experimental observation, this being in connection with 1,3-eliminations from 2-norbornyl tosylates for which a truly concerted process may not apply.

For only two of the 33 different systems considered in this and earlier papers[1,2] are there major discrepancies between the PLM result and experimental observation. In view of this high degree of agreement it is unlikely that the concordance is purely fortuitous. However, the apparent success of the PLM method does not necessarily imply that least motion of atoms is itself the factor which determines stereochemical pathways. It may well transpire that the least motion type of calculation, by virtue of its geometric constraints and hence its implicit adherence to requirements of local symmetry, is successfully simulating some more important stereoelectronic factors.

Acknowledgments. The authors wish to thank many people who have shown interest in this work and who have suggested systems for our consideration. In particular we thank Professors A. Nickon and N. H. Werstiuk for several discussions. The financial support of the National Research Council of Canada is gratefully acknowledged. We also thank the Sir George Williams University Computer Centre and the Institute of Computer Science at the University of Toronto for the use of computer facilities.

Chemistry of *cis*- and *trans*-2,3-Di-*tert*-butylthiiranes (Episulfides). Some Observations on the Consequences of Steric Overcrowding in Small Ring Compounds

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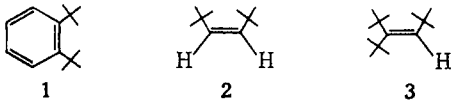
Abstract: Chemical reactions of *cis*- and *trans*-2,3-di-*tert*-butylthiiranes (episulfides) have been investigated. The cis isomer has extra steric strain because of the interference of the bulky *tert*-butyl groups. One side of the molecule is exposed to attack by various reagents. The trans isomer, although probably less strained, is better shielded from attack on either side of the ring. The sulfoxides from both isomers have been prepared as well as an *S*-methylsulfonium salt from the cis isomer. Chlorine cleaves a sulfur–carbon bond of the cis isomer but gives a complex reaction with the trans isomer. Somewhat related behavior is seen with *tert*-butyl hypochlorite. Protonation of both the cis and trans isomers on the sulfur atom occurs in fluorosulfonic acid. In none of the derivatives prepared was there any evidence for ring opening to a presumably less strained 2-thia analog of an allyl cation. The *S*-methylsulfonium salt underwent ring opening in the expected trans fashion with a variety of nucleophiles (water, methanol, chloride, bromide). No evidence for initial attack on sulfur was forthcoming although precedent exists for this type of reaction.

A leitmotiv of organic chemistry is the juxtapositioning of *tert*-butyl groups. Classic examples in which these bulky substituents are positioned on adjacent trivalent carbon atoms are found in *o*-di-*tert*-butylbenzene (**1**),[1] *cis*-1,2-di-*tert*-butylethylene (**2**),[2] and 1,1,2-tri-



1 2 3

tert-butylethylene (**3**).[3] The steric crowding introduces undeniable strain (22.3 kcal/mol in **1** relative to the para isomer,[1] 10 kcal/mol in **2** relative to the trans isomer,[4] apparently unknown in **3**). Hope of discovering the means by which such strain manifests itself in structural features, spectral properties, and chemical reactivity has provided a major impetus for the synthesis and examination of these types of compounds.[5,6]

Our own interest in this general area was stimulated when the *cis*- and *trans*-2,3-di-*tert*-butylthiiranes (episulfides) **4** and **5** became available to us through the routes in eq 1 and 2.[7] *tert*-Butyl groups and other bulky aliphatic substituents are often useful in stabilizing sensitive three-membered rings but in the examples reported thus far[8] the *tert*-butyl groups appear to be in the sterically

(1) (a) For a compilation of references, see E. M. Arnett, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5889 (1967). (b) For *o*-di-*tert*-butyl aromatics, see Ae. de Groot and H. Wynberg, *J. Org. Chem.*, **31**, 3954 (1966). (c) For a discussion of much of the thought that led to interest in *o*-di-*tert*-butyl compounds, see H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972.

(2) W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **81**, 1611 (1959).

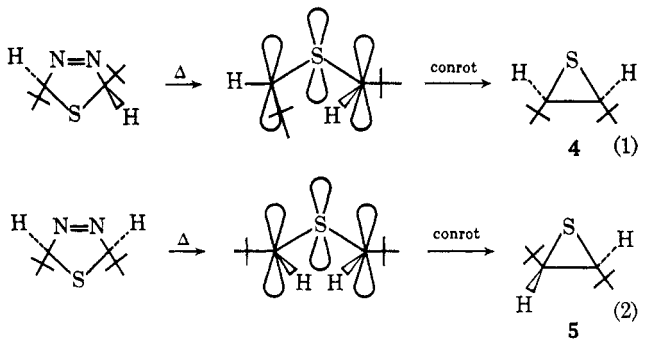
(3) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 4125 (1970).

(4) (a) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958); (b) M. S. Newman, "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, p 248; (c) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972); (d) M. B. Robin, G. N. Taylor, and N. A. Kuebler, *J. Org. Chem.*, **38**, 1049 (1973).

