyl-1-phenylthiolanium Tetrafluoroborate

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Kinetics of sulfur inversion in the title compound was studied by the classical method to afford the following kinetic parameters for the process (1*r*,3*R*,4*S*)→(1*s*,3*R*,4*S*): $\Delta H^{\ddagger}$ 25.7±0.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ −2.2± 0.8 cal mol^{-1} K^{-1}. X-Ray crystallography of one isomer (1*r*,3*R*,4*S*) in which the methyl groups are cis to the phenyl group shows some abnormal bond lengths and conformations due to the steric congestion in the 3,4-region of the thiolane ring. The anomalies in the structure are pointed out by comparing the structure with those closely related and the correlation of them with the barrier height to inversion is discussed.

Although racemization of optically active sulfonium ions attracted interests of many investigators[1] since the discovery of fairly facile racemization of this class of compounds by Darwish et al.[2] through sulfur inversion, the reports have mainly concerned with racemization at one point of temperature and the literatures which report enthalpy and entropy of activation are very few.[3] During the course of work on dissociation of molecular species by the dynamic NMR technique, we have come across an idea that entropies of activation can be used as decisive information in diagnosing the mechanism of topomerization,[4] and have felt the necessity of providing the kinetic data of sulfur inversion at various temperatures.

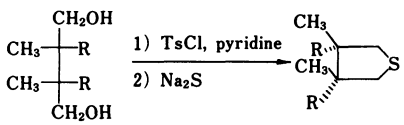
Our first aim of the investigation was to design a molecule that suits to both classical and NMR study of the kinetics of sulfur inversion. In principle, any barrier to a transformation may be reduced by either stabilization of the transition state for the transformation or the destabilization of the ground state. Since normal sulfonium salts racemize with a barrier of ca. 26—35 kcal mol^{-1},[1] it is necessary to design a molecule that possesses a lower barrier to sulfur inversion than usual, if we wish to investigate the inversion by the dynamic NMR technique. For the stabilization of the transition state for inversion, it seemed that we could do little: Although introduction of a phenyl group into the sulfonium moiety is known to cause reduction in the inversion barrier,[5] this may not be ascribed to the stabilization of the transition state, because the substituent constant (σ) of a methylthio group is close to zero,[6] and this is believed to be caused by poor 2p–3p conjugation relative to the 2p–2p case.[7] Thus we decided to work on destabilization of the ground state by introducing the steric effects. This paper reports the results of such investigations: Although the barrier was not reduced large enough to be amenable to the dynamic NMR investigation, it was indeed reduced by destabilizing the ground state by steric congestion, that is discussed from the molecular structure obtained by X-ray crystallography, even for a cyclic compound.

We decided to use a sulfonium salt which could be derived from a cyclic sulfide for two reasons. The first is the difficulty of selecting suitable alkyl groups in the open chains. The mechanism of racemization of sulfonium compounds is known to be three fold:[8] Simple sulfur inversion, sulfur inversion after dissociation when a stable carbocation is formed, and sulfur inversion with intermediates of a thioether and a product which is derived by the attak of the nucleophile on one of the alkyl groups attached to the sulfonium-sulfur. Since we are concerned in the entropy of activation of pure sulfur-inversion, any possibility of the dissociation mechanism must be avoided. There is a report that claims that even *t*-butylethylmethylsulfonium ion racemizes by a dissociation mechanism from a study of volume of activation.[9] We preferred therefore to use primary alkyl groups or aryl groups where possible in the sulfonium salt that gives large rates of inversion. This type of molecular design is not possible in the noncyclic compounds, because the bulky groups which are not directly bonded to the sulfonium-sulfur will avoid each other by taking a suitable conformation. The second is to use this restriction of the freedom of taking conformations in the cyclic compounds. Even though a sulfur atom may be bonded to two primary alkyl groups in a cyclic sulfide, it is possible to give large steric congestion by introducing substituents to the beta or farther positions relative to the sulfur.

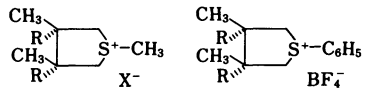
A literature reports that compounds **1** and **2** change their optical activity with rate constants, 1.08×10^{-4} and 0.81×10^{-4} s^{-1}, respectively at 100 °C in acetic acid.[10] If we could add another pair of *gem*-dimethyl groups in another beta-position relative to the sulfur, there could be a low barrier to inversion of sulfur. Because of the ease of syntheses, we selected the five-membered sulfide as a target molecule, though the 5-membered ring system could give higher barrier to inversion due to the small bond angle in the planar structure than the 6-membered.

1 2

2,2,3,3-Tetramethyl-1,4-butanediol (**3a**) had been known.[11] This compound was treated with *p*-toluenesulfonyl chloride in the presence of pyridine to afford the desired product, 3,3,4,4-tetramethylthiolane (**4a**). The thiolane was converted to 1,3,3,4,4-pentamethylthiolanium salts (**5a**): The iodide decomposed very easily because of the nucleophilic attack of the iodide ion, the tosylate also decomposed at above 100 °C, and the trifluoromethanesulfonate survived heating at above 150 °C. However, these compounds did not show evidence that the sulfur-inversion was taking place on the NMR time scale under the conditions of heating mentioned above. Although we introduced a phenyl group to the sulfur atom of the thiolane in a hope that **6a** should further lower the barrier to inversion, that trial did not work as expected. No change in the NMR line shapes was observed at 200 °C at 60 MHz.



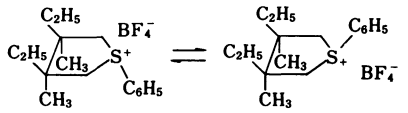
3 a : R=CH3, b : R=C2H5 4



5 6

At this point we turned our attention to the synthesis of other compounds that might fit to the classical equilibration and decided to synthesize derivatives of *meso*-3,4-diethyl-3,4-dimethylthiolane (**4b**). The syntheses could be carried out analogously with the tetramethyl compound, although the corresponding diol **3b** was unknown. Methylation of the thiolane **4b** with methyl trifluoromethanesulfonate afforded a mixture of stereoisomers of **5b** (X=CF_3SO_3) which could not be separated, whereas phenylation of **4b** with diphenyliodonium tetrafluoroborate in the presence of copper(II) benzoate afforded a mixture of stereoisomers of **6b** which could give one pure isomer by recrystallization from ethanol. The stereochemistry of the recrystallized isomer was expected to be (1*r*,3*R*,4*S*)-**6b** from the kinetic consideration, because this isomer was the major product as well as because this form was the preferred of the two at equilibrium. However, it was not possible to determine the stereochemistry unambiguously by the chemical means. That the stereochemistry of this product is really 1*r*,3*R*,4*S* was established by X-ray crystallography.

The isomerization of **6b** in chloroform-*d* solutions was followed by ^{1}H NMR technique, using the signals due to 2,5-methylene protons, which show completely separated AB signals at 270 MHz for the two isomers. The rate constants thus obtained at 5 temperatures are listed in Table 1. From these results, the following activation parameters were obtained: $\Delta H^{\ddagger}$ 25.7±0.3 kcal mol^{-1} (1 cal=4.184 J), $\Delta S^{\ddagger}$ −2.2±0.8 cal mol^{-1} K^{-1}. The feature of the kinetic parameters is the near-zero entropy of activation and confirms that, if pure sulfur-inversion takes place, the entropy of activation is close to zero as is described in the literature.[3] This result is reasonable in that during the inversion of sulfur net charge does not change nor a new particle is formed.



(1*r*,3*R*,4*S*)-**6b** (1*s*,3*R*,4*S*)-**6b**

That we do not observe other reactions but real inversion of sulfur was proved by enriching the other isomer: the solution obtained by the equilibration of **6b**, that contained the product and the starting material in ca. 3:4 ratio was concentrated and fractionally recrystallized from ethanol. It was possible to enrich the product to 6:1 purity. Satisfactory elementary analyses of the enriched product and expected ^{1}H NMR spectra support the structure of the isomer. Furthermore, the product, when heated in chloroform-*d*, afforded the identical mixture of the isomers of **6b**, which was obtained by heating the original isomer.

Table 1. Rate Constants of Sulfur-Inversion in *meso*-3,4-Diethyl-3,4-dimethylthiolanium Tetrafluoroborate in Chloroform-*d*

Temp/°C	$k/10^{-5}$ s^{-1} (1*r*,3*R*,4*S*)→(1*s*,3*R*,4*S*)	*K* (1*s*,3*R*,4*S*)/(1*r*,3*R*,4*S*)
60.3	3.42±0.03	0.76
65.3	6.14±0.06	0.74
70.3	10.8 ±0.1	0.74
75.3	18.8 ±0.1	0.75
80.3	32.6 ±0.1	0.77

Table 2. Atomic Positional Parameters ($\times 10^4$) with Estimated Deviations in Parentheses and Equivalent Isotropic Thermal Parameters of (1*r*,3*R*,4*S*)-3,4-Diethyl-3,4-dimethyl-1-phenylthiolanium Tetrafluoroborate

Atom	*x*	*y*	*z*	B_{eq}[a]	Atom	*x*	*y*	*z*	B_{eq}[a]
S	−2847(1)	629(1)	−3469(1)	3.6	$C_{3'}$	−207(6)	4134(5)	−2326(6)	5.2
C_2	−3571(4)	−380(5)	−1635(5)	3.7	$C_{4'}$	1005(5)	4511(5)	−3093(6)	5.2
C_3	−3156(4)	−1783(5)	−1036(5)	3.4	$C_{5'}$	1029(5)	3670(5)	−3934(6)	5.1
C_4	−3096(4)	−2214(5)	−2455(5)	3.4	$C_{6'}$	−91(5)	2486(5)	−4009(5)	4.7
C_5	−2174(4)	−794(5)	−3523(5)	3.9	B	−2108(6)	1388(7)	−7793(7)	4.9
C_{3a}	−1674(5)	−1422(6)	−243(6)	4.9	F_1*	−2908(5)	1135(6)	−8981(5)	9.9
C_{3b}	−4232(5)	−2958(5)	49(5)	4.5	F_2*	−1288(5)	505(6)	−7309(6)	10.4
$C_{3b'}$	−4404(6)	2606(6)	1411(6)	6.1	F_3*	−2896(6)	1293(9)	−6812(5)	14.7
C_{4a}	−2344(5)	−3363(5)	−2100(6)	5.1	F_4*	−1389(9)	2844(7)	−8462(10)	18.4
C_{4b}	−4588(5)	−2759(5)	−3147(5)	4.2	$F_{1'}$*	−3333(14)	277(14)	−7079(19)	3.6
$C_{4b'}$	−4710(6)	−2995(7)	−4651(6)	6.4	$F_{2'}$*	−1823(28)	2178(21)	−7006(24)	8.6
$C_{1'}$	−1292(5)	2094(4)	−3227(5)	3.5	$F_{3'}$*	−1014(22)	1535(46)	−6928(25)	16.2
$C_{2'}$	−1351(5)	2941(5)	−2393(5)	4.4	$F_{4'}$*	−1692(40)	1253(49)	−8867(32)	18.4