(5) The effects of the considerable steric interaction in these types of compounds are often remarkably muted. Available evidence suggests that in **1** there is no significant deviation from planarity of the π system;[4d,6a] the same holds true in *o*-di-*tert*-butylquinoxaline, the crystal structure of which has been determined.[6b] Bending from planarity of an aromatic system is accomplished in an [8]paracyclophane,[6c] however, and calculations indicate that mild deviations from planarity of the benzene ring require remarkably little energy.[6d] In **2** there appears to be no appreciable twisting of the carbon–carbon double bond.[6e]

(6) (a) E. H. Wiebenga and E. Bouwhuis, *Tetrahedron*, **25**, 453 (1969); (b) G. J. Visser, A. Vos, Ae. de Groot, and H. Wynberg, *J. Amer. Chem. Soc.*, **90**, 3253 (1968); (c) M. G. Newton, T. J. Walter, and N. L. Allinger, *ibid.*, **94**, 5652 (1972); also C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (d) H. Wynberg, W. Nieuwpoort, and H. T. Jonkman, *Tetrahedron Lett.*, 4623 (1973); (e) M. B. Robin, G. N. Taylor, N. A. Kuebler, and R. D. Bach, *J. Org. Chem.*, **38**, 1049 (1973); see also N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972), and ref 6a.

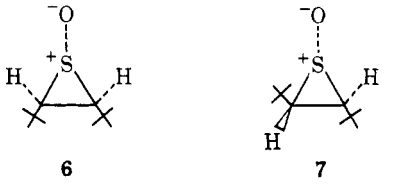
(7) J. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972).



more favorable trans arrangement. With both **4** and **5** available (the cis orientation of *tert*-butyl groups in **4** is to the best of our knowledge unique among three-membered rings) an exceptional opportunity was offered to learn more about the effect on steric strain on three-membered rings using in this case the sulfur atom as a site for chemical manipulation.

Results and Discussion

A. Oxidation, Chlorination, and Alkylation of 4 and 5. The sulfoxides **6** and **7** were prepared by oxidation

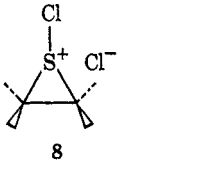


6 **7**

of **4** and **5** with a single equivalent of *m*-chloroperbenzoic acid. The anti configuration for **6** is anticipated on the basis of attack from the less shielded side of **4** and is consistent with a downfield shift of 0.29 ppm of the methine hydrogens compared to those in **4**.[9] The methine hydrogens are also shifted 9.93 ppm downfield in the presence of 0.33 equiv of europium(III) trisdipivaloylmethane as expected for complexation with the oxygen atom from the least hindered side of the molecule.

All attempts to form sulfones from **6** or **7** or from **4** or **5** failed. Reagents investigated included *m*-chloroperbenzoic acid, sodium peroxide in methane sulfonic acid, 30% hydrogen peroxide in acetic acid, 3% hydrogen peroxide in water, ozone, and aqueous potassium permanganate. Cis isomer **6** was resistant to further reaction, probably because of steric hindrance to attack on the side of the *tert*-butyl groups. On the other hand, both **5** and **7** were consumed with excess oxidizing agent but no stable products could be isolated.

Thiiranes are known to be attacked readily by chlorine[10] leading to cleavage of a carbon–sulfur bond. Chlorinated disulfides are usually obtained as products. A chlorosulfonium ion **8** is presumed to be an intermediate in these reactions. With chlorine in methylene chloride at −80° **4** gave **9** in 95% yield (eq 3). The



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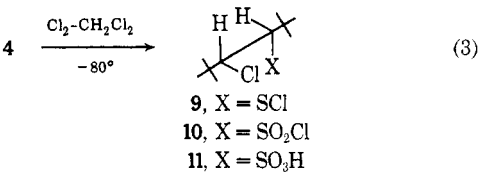
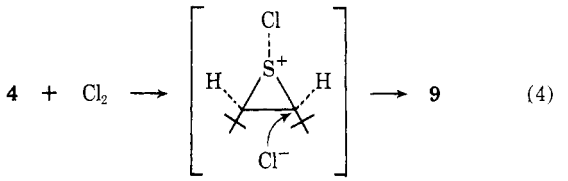


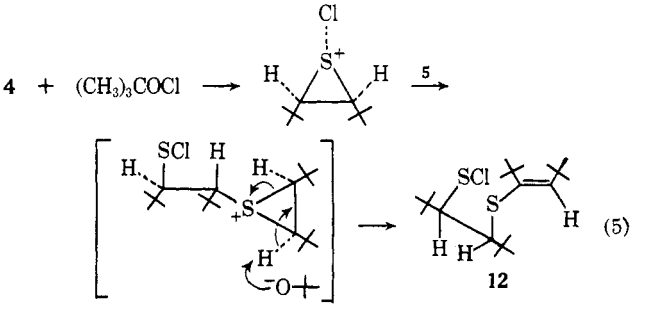
product was clearly a single diastereomer. Arguments for the threo configurational assignment for this and related compounds are offered in section C. The presence of the sulfenyl chloride functionality was established by oxidation with *m*-chloroperbenzoic acid to a sulfonyl chloride **10** (ir 1373 and 1162 cm^{-1}), which was hydrolyzed to the corresponding sulfonic acid **11** (Experimental Section). We are not aware of other examples in which a sulfenyl chloride is isolated on chlorination of a thiirane.

Attempts to chlorinate trans isomer **5** led to complex product mixtures from which no identifiable products could be obtained.