* Occupancies for the disordered atoms are 0.85 for F_1—F_4 and 0.15 for $F_{1'}$—$F_{4'}$.
a) Equivalent isotropic temperature factor defined by Hamilton.[12]

Table 3. Selected Bond Distances in (1*r*,3*R*,4*S*)-3,4-Diethyl-3,4-dimethyl-1-phenylthiolanium Tetrafluoroborate

Atom(1)–Atom(2)	Distance/Å	Atom (1)–Atom(2)	Distance/Å
S–C_2	1.825(4)	C_3–C_{3b}	1.512(6)
S–C_5	1.831(6)	C_4–C_5	1.537(5)
S–$C_{1'}$	1.793(4)	C_4–C_{4a}	1.531(8)
C_2–C_3	1.535(7)	C_4–C_{4b}	1.527(6)
C_3–C_4	1.586(7)	C_{3b}–$C_{3b'}$	1.521(9)
C_3–C_{3a}	1.558(7)	C_{4b}–$C_{4b'}$	1.524(9)

The observed barrier to sulfur-inversion is indeed lower than that in **1** by ca. 2 kcal mol^{-1} and represents the lowest barrier known so far for purely aliphatic cyclic sulfonium salts, yet it is higher than that in 1-adamantylethylmethylsulfonium perchlorate.[3] We were thus interested in the investigation of the cause for the relatively high barrier to sulfur-inversion in compound **6b**, irrespective to the fact that the molecular models of the compound suggested that the high degree of congestion was possible in the molecule. Thus X-ray crystallography of the starting material **6b** was carried out. This as well provides unambiguous assignment of the stereochemistry of the isomers involved.

Atomic coordinates, bond lengths, bond angles, and some selected dihedral angles are given in Tables 2, 3, 4, and 5, respectively. The ORTEP diagram is given in Fig. 1 for the enantiomer of the molecule that is defined by the atomic coordinates in Table 2, for the convenience of the comparison with the molecule of **8**. It is clear that the prediction of stereochemistry given by considering both kinetic and thermodynamic preference is correct. The originally preferred compound is (1*r*,3*R*,4*S*)-3,4-diethyl-3,4-dimethyl-1-phenylthiolanium tetrafluoroborate. Thus the product by equilibration must be (1*s*,3*R*,4*S*)-3,4-diethyl-3,4-dimethyl-1-phenylthiolanium tetrafluoroborate.

The compound **6b** has some interesting structural features that follow. These must be caused by the presence of neighboring two pairs of *gem*-ethyl-and-methyl groups which interact strongly with each other. The methyls of the ethyl groups are directing outward relative to the five-membered ring to avoid the interaction with other groups. The C_3–C_4 bond is

Table 4. Selected Bond Angles in (1*r*,3*R*,4*S*)-3,4-Diethyl-3,4-dimethyl-1-phenylthiolanium Tetrafluoroborate

Atom(1)–Atom(2)–Atom(3)	Angle/°
C_2–S–C_5	94.5(2)
C_2–S–$C_{1'}$	106.4(2)
C_5–S–$C_{1'}$	105.3(2)
S–C_2–C_3	107.8(4)
C_2–C_3–C_4	105.4(3)
C_2–C_3–C_{3a}	108.3(4)
C_2–C_3–C_{3b}	110.0(4)
C_4–C_3–C_{3a}	109.9(4)
C_4–C_3–C_{3b}	113.0(4)
C_{3a}–C_3–C_{3b}	110.0(3)
C_3–C_4–C_5	104.5(4)
C_3–C_4–C_{4a}	112.0(4)
C_3–C_4–C_{4b}	111.2(4)
C_5–C_4–C_{4a}	107.7(4)
C_5–C_4–C_{4b}	111.3(3)
C_{4a}–C_4–C_{4b}	110.0(4)
S–C_5–C_4	104.7(4)
C_3–C_{3b}–$C_{3b'}$	116.4(4)
C_4–C_{4b}–$C_{4b'}$	117.9(5)

very long as an sp^3–sp^3 carbon bond and is even longer than the C–C bond in tetramethylsuccinonitrile.[13] This is probably caused by the fact that the steric size of a cyano group is smaller than a methylene group.