The chlorination of **4** can be explained by the mechanism of eq 4. As a consequence of this mechanism we



anticipated that a source of positive chlorine in which the anionic portion has a greater steric bulk than chloride would open the ring less readily, perhaps allowing the isolation of intermediates. *tert*-Butyl hypochlorite seemed an ideal candidate.[11] Treatment of **4** with this reagent at −10° led to smooth reaction. Although the hope that stable intermediates might be obtained was not met in fact, the reaction did take a considerably different course from that involved in the reaction with chlorine. Product **12** was isolated in 60% yield along



(8) Representative examples are 2,3-di-*tert*-butylaziridine [J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, **89**, 362 (1967)], 2,3-di-*tert*-butylaziridinones (and other bulky substituents) [F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969)], *trans*-2,3-di-*tert*-butylcyclopropanone [J. F. Pazos and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 1030 (1967)], and di-*tert*-butyloxadiaziridine [F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970)]. In this case bulky groups are not mandatory for stabilization. 2,3-Di-*tert*-butylthiadiazirine 1,1-dioxide: J. W. Timberlake and M. L. Hodges, *J. Amer. Chem. Soc.*, **95**, 634 (1973). The same effect can be achieved with adamantyl; see, for example, adamantanespiro-2′-(*N*-1-adamantylaziridone) [E. R. Talaty and A. E. Dupuy, *Chem. Commun.*, 790 (1968)].

(9) (a) Compare with K. Kondo and A. Negishi, *Tetrahedron*, **27**, 4821 (1971). Shifts of methine protons syn to an SO group are less trustworthy than those of methyl groups. The europium shift reagent experiment is more definitive. (b) See also B. J. Hutchinson, K. K. Andersen, and A. R. Katritzky, *J. Amer. Chem. Soc.*, **91**, 3939 (1969).

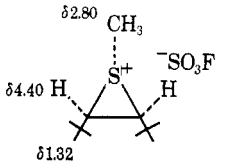
(10) N. V. Schwartz, *J. Org. Chem.*, **33**, 2895 (1968).

(11) C. R. Johnson and J. J. Rigau, *J. Amer. Chem. Soc.*, **91**, 5398 (1969).

with a higher molecular weight material that we could not identify. The structural assignment for **12** rests on elemental composition and the pmr spectrum that showed two methine protons with the unique coupling characteristics seen in **9** as well as other ring-opened products (section C), a single vinylic proton, and four different *tert*-butyl groups. The *tert*-butyl groups on the double bond could conceivably be *E* rather than *Z* as indicated. A possible mechanism for the formation of **12** is given in eq 5; *tert*-butoxide is apparently indeed incapable of nucleophilic displacement at a neopentyl carbon and can terminate the reaction only by abstracting a methine proton.

In contrast, *trans*-thiirane **5** was not attacked appreciably by *tert*-butyl hypochlorite at 0° even on standing 2 weeks.

Methylation of **4** took place on treatment with methyl fluorosulfonate at about 0° in methylene chloride leading to sulfonium salt **13**, which could be isolated in

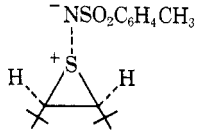


13

crystalline form. This salt is very sensitive to moisture and also decomposes even on standing a few hours at 20°. It is best handled as a solution in methylene chloride with efficient exclusion of moisture. The structure is based chiefly on the nmr data ($CDCl_3$) shown and on the reactions described in the following section. The indicated stereochemistry rests on the assumption that substitution will occur from the least hindered side of the molecule. Owing to the instability of **13** an elemental analysis could not be obtained. To the best of our knowledge, this is the second sulfonium salt from a thiirane to be defined in any detail. Helmkamp and coworkers[12] have previously described the *S*-methyl salt of cyclooctene sulfide.

Ambient or higher temperatures were required to cause reaction between trans isomer **5** and methyl fluorosulfonate. No characterizable products were isolated. Methylation likely occurs analogously to **4** but the increased steric hindrance to bimolecular substitution forces the use of higher temperatures at which the derived salt is not stable.

We mention briefly some attempted but failed reactions. The *p*-toluenesulfonylsulfinimide **14** could not

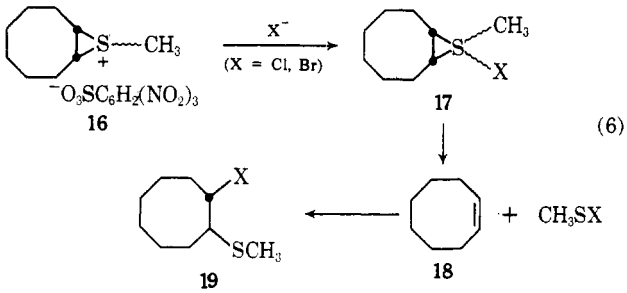


14 (not formed)

15 (not formed)

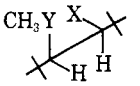
be obtained on treatment of **4** with *p*-toluenesulfonyl azide in methanol with a copper catalyst[13] or in water with chloramine-T or by exchange of sulfoxide **6** with *N*-sulfinyl-*p*-toluenesulfonamide or *N*,*N*′-bis(*p*-toluenesulfonyl)sulfur diimide.[14] Neither **4** nor **5** could be opened with dry hydrogen chloride in methylene chloride although this reaction is characteristic of other thiiranes.[10] Some attempts were made to prepare the unusual ring structure **15**[15] by elimination of water from sulfoxide **6** induced by acetic anhydride (the Pummerer reaction followed by loss of acetic acid was hoped for); **6** was continually recovered unchanged, however. Reactions of **7** were less well investigated owing to a shortage of material. An attempt to prepare **15** by dehydrogenation with diethyl azodicarboxylate was also fruitless.[16] Attempts to prepare a complex from **4** and iron pentacarbonyl or diiron nonacarbonyl in refluxing benzene[17] led to extensive color changes but **4** was recovered essentially unchanged.

B. Reactions of Sulfonium Salt 13. Sulfonium salts of thiiranes have long been postulated as intermediates in the solvolyses of β-thio-substituted halides[18] and in the addition of sulfenyl halides to olefins.[19] Helmkamp and coworkers[12a] made the unanticipated observation that **16**, although it ultimately provides **19** on



(6)

treatment with chloride or bromide, reacts initially at sulfur providing an unstable σ-sulfurane **17**[20] that decomposes to methanesulfenyl halide and cyclooctene. Subsequent reaction between these two reagents provides ultimately **19** (eq 6). Apparently in this case the rate of nucleophilic attack at sulfur is appreciably greater than SN2 displacement at carbon. With these results in mind, the chemistry of **13** was investigated. In actual fact, ring opening took place. With relatively soft nucleophiles **13** afforded **20**–**24**, all of which



20, Y = S; X = OH
21, Y = S; X = OCH_3
22, Y = S; X = Cl
23, Y = S; X = Br
24, Y = S; X = $NHC(O)CH_3$
25, Y = SO_2; X = OH
26, Y = SO_2; X = OH
27, Y = SO; X = OCH_3
28, Y = SO_2; X = OCH_3

are assigned threo structures on the basis of the arguments in the following section. Reaction with water

(12) (a) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963); **29**, 2702 (1964); D. C. Owsley, G. K. Helmkamp, and S. N. Spurlock, *J. Amer. Chem. Soc.*, **91**, 3606 (1969). (b) For less well defined examples, see L. Goodman, A. Benitez, and B. R. Baker, *ibid.*, **80**, 1680 (1958), and P. P. Budnikoff and E. A. Schilow, *Ber.*, **55**, 3848 (1922).

(13) H. Kwant and A. A. Kahn, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).

(14) (a) G. Schultz and G. Kresze, *Angew. Chem.*, **75**, 1022 (1963); (b) G. Kresze, *Tetrahedron Lett.*, 1671 (1966); (c) D. J. Cram, *et al.*, *J. Amer. Chem. Soc.*, **92**, 7369 (1970).

(15) For the corresponding oxides, see L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spienak, *J. Amer. Chem. Soc.*, **93**, 476 (1971), and L. A. Carpino and H.-W. Chen, *ibid.*, **93**, 785 (1971).

(16) F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966).

(17) R. B. King, *Inorg. Chem.*, **2**, 236 (1963).

(18) A. Streitweiser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 108–110.

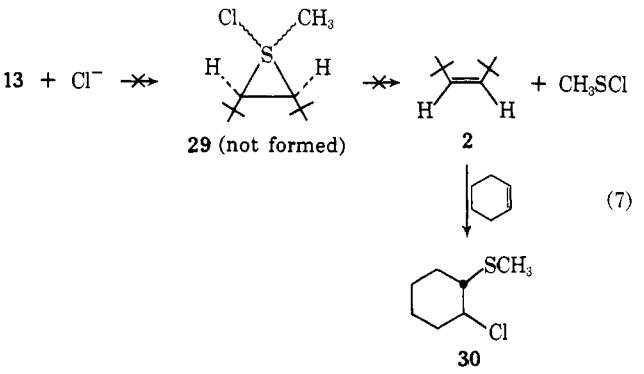
(19) (a) W. A. Thaler, W. H. Mueller, and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2069 (1968), and previous papers from the Esso group. (b) For a review see W. H. Mueller, *Angew. Chem.*, **81**, 475 (1969).

(20) Nomenclature suggested by B. M. Trost and S. D. Ziman, *J. Org. Chem.*, **38**, 932 (1973), ref 21.

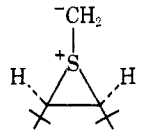
gave **20** (73% yield) and with methanol **21** was obtained (86% yield). To establish that sulfur was bivalent, *i.e.*, that a σ-sulfurane analogous to **17** was not the product, oxidation to the respective sulfoxides and sulfones **25–28** was carried out with the required amount of *m*-chloroperbenzoic acid.[21] The hydroxyl groups in **20**, **25**, and **26** exchanged readily with deuterium oxide. Sulfones **26** and **28** exchanged at the methyl groups in deuteriomethanol–methoxide but the forcing conditions required to obtain exchange at the more hindered methine positions led to some decomposition.

With lithium chloride and lithium bromide in acetonitrile, **22** (80% yield) and **23** (40% yield) were obtained together with **24** (after aqueous work-up) in 5 and 59% yields, respectively. Acetonitrile reacted spontaneously with **13** giving, after aqueous work-up, a mixture of **20** and **24**. The yield of **23** was raised to 69% when **13** was allowed to react with lithium bromide suspended in ether. With lithium fluoride in acetonitrile only **24** (90% yield) was obtained. When treated with either lithium iodide or tetrabutylammonium iodide, **13** failed to give an iodide. However, free iodine was formed in these reactions and in the latter small amounts of *cis*- and *trans*-di-*tert*-butylethylenes were noted. Phenol, *p*-dimethoxybenzene (to see if **13** was capable of accomplishing electrophilic substitution), acetic acid, and *n*-butylthiol failed to give any identifiable products with **13**.

The ring opening, at least on the basis of the evidence now available, appears to involve attack of a nucleophile at a (sterically badly hindered) neopentyl carbon rather than by a mechanism analogous to that of eq 6. This conclusion is chiefly based on experiments using **13** and lithium chloride. If a sulfurane **29** were involved (eq 7), then fragmentation would produce **2** and methanesulfenyl chloride. In independent experiments methanesulfenyl chloride and **2** did not react; no **22** could be detected. Moreover, when run in the presence of a large excess of cyclohexene, the reaction of **13** and lithium chloride gave only **22** with no trace of either **2** or **30** (eq 7). Helmkamp and coworkers[12a] described a similar experiment with **16** leading to **18** and **30**. We repeated this experiment to test our method and we were able to reproduce the described results fully.