Table 5. Selected Torsion Angles in (1*r*,3*R*,4*S*)-3,4-Diethyl-3,4-dimethyl-1-phenylthiolanium Tetrafluoroborate

Atom(1)–Atom(2)–Atom(3)–Atom(4)	Angle/°
C_5–S–C_2–C_3	4.6(3)
$C_{1'}$–S–C_2–C_3	−102.8(3)
C_2–S–C_5–C_4	24.0(3)
$C_{1'}$–S–C_5–C_4	132.4(3)
C_2–S–$C_{1'}$–$C_{2'}$	−46.3(4)
C_2–S–$C_{1'}$–$C_{6'}$	141.1(4)
C_5–S–$C_{1'}$–$C_{2'}$	−145.8(4)
C_5–S–$C_{1'}$–$C_{6'}$	41.6(4)
S–C_2–C_3–C_4	−31.2(4)
S–C_2–C_3–C_{3a}	86.4(4)
S–C_2–C_3–C_{3b}	−153.3(3)
C_2–C_3–C_4–C_5	49.5(4)
C_2–C_3–C_4–C_{4a}	165.8(4)
C_2–C_3–C_4–C_{4b}	−70.6(4)
C_{3a}–C_3–C_4–C_5	−67.0(4)
C_{3a}–C_3–C_4–C_{4a}	49.3(5)
C_{3a}–C_3–C_4–C_{4b}	172.9(4)
C_{3b}–C_3–C_4–C_5	169.7(4)
C_{3b}–C_3–C_4–C_{4a}	−74.0(5)
C_{3b}–C_3–C_4–C_{4b}	49.6(5)
C_3–C_4–C_5–S	−45.0(4)
C_{4a}–C_4–C_5–S	−164.3(3)
C_{4b}–C_4–C_5–S	75.0(4)

Another interesting feature is that the C_4 occupies the tip of the envelope conformation of the thiolane ring in contrast to the fact that the sulfur atom occupies the tip position in 1-methylthiolanium iodide.[14] The cause was again considered to be the steric effects at the 3 and 4 positions, because, if the sulfur atom occupies the tip, the methyl and the ethyl groups at 3,4-positions must take near-eclipsing conformations

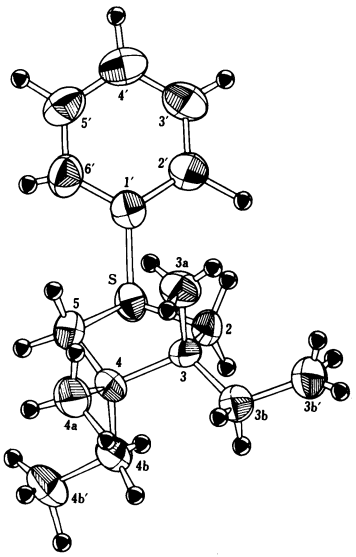


Fig. 1. An ORTEP diagram of (1*r*,3*R*,4*S*)-3,4-diethyl-3,4-dimethyl-1-phenylthiolanium ion. Number of atoms corresponds with that in Tables 2—5.

Table 6. Atomic Positional Parameters (×10^4) with Estimated Standard Deviations in Parentheses and Equivalent Isotropic Thermal Parameters of 1-Phenylthiolanium Perchlorate

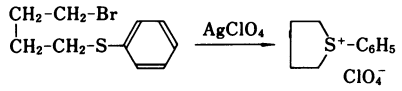
	Molecule 1					Molecule 2			
Atom	*x*	*y*	*z*	B_{eq}[a]	Atom	*x*	*y*	*z*	B_{eq}[a]
S	6675(2)	9141(2)	1494(3)	4.4	S	2918(2)	4061(2)	3444(3)	4.9
C_2	6754(8)	9178(8)	3254(12)	5.7	C_2	2943(9)	4225(8)	1727(13)	6.3
C_3	6108(10)	8468(9)	3689(14)	7.9	C_3	3556(11)	4269(11)	1170(16)	10.7
C_4	5312(8)	8462(9)	2757(13)	6.7	C_4	4146(10)	3627(9)	1764(17)	9.5
C_5	5609(8)	8554(8)	1386(12)	5.4	C_5	4069(8)	3648(8)	3279(16)	7.2
$C_{1'}$	7525(7)	8395(7)	1082(12)	4.0	$C_{1'}$	2246(7)	3163(7)	3844(12)	4.1
$C_{2'}$	7507(9)	7568(7)	1513(12)	5.2	$C_{2'}$	2289(9)	2406(7)	3169(13)	5.4
$C_{3'}$	8251(9)	7046(8)	1189(13)	6.4	$C_{3'}$	1755(8)	1746(7)	3600(14)	6.1
$C_{4'}$	8888(8)	7334(9)	459(14)	6.6	$C_{4'}$	1217(8)	1839(8)	4622(12)	5.6
$C_{5'}$	8888(8)	8139(10)	8(12)	6.8	$C_{5'}$	1174(8)	2572(9)	5274(14)	6.5
$C_{6'}$	8209(8)	8683(8)	334(12)	5.3	$C_{6'}$	1691(8)	3257(8)	4904(12)	5.6
Cl	5590(2)	9223(2)	7783(3)	5.4	Cl	4103(2)	4302(2)	7264(3)	5.7
O_1*	5479(12)	9533(11)	6420(15)	11.1	O_1*	4354(12)	3565(9)	8003(18)	9.4
O_2*	4738(9)	9378(8)	8320(14)	7.6	O_2*	3378(15)	4134(14)	6586(22)	14.4
O_3*	5704(10)	8378(10)	8003(16)	9.2	O_3*	4624(10)	4657(10)	6314(15)	8.0
O_4*	6140(9)	9788(9)	8501(13)	7.5	O_4*	4067(12)	5044(11)	8092(18)	10.4
$O_{1'}$*	5440(27)	8444(28)	6928(40)	16.3	$O_{1'}$*	3210(15)	4554(17)	7439(27)	11.4
$O_{2'}$*	6074(17)	8566(19)	8652(19)	9.2	$O_{2'}$*	4039(18)	3462(21)	6411(38)	15.1
$O_{3'}$*	5887(16)	9294(18)	6596(28)	8.6	$O_{3'}$*	4990(17)	4479(17)	6994(38)	13.6
$O_{4'}$*	4450(15)	3943(15)	8325(20)	5.9	$O_{4'}$*	4672(17)	9414(19)	7670(39)	13.9

* Occupancies for the disordered atoms are 0.65 for O_1—O_4 and 0.35 for $O_{1'}$—$O_{4'}$, in molecule 1, and 0.60 for O_1—O_4 and 0.40 for $O_{1'}$—$O_{4'}$ in molecule 2, respectively.

a) Equivalent isotropic temperature factor defined by Hamilton.[12]

that are of very high energy.

Another interesting point in the structure of **6b** is that the 1-phenyl group takes a conformation that is nearly perpendicular to the lone-pair orbital of the sulfur atom. This makes an interesting contrast to the structure of dimethylphenylsulfonium ion in which the phenyl group nearly bisects the CH_3–S–CH_3 angle.[15] To get further insight into the implication of the structure, we have carried out the X-ray crystallography of 1-phenylthiolanium perchlorate (**8**) which was easily prepared by treating (4-bromobutylthio)benzene (**7**) with silver perchlorate. The results are shown in Tables 6, 7, 8, and 9.



7 8

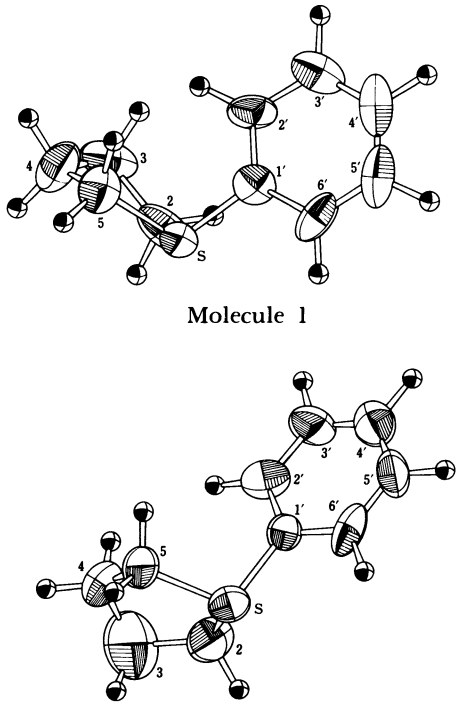
The diffraction data were best interpreted by assuming that there were two kinds of molecules in the crystals in addition to their enantiomers. The two independent molecules are those which differ in the positions of the carbon-3 of the thiolane ring. Thus they are diastereomers. However, their structures are similar except that the position of C_3 which is up or down relative to the plane made by others, C_2–S–C_5–C_4: the torsion angle $C_{1'}$–S–C_2–C_3 in molecule 2 is much larger than that in molecule 1, reflecting the relative positions of C_3. The ORTEP diagrams of these molecules are shown in Fig. 2. Thus only one form (molecule 2) will be used for comparison of the structures of **6b** and **8** that follows. It is interesting that in these molecules C_3 occupies the tip of the envelope. However, the cause for the difference between **8** and 1-methylthiolanium ion[14] is not well understood at present.

Table 7. Selected Bond Distances (Å) in 1-Phenylthiolanium Perchlorate

Atom(1)–Atom(2)	Molecule 1	Molecule 2
S–C_2	1.808(12)	1.803(13)
S–C_5	1.826(12)	1.842(12)
S–$C_{1'}$	1.801(12)	1.806(11)
C_2–C_3	1.565(19)	1.515(22)
C_3–C_4	1.462(19)	1.442(22)
C_4–C_5	1.515(19)	1.572(25)

Table 8. Selected Bond Angles (°) in 1-Phenylthiolanium Perchlorate

Atom(1)–Atom(2)–Atom(3)	Molecule 1	Molecule 2
C_2–S–C_5	94.1(6)	96.0(7)
C_2–S–$C_{1'}$	105.1(6)	104.5(6)
C_5–S–$C_{1'}$	105.2(5)	105.3(5)
S–C_2–C_3	105.4(9)	103.4(9)
C_2–C_3–C_4	107.1(11)	109.2(14)
C_3–C_4–C_5	109.7(11)	108.8(13)
S–C_5–C_4	107.4(8)	103.5(9)



Molecule 1

Molecule 2

Fig. 2. ORTEP diagrams of two forms of 1-phenylthiolanium ion. Number of atoms corresponds with that in Tables 6—9.