Efforts were undertaken to deprotonate **13** to give ylide **31**. However, on treatment with methyllithium, *n*-butyllithium, or diisopropylamide only undefinable products were obtained.



31 (not formed)

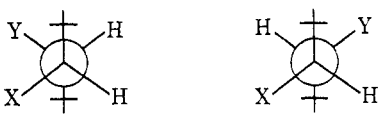
C. Structures of the Ring-Opened Products. All the products derived from ring opening of **13** and the chlorination product **9** have in common two distinguishable absorptions for the *tert*-butyl groups and two separate methine absorptions with the chemical shifts expected for the heteroatom substitution pattern (Table I). These absorptions were sharp or slightly broadened singlets (save in **24** in which the N–H was coupled to a methine proton; however, the methine protons themselves were not coupled). The only derivative in which any coupling of the methine protons could be discerned was **28** in which a coupling constant of $J = 2.5$ Hz (60 MHz) was measured. Precursors **21** and **27** failed to show this coupling.

Table I. 60-MHz Pmr Data[a] for Ring-Opened Products from **4**

Compd	*t*-Bu	Methine	Other
20[b]	0.96, 1.02	2.36, 3.42	2.17 (br s, OH) 2.19 (s, CH_3S)
21[b]	1.00, 1.05	2.30, 3.06	2.12 (s, CH_3S) 3.49 (s, CH_3O)
22[b]	1.05, 1.10	2.56, 4.08	2.18 (s, CH_3S)
23[c]	1.00, 1.13	2.56, 4.31	2.00 (s, CH_3S)
24[b]	0.93, 1.00	2.37, 4.10 (d, J = 10.5 Hz)	1.99 (s, CH_3CO) 2.20 (s, CH_3S) 6.10 (br, NH)
25[b]	1.01, 1.10	3.04, 3.88	2.83 (br s, OH) 2.85 (s, CH_3SO)
26[b]	1.01, 1.30	3.08, 3.70	3.08 (s, CH_3SO_2) 3.44 (br s, OH)
27[b]	1.02, 1.26	2.93, 3.15	2.87 (s, CH_3SO) 3.48 (CH_3O)
28[b]	1.00, 1.30	3.12 (d, J = 2.5 Hz) 3.31 (d, J = 2.5 Hz)	3.12 (CH_3SO_2) 3.60 (CH_3O)
9[c]	1.12[d]	3.22, 4.01	

[a] Chemical shifts as δ values from TMS; unless otherwise noted absorptions are singlets. [b] In $CDCl_3$. [c] In CCl_4. [d] *t*-Bu absorptions overlap in this case.

These common features point in turn to common stereochemical arrangements with the choice being between threo (**32a**) or erythro (**32b**). The bulkiness of



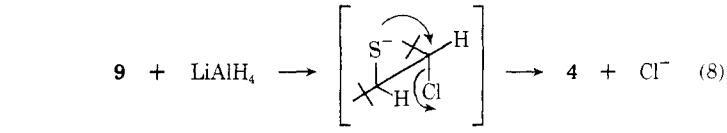
32a **32b**

the *tert*-butyl groups makes it reasonable that the illustrated conformers are most favored. The trans-coplanar arrangement of the methine hydrogens in **32b** should lead to appreciable coupling. On the other hand, the gauche-oriented methine protons of **32a** would, at best, couple less strongly and in view of the presence of two electronegative substituents, X and Y, coupled with sensitivity of J_{vic} to small changes in angle near 60°, small or nonexistent coupling is to be ex-

(21) A sulfurane can presumably consume no more than 1 equiv of oxidizing agent; see, for example, E. F. Perozzi and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5519 (1972). No evidence could be obtained for any intermediates that might have characteristics of a σ-sulfurane; see, for example, J. C. Martin and R. J. Arhart, *ibid.*, **94**, 4997 (1972).

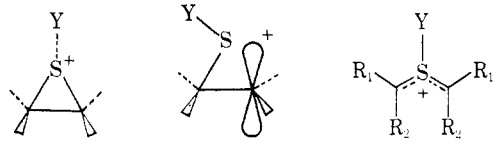
pected.[22] Unfortunately all efforts to obtain examples of **32b** by ring opening of *trans*-**5** were unsuccessful.

Independent chemical confirmation for the threo assignment was sought. A structural proof was desired in which the elements of X and Y would be eliminated in a trans manner leading to *cis*-di-*tert*-butylethylene (**2**). It was considered essential in any demonstration of stereochemistry by chemical reaction that the sterically *least favored* product be formed, since in these highly hindered molecules steric factors might change the course of an elimination from the stereochemistry normally encountered in simpler compounds. In our hands a variety of schemes to bring about trans elimination failed. What did succeed was conversion of **9** back to **4** in high yield on treatment with lithium aluminum hydride. A reasonable mechanism is that shown in eq 8. The formation of sterically less favored **4** in-



stead of **5** speaks for an intramolecular SN2 displacement as shown supporting the assigned stereochemistry and also that assigned for **20–28** by spectral analogy.

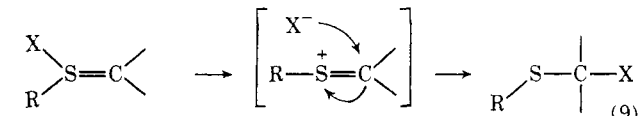
D. Structure of the Three-Membered Rings. Protonated Episulfides. The sulfur atom of not only **4** and **5** but of other thiiranes is subject to attack by good electrophiles. There is reason to wonder about the structure of the intermediates that are formed. Forms **33** and **34** (the sulfur atom possibly undergoing a rapid,



33 34 35

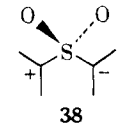
reversible 1,2 shift) have been most commonly considered with the weight of evidence being in favor of **33** at least as extrapolated from the results of the addition of sulfenyl halides to unsymmetrical olefins.[19] A third structural possibility that appears to have received little, if any, consideration is **35**. We felt that particularly in the reactions of **4** that **35** (R_1 = *tert*-butyl) had a chance of existence. Attack of the electrophile on sulfur followed by or concomitant with outward disrotatory rotation of the *tert*-butyl groups would relieve the strain arising from steric interaction. Excellent precedent for this type of reaction is found in the solvolyses of cyclopropyl halides[23] and *N*-chloroaziridines.[24]

The retention of the ring carbon–carbon bond in the various ring-opened products from **5** need not be *a priori* evidence against **35**. Compounds having the structural elements of **36** are well known to rearrange,



as shown in eq 9, to structure **37**. Attack of a nucleophile X^- at a neopentyl carbon of **35** followed by the rearrangement of eq 9 (X being the substituted neopentyl group) would give the ring-opened products. It is not easy to predict whether steric factors in such a rearrangement would dictate the observed exclusive formation of threo products.

In connection with the above considerations we note that the ring carbon–carbon bond of crystalline *cis*-2,3-diphenylthiirane *S*-dioxide is abnormally long, 1.60 Å, although there seems to be no evidence of any outward disrotatory twisting of the phenyl groups.[27] This bond lengthening has been attributed to electron donation from the sulfur dioxide segment to an antibonding orbital between the two carbon atoms.[28] In addition, experimental evidence has been accumulated that implicates dipolar ions of type **38** as intermediates in cer-



38

tain intramolecular cycloadditions.[29a] Moreover, **35** (Y = CH_3) forms an integral part of *S*-methylthiophenium ions.[29b]

We attempted to probe structures of charged intermediates formed from **4** and **5** by using pmr and cmr spectroscopy. Although the S-methylated salt **13** was available, our failure to alkylate **5** deprived us of a nearly indispensable reference compound. To obtain reasonably stable positively charged species from **4** and **5**, attention was turned to a reaction with minimal steric requirements, namely protonation. This succeeded quite well. When added slowly with vigorous mixing to a solution of fluorosulfonic acid at −60°, both **4** and **5** were completely protonated. The pmr spectra of the derived ions as well as those of some reference compounds are collected in Table II. The ion **39** derived from **5** on quenching in methanol–sodium methoxide reaffords the parent compound in at least 80% yield. The chemical shifts of the methine protons (δ 4.90 and 4.96) agree very well with shifts of protons α to protonated sulfur found by Olah and coworkers[30] in alicyclic sulfides (see the spectrum of protonated diisopropyl sulfide in Table II for reference).

(22) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, London, 1966, pp 678–681. (b) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, pp 103–105. (c) *cis*-Di-*tert*-butylethylene (**2**) undergoes trans oxymercuration to give a threo adduct with a 1.6-Hz coupling (60 MHz) between the gauche-oriented methine protons: R. D. Bach and R. F. Richter, *J. Org. Chem.*, **38**, 3442 (1973). Rather surprisingly, *trans*-di-*tert*-ethylene gives the same oxymercuration product as obtained from **2**. It is not at all clear why one isomer reacts *via* trans and the other *via* syn addition.

(23) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, **87**, 4006 (1965); (b) P. v. R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Panst, *ibid.*, **88**, 2868 (1966); (c) U. Schöllkopf, F. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. van Dine, *Tetrahedron Lett.*, 3639 (1967); (d) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

(24) (a) P. G. Gassman and D. K. Dygos, *J. Amer. Chem. Soc.*, **91**, 1543 (1969); (b) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(25) (a) D. L. Tuleen, *J. Org. Chem.*, **32**, 4006 (1967); (b) D. L. Tuleen and V. C. Marcum, *ibid.*, **32**, 304 (1967).

(26) (a) L. Horner and P. Kaiser, *Justus Liebigs Ann. Chem.*, **626**, 19 (1959); (b) C. R. Johnson and W. D. Philips, *Tetrahedron Lett.*, 2101 (1965).

(27) R. Desiderato and R. L. Sass, *Acta Crystallogr.*, **23**, 430 (1967).

(28) R. Hoffmann, H. Fujimoto, J. R. Swenson, and C-C. Wan, *J. Amer. Chem. Soc.*, **95**, 7644 (1973).

(29) (a) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **95**, 2230 (1973); (b) R. M. Achesin and D. R. Hanson, *J. Chem. Soc. C*, 1764 (1970).

(30) G. A. Olah, D. H. O'Brien, and C. V. Pittman, *J. Amer. Chem. Soc.*, **89**, 2996 (1967).