Table 9. Selected Torsion Angles (°) in 1-Phenylthiolanium Perchlorate

Atom(1)–Atom(2)–Atom(3)–Atom(4)	Molecule 1	Molecule 2
C_5–S–C_2–C_3	18.6(9)	−21.2(10)
$C_{1'}$–S–C_2–C_3	−88.2(9)	−128.6(9)
C_2–S–C_5–C_4	4.1(9)	−2.7(10)
$C_{1'}$–S–C_5–C_4	111.1(9)	104.1(9)
C_2–S–$C_{1'}$–$C_{2'}$	59.1(11)	54.4(11)
C_2–S–$C_{1'}$–$C_{6'}$	−119.8(9)	−127.4(9)
C_5–S–$C_{1'}$–$C_{2'}$	−39.4(11)	−46.1(11)
C_5–S–$C_{1'}$–$C_{6'}$	141.6(9)	132.1(9)
S–C_2–C_3–C_4	−37.9(12)	42.4(14)
C_2–C_3–C_4–C_5	42.9(14)	−46.9(16)
C_3–C_4–C_5–S	−28.1(13)	28.0(14)

The feature of the structure of **8** is that the phenyl group nearly bisects the angle C_2–S–C_5 although it is tilted a little toward C_4. It seems that in normal dialkylphenylsulfonium ions the phenyl group nearly bisects the C–S–C angle. The tilting of the phenyl group to a small degree in **8** must be caused by avoiding the van der Waals repulsion between the groups concerned. Since, if the phenyl group takes the similar conformation as in **8**, severe steric interactions between the 3-methyl group and the phenyl group are unavoidable in **6b**, the phenyl group seems to take the conformation that is observed by the X-ray crystallography. Indeed, the distance between $C_{2'}$ and the methyl group at C_3 and that between $C_{6'}$ and the same methyl group in **6b** are 4.16 and 4.37 Å, respectively. That is, the ortho carbons of the phenyl group are at about the same distance from the methyl group and are in close contact at about the sum of the van der Waals radii.

The sulfur pyramid in **6b** is not significantly different from that in the 1-phenylthiolanium perchlorate (**8**). However, the five-membered ring is a little more distorted in **6b** than in **8**. This is because, due to the steric effects in the 3,4-positions, the conformation about the C_3–C_4 bond is very close to the perfectly staggered. The carbon atom that occupies the tip of the envelope is 0.68 and 0.58 Å out of the average plane that is made by the other four atoms of the ring in **6b** and **8**, respectively.

We summarize from the structural features of the thiolanium ion discussed above that **6b** has an unusual structure about the C_3–C_4 region because of the steric effects of the two methyl and two ethyl groups. However, this abnormality may not affect the structure of the sulfur pyramid except that the phenyl conformation is unusual in **6b**. Although there is no evidence that the structure of the molecule in the solid state is taken in solution, it is tempting to consider that the lowering of the sulfur-inversion barrier in **6b** to a small extent relative to **1** is ascribable to the fact that the sulfur pyramid is not unusual except that the phenyl group takes a conformation that is perpendicular to the direction of the lone pair orbital of the sulfur atom. Namely the steric effect of the four alkyl groups in 3 and 4 positions appears only at the unusual conformations about the S–$C_{1'}$ bond as far as the barrier to sulfur-inversion concerns.

Experimental

Determination of Rates of Sulfur-Inversion. **6b** was dissolved in chloroform-*d* to make up ca. 0.1 mol L^{-1} solutions. The solution was heated in a thermostatted bath at a given temperature. The starting material and the product were analyzed with the use of ^1H NMR spectra of the methylene protons at 270 MHz. The spectrometer was a JEOL GX-270. The integration method and the weight method afforded agreeable data within the error limit. The data were treated by assuming the reversible first order reaction and the rate constants were put into the Eyring equation to afford kinetic parameters.

X-Ray Crystallography. Crystals suitable for the crystallography were grown from dichloromethane–hexane and acetone–hexane, respectively, for **6b** and **8**.

Colorless crystals (0.5×0.3×0.3 mm) were mounted on a Rigaku AFC-5 automated four-circle diffractometer and the intensity data were collected using Mo $K\alpha$ radiation (λ=0.71073 Å). The ω–2θ scan technique was employed at a scan rate of 3° min^{-1} in ω, and the scan range was calculated by $1.1°+0.5°\tan\theta$. For **6b**, 4218 independent reflections within the range $2\theta<55°$ were measured, and 1851 reflections with $|F_o|>3\sigma|F_o|$ were judged as observed and were used for the structure determination and refinement. For **8**, the total number of measured reflections and the observed reflections were 4644 ($2\theta<50°$) and 1299, respectively. The crystal data and the methods of structure determination were as follows.

6b: $C_{16}H_{25}BF_4S$, F.W.=336.24, triclinic, space group $P\bar{1}$, a=10.025(2), b=10.268(2), c=9.599(1) Å, α=69.91(1)°, β=99.42(2)°, γ=110.68(1)°, V=867.2 Å^3, Z=2, D_c=1.29 g cm^{-3}, μ=2.21 cm^{-1}. The structure was solved by direct methods (MULTAN 78) and refined by the block-diagonal least-squares technique with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogens. All the hydrogen atoms were located on a difference map but their positional parameters were not refined. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[16] Difference syntheses revealed the disorder of the tetrafluoroborate anion, and their positional and anisotropic thermal parameters were refined. The weighting scheme $w=[\sigma_c^2+(0.02|F_o|^2)]^{-1}$ was employed. The final R and R_w values were 6.13 and 8.44%, respectively.

8: $C_{10}H_{13}ClO_4S$, F.W.=264.72, monoclinic, space group $P2_1/n$, a=14.760(1), b=15.928(2), c=10.294(1) Å, β=94.18(1)°, V=2413.6 Å^3, Z=8, D_c=1.46 g cm^{-3}, μ=4.81 cm^{-1}. The structure was solved by direct methods (MULTAN 78), assuming the temperature factor of 2.30, to reveal the positions of four heavy atoms. Two kinds of independent molecules were found in a unit cell. Calculation of structure factors based on the four atoms gave an R value of 55.8%. The Fourier syntheses and successive difference syntheses indicated all the non-hydrogen atoms in addition to the disorder of the perchlorate anion, the positional and anisotropic thermal parameters of which were refined by the block-diagonal least-squares technique. The positions of all hydrogens were obtained by calculation. The positional and isotropic thermal parameters (assumed to be 10.5) of hydrogens were not refined, but were included in the calculation of structure factors. The final R and R_w values were 5.99 and 7.82%, respectively.