Table II. Pmr Chemicals Shifts and Coupling Constants of Some Protonated Thiiranes in Fluorosulfonic Acid at −50 to −80° Measured at 60 MHz

Ion	Chemical shifts[a] (J_{H-H}, Hz) 2,3-H	$(CH_3)_2C$	SH	CH_3
39	4.96 (d, J = 6), 4.90 (d, J = 8)	1.52 (s), 1.49 (s)	3.01 (dd, J = ~6, 8)	
40	4.95 (d, J = 8)	1.70 (s)	3.54 (t, J = 8)	
41	4.72 (d, J = 8)	1.70 (s, ?)[b]	2.68 (t, J = 8)	
42			2.37 (s)	1.88 (s), 2.04 (s)
$[(CH_3)_2CH]_2\overset{+}{S}H$	4.33 (septet, J = 7)[c]		6.46 (t, J = 7)	2.06 (d, J = 3),[d] 1.93 (d, J = 3)

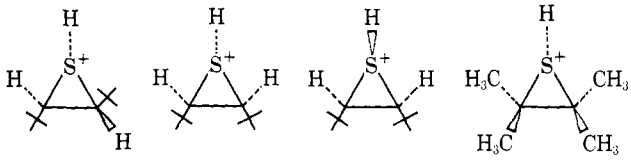
[a] Referred to external TMS. [b] Absorption apparently lies under that of **40**. [c] Methine protons. [d] Geminal methyl groups.

Table III. Cmr Chemical Shifts and $J_{^{13}C-H}$ Couplings for Some Selected Compounds Measured at 25.2 MHz

Compd	Chemical shifts[a] ($J_{^{13}C-H}$, Hz) 2,3-C	$(CH_3)_3C$	$(CH_3)_3C$	SCH_3	CH_3
4[b]	55.6 (d, J = 155)	32.3	30.5 (q, J = 126)		
5[b]	50.7 (d, J = 160)	31.6	27.7 (q, J = 124)		
6[b]	71.4 (d, J = 157)	31.8	30.8 (q, J = 126)		
7[b]	63.8 (d, J = 155),	33.2	29.5 (q, J = 122),		
	58.3 (d, J = 157)	30.8	28.1 (q, J = 122)		
13[b]	76.2 (d, J = 165)	34.2	30.8 (q, J = 126)	27.6 (q, J = 128)	
39[c]	74.5 (d, J = 167),	37.2	30.2 (q, J = 120)[d]		
	75.1 (d, J = 167)	37.7			
40[c]	78.3 (d, J = 127)	38.3	34.0 (q, J = 125)		
$[(CH_3)_2CH]_2\overset{+}{S}CH_3$, $\bar{S}O_3F$[b]	43.3 (d, J = 146)[e]			14.3 (q, J = 145)	17.8 (q, J = 130)

[a] All chemical shifts are referred to TMS. [b] In $CDCl_3$. [c] In FSO_3H at −50°. [d] All methyl carbons resonate at the same frequency. [e] Tertiary carbons α to sulfonium center.

The 1,3 protons of the allyl cation, which might serve as a reference material for any derivative of **35**, absorb in contrast at δ 8.97 in SO_2–SbF_5 mixtures.[31] The clear nonequivalence of the *tert*-butyl groups and the methine protons are expected consequences of a pyramidal sulfur atom. No temperature-dependent changes were observed in the spectrum between +20 and −110°. The most logical structure for **39** is indeed the simplest,



39 **40** **41** **42**

namely a protonated three-membered ring, as indicated. An open carbonium ion analogous to **34** seems unlikely since quenching should lead to ring opening.

Protonation of **4** led to a more complicated spectrum in which two ions, **40** and **41**, could be distinguished, present in about 80:20 mixture. Quenching led to recovery of **4** in minimally 80% yield. The fairly close analogy in chemical shifts with **39** suggests that in this important case the ring also must be closed. We suggest that **40** (major) and **41** (minor) are geometrical isomers as indicated. Proton exchange in protonated sulfides is slow relative to the nmr time scale, making the observation of geometrical isomerism possible—note the appearance of diastereotopic methyl groups in protonated diisopropyl sulfide (Table II).[30]

To obtain a reference material for the ions derived from **4** and **5**, 2,2,3,3-tetramethylthiirane was protonated leading to an ion assigned structure **42**. In this case protonation was accompanied in our hands by considerable polymerization. Here the one notable feature of the spectra of **39–41**, namely, the remarkably large upfield shift of about 4 ppm of the S–H absorption relative to alicyclic derivatives, is again reproduced. The high-field absorption of the S–H appears to be the only anomalous or unexpected feature of the spectra. The J_{SH-CH} coupling constants for **40–42** are of the same magnitude as observed in alicyclic protonated sulfides.

These pmr data argue strongly against the formation of ions like **35** even from **4**, which would seem the most logical candidate for such a reaction. To probe into any more subtle structural differences between **4** and **5** and their derivatives, a number of cmr spectra were measured. These are listed in Table III. Cmr chemical shifts are supposedly more sensitive to charge density at a carbon atom than pmr chemical shifts. Cmr spectroscopy has proven to be particularly useful in understanding the structure of carbonium ions.[32,33]

The effect of introducing a semipolar bond on sulfur (**6** and **7**) or a formal charge (**13**, **39**, **40**) is reflected in a moderate downfield shift of the ring carbon atoms.[34] However, the chemical shifts of these carbon atoms lie at far higher field than, for example, the terminal carbons of various allyl cations, which absorb between 200 and 240 ppm from TMS in super acids.[32,35] The differences in spectra between the *cis*- and *trans*-di-*tert*-butyl derivatives are frustratingly small. Cmr

(31) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **86**, 5682 (1964).

(32) For spectra of allyl carbonium ions, see G. A. Olah, P. R. Clifford, Y. Halpern, and R. G. Johanson, *J. Amer. Chem. Soc.*, **93**, 4219 (1971).

(33) For pertinent criticism, see H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973).

(34) Ion **41** was recognizable only in a peak for the ring carbons at δ 79.4. The relatively poor resolution in fluorosulfonic acid prevented the identification of other absorptions.