All the calculations were carried out on a HITAC M-200H computer with crystallographic computation program system, MULTAN and UNICS III, filed at the Computer Center of the Institute for Molecular Science. The complete F_o–F_c data are deposited as Document No. 8771 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

3,3,4,4-Tetramethylthiolane (4a). To a mixture of 5.4 g (37 mmol) of 2,2,3,3-tetramethyl-1,4-butanediol[11] and 17 mL of dry pyridine, was added 16.8 g (88 mmol) of *p*-

toluenesulfonyl chloride in portions with ice-cooling and stirring. After several hours of stirring, the mixture was allowed to stand in a refrigerator and then poured into 100 mL of water. The precipitates were collected by filtration to give the crude ditosylate, mp 98—107 °C, in 80% yield. ^{1}H NMR ($CDCl_3$) δ=0.83 (12H, s), 2.44 (6H, s), 3.79 (4H, s), 7.36 and 7.69 (8H, ABq, J=8.4 Hz). This crude ditosylate was directly used for the next reaction.

To a solution of 3.0 g (6.6 mmol) of the crude ditosylate in 100 mL of *N,N*-dimethylformamide, was added 3.0 g (13 mmol) of sodium sulfide nonahydrate. The whole was heated under reflux for 2 h and steam-distilled to give 0.7 g (74%) of the desired compound. The pure sample was obtained by sublimation, mp 151—152 °C (sealed tube). High resolution MS: M^+ 144.0973. Calcd for $C_8H_{16}S$: M^+ 144.0973. ^{1}H NMR ($CDCl_3$) δ=0.98 (12H, s), 2.69 (4H, s).

1,3,3,4,4-Pentamethylthiolanium Trifluoromethanesulfonate (5a: X=CF_3SO_3). To a solution of 0.1 g (0.7 mmol) of the thiolane in 2 mL of carefully dried (distilled from CaH_2) dichloromethane, was added 0.1 mL (0.15 g or 0.9 mmol) of methyl trifluoromethanesulfonate and stirred for 1.5 h at room temperature. Addition of ether to the mixture afforded 0.17 g (80%) of the desired compound, mp 120.5—122.0 °C. Recrystallization from ethanol afforded the pure sample, mp 123.5—124.5 °C. Found: C, 38.69; H, 6.16; S, 20.99%. Calcd for $C_{10}H_{19}F_3S_2O_3$: C, 38.95; H, 6.12; S, 20.79%. ^{1}H NMR ($CDCl_3$) δ=1.10 (6H, s), 1.23 (6H, s), 3.22 (3H, s), 3.44 and 3.68 (4H, ABq, J=13.5 Hz).

3,3,4,4-Tetramethyl-1-phenylthiolanium Tetrafluoroborate (6a). A solution of 0.12 g (0.83 mmol) of the thiolane, 0.31 g (0.84 mmol) of diphenyliodonium tetrafluoroborate,[17] and 10 mg of copper(II) benzoate in 3 mL of *N,N*-dimethylformamide was heated in an oil bath at 120—125 °C for 4 h. After the mixture was cooled, ether was added to the mixture and the precipitates were collected by filtration. Recrystallization from ethanol afforded 0.16 g (63%) of the desired product, mp 241.0—245.5 °C. Found: C, 54.51; H, 6.57; S, 10.87%. Calcd for $C_{14}H_{21}BF_4S$: C, 54.56; H, 6.87; S, 10.40%. ^{1}H NMR (DMSO-d_6) δ=1.06 (6H, s), 1.12 (6H, s), 3.97 and 4.07 (4H, ABq, J=13.5 Hz), 7.6—7.8 (3H, m), 7.9—8.1 (2H, m).

***meso*-2,3-Diethyl-2,3-dimethyl-1,4-butanediol (3b).** A solution of 14.0 g of *meso*-2,3-diethyl-2,3-dimethylsuccinic acid[18] in 50 mL of methanol was heated with 5 mL of sulfuric acid for 12 h and poured into water. The mixture was extracted with ether and the ether extracts were dried over magnesium sulfate. Evaporation of the solvent afforded 14.7 g of the crude half-ester of the succinic acid derivative. ^{1}H NMR ($CDCl_3$) δ=0.82 (3H, t, J=7.5 Hz), 0.87 (3H, t, J=7.5 Hz), 1.17 (3H, s), 1.20 (3H, s), 1.5—2.4 (4H, m), 3.68 (3H, s), 10.7 (1H, br s). A solution of the crude monomethyl ester (11.9 g or 55 mmol) in 50 mL of ether was added to 4.0 g (0.1 mol) of lithium tetrahydridoaluminate in 200 mL of ether with ice-cooling and the mixture was heated for 14 h. The mixture was treated with water and then with dilute sulfuric acid with ice-cooling and the ether layer was separated. The aqueous layer was extracted several times with ether. The combined ether extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent afforded 9.4 g (78% based on the succinic acid) of the desired diol, which was purified by recrystallization from dichloromethane–pentane, mp 33.0—34.5 °C. Found: C, 68.67; H, 12.96%. Calcd for $C_{10}H_{22}O_2$: C, 68.92; H, 12.72%. ^{1}H NMR ($CDCl_3$) δ=0.77 (6H, s), 0.83 (6H, t, J=7.5 Hz), 1.1—1.7 (4H, m), 3.46 (4H, s), 4.55 (2H, br s).

***meso*-3,4-Diethyl-3,4-dimethylthiolane (4b).** This compound was obtained in a similar manner as described for the tetramethyl compound **4a**, starting from **3b**; tosylation of the diol followed by treatment with sodium sulfide. The yield was 66%. It was obtained as an oil. High resolution MS: M^+ 172.1308. Calcd for $C_{10}H_{20}S$: M^+ 172.1286. ^{1}H NMR ($CDCl_3$) δ=0.77 (6H, t, J=7.5 Hz), 0.93 (6H, s), 1.17 (4H, q, J=7.5 Hz), 2.58 and 2.73 (4H, ABq, J=10.5 Hz).

Methylation of 4b with Methyl Trifluoromethanesulfonate. To a solution of 0.1 g (0.6 mmol) of the thiolane (**4b**) in 2 mL of dry dichloromethane was added 0.1 mL (0.15 g or 0.9 mmol) of methyl trifluoromethanesulfonate. The product was a ca. 1:1.3 mixture of two isomers which were not assigned. Attempted separation of the stereoisomers failed. The following ^{1}H NMR ($CDCl_3$, δ) were collected. One isomer: 0.98 (6H, t, J=7.5 Hz), 1.05 (6H, s), 1.3—1.5 (4H, m), 3.12 (3H, s), 3.44 and 3.60 (4H, ABq, J=13.7 Hz). Other isomer: 1.01 (6H, t, J=7.5 Hz), 1.16 (6H, s), 1.54 (4H, q, J=7.5 Hz), 3.17 (3H, s), 3.30 and 3.80 (4H, ABq, J=13.6 Hz). The assignment of the peaks at δ 0.98 and 1.01 for the methyl protons may be reversed because their intensities were equal.

(1*r*,3*R*,4*S*)-3,4-Diethyl-3,4-dimethyl-1-phenylthiolanium Tetrafluoroborate (6b). The thiolane (0.60 g or 3.5 mmol) and 1.30 g (3.53 mmol) of diphenyliodonium tetrafluoroborate were treated similarly as described for the synthesis of **4a**. The precipitate (0.75 g) obtained by adding ether to the reaction mixture was recrystallized from ethanol to give 0.32 g (27%) of the desired material, mp 156.5—157.5 °C. Found: C, 57.00; H, 7.37; S, 9.39%. Calcd for $C_{16}H_{25}BF_4S$: C, 57.15; H, 7.49; S, 9.53%. ^{1}H NMR ($CDCl_3$) δ=0.99 (6H, t, J=7.4 Hz), 1.07 (6H, s), 1.49 (4H, q, J=7.4 Hz), 3.58 and 4.20 (4H, ABq, J=13.4 Hz), 7.56—7.61 (3H, m), 7.82—7.86 (2H, m). The crude product contained some stereoisomer of **6b** which was apparently removed by recrystallization.

After equilibration of **6b** by heating, the chloroform solution was concentrated to produce crystals that contained mainly (1*r*,3*R*,4*S*)-**6b**. The repetition of the procedure finally gave a 1:6 mixture of (1*r*,3*R*,4*S*)-**6b** and (1*s*,3*R*,4*S*)-**6b**. Recrystallization of the mixture from ethanol or dichloromethane–hexane did not improve the purity. Found: C, 56.98; H, 7.60%. Calcd for $C_{16}H_{25}BF_4S$: C, 57.15; H, 7.49%. The following ^{1}H NMR data ($CDCl_3$, δ) of (1*s*,3*R*,4*S*)-**6b** were obtained by subtracting the signals due to (1*r*,3*R*,4*S*)-**6b**: 0.89 (6H, t, J=7.3 Hz), 1.11 (6H, s), 1.39 and 1.49 (4H, AB part of ABX_3, J_{AB}=14.1 Hz, J_{AX}=J_{BX}=7.3 Hz), 3.74 and 4.06 (4H, ABq, J=13.2 Hz), 7.61—7.63 (3H, m), 7.78—7.81 (2H, m).

1-Phenylthiolanium Perchlorate (8). To a solution of 0.24 g (0.98 mmol) of (4-bromobutylthio)benzene (**7**)[19] in 20 mL of dichloromethane was added 0.20 g (0.96 mmol) of silver perchlorate and the whole was stirred overnight at room temperature. The precipitate was removed by filtration and the filtrate was concentrated in vacuo. The crystals thus obtained were recrystallized from ethanol to afford 0.20 g (77%) of the desired product, mp 90.0—91.5 °C. Found: C, 45.12; H, 4.96%. Calcd for $C_{10}H_{13}ClO_4S$: C, 45.37; H, 4.95%. ^{1}H NMR ($CDCl_3$) δ=2.55—2.61 (4H, m), 3.66—3.76 (2H, m), 4.17—4.26 (2H, m), 7.61—7.73 (3H, m), 7.80—7.82 (2H, m).

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