(35) Comparison with some of the data given by G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969), leads to the crude guess that the chemical shift of the 2,3 carbons in an open, but rapidly equilibrating ion such as **34** (Y = H or CH_3) should be around 190 ppm downfield from TMS. All observed values are at more than a 100-ppm field higher than this.

spectroscopy gives no hint, either in chemical shift or ^{13}C–H coupling, that the cis-oriented *tert*-butyl groups in **4**, **6**, **13**, and **40** force any unusual changes in geometry. At least on the basis of the spectroscopic data now in hand, we must conclude that there is no detectable tendency toward ring opening in any case investigated here, despite the fact that this would provide a seemingly attractive manner for compounds derived from **4** to relieve strain.

General Comments. Two points arise on consideration of the results. First, the *tert*-butyl groups protect **4** and **5** from attack by external reagents. In **5**, as in other *trans*-di-*tert*-butyl-substituted three-membered rings, both faces of the ring are shielded since the hydrogens of the methyl groups are ideally arranged to hinder attack on sulfur.[36] On the other hand in **4** one face of the ring is exposed and is readily attacked. This allows the development of a fairly broad chemistry for **4**. Approach of an entity from the *tert*-butyl shielded face of **4** seems almost impossible, however.

The second point is the readiness with which the unavoidable strain in **4** and its derivatives is accommodated without significant effects on structural properties. Although more refined measurements or experiments might reveal more clearly the effects of strain, it is clear that at least in these compounds steric hindrance is a poor driving force for bringing about significant structural modification even when seemingly feasible routes for strain relief are available.

Experimental Section

Melting points were determined on various oil bath units; both melting and boiling points are uncorrected. Infrared (ir) spectra were obtained on Unicam SF-200 and Perkin-Elmer 257 instruments. Proton nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 spectrometer; values are reported in parts per million (ppm) δ downfield from tetramethylsilane (TMS), which was used as an internal standard. A Jeolco C-60HL spectrometer was used for low-temperature pmr spectroscopy. Carbon-13 nuclear magnetic resonance spectra were determined on a Varian XL-100-15 spectrometer system equipped for pulsed Fourier transform operation at 25.2 MHz; deuteriochloroform or hexadeuterioacetone (spectra in fluorosulfonic acid) was used as an internal standard; reported values have been corrected to parts per million downfield from TMS by taking the shift of $CDCl_3$ as δ 76.9 and of C_2D_6O as δ 207. Most nmr spectra are given in the text. Mass spectra were obtained on an AEI MS 9 instrument. Elemental analyses were carried out by the analytical section of this department. Gas–liquid chromatography (glc) was done on a F & M 810 chromatograph equipped with glass injector port and a splitter which directed 10% of the column effluent to the flame ionization detector; the remainder was available for collection. A glass 6 mm by 100 cm column with 16% SE-30 on Chromosorb W AW (30–60 mesh) was used for all separations; the injector port temperature was typically 270°; detector and splitter, 250°.

Solvents, distilled from an appropriate drying agent (sodium, phosphorus pentoxide, calcium hydride, or anhydrous sodium sulfate) were stored over Linde 3A molecular sieves. Silica gel, 60–120 mesh, was used for all column chromatography. Solvents were removed on a film evaporator under aspirator vacuum.

cis-**2,3-Di-*tert*-butylthiirane (4)** was synthesized in quantitative yield by heating *trans*-2,5-di-*tert*-butyl-1,3,4-Δ^3-thiadiazoline dissolved in a small amount of diethyl ether in a sealed tube at 100° for 8 hr.[7] Removal of solvent gave the product which was *ca.* 99% pure as determined by glc analysis.

cis-**2,3-Di-*tert*-butylthiirane *S*-oxide (6)** was prepared by oxidation of **4** with *m*-chloroperbenzoic acid. The compound is a colorless, hydroscopic liquid, bp 80–81° (0.10 Torr), obtained in 86% yield: nmr ($CDCl_3$) δ 3.07 (s, 2 H, methine H), 1.18 (s, 18 H, *t*-Bu); ir (neat) 1072 cm^{-1} (S→O). *Anal.* Calcd for $C_{10}H_{20}OS$: C, 63.77; H, 10.71; S, 17.03. Found: C, 63.55; H, 10.68; S, 16.97.

Repeated attempts to oxidize either **4** or **6** to *cis*-2,3-di-*tert*-butylthiirane *S*-dioxide met uniformly with failure. Stirring **4** with 3 equiv of *m*-chloroperbenzoic at 50° for 12 hr or at room temperature for 10 days gave only **6** in 60–80% yield; neither the sulfone nor *cis*-di-*tert*-butylethylene was detected in the reaction product. Hydrogen peroxide (30%) in acetic acid,[37] 30% hydrogen peroxide in an equal volume of dioxane and aqueous potassium permanganate, or 100% hydrogen peroxide generated from sodium peroxide and methanesulfonic acid[38] failed to give any reaction; starting material was recovered in good yield even when the reactants were heated to 40–50° for 42–48 hr.

trans-**2,3-Di-*tert*-butylthiirane (5)** was separated from the mother liquors of the synthesis of *trans*-2,5-di-*tert*-1,3,4-Δ^3-thiadiazoline by careful column chromatography over silica gel using a 150-cm column with a 3-cm diameter. Elution with pentane gave a forerun of sulfur followed by **5**, a faintly yellow liquid, which was more than 99% pure by glc analysis.

trans-**2,3-Di-*tert*-butylthiirane *S*-oxide (7)**, a white solid, mp 69–70°, was synthesized in 80% yield by the *m*-chloroperbenzoic acid oxidation of **5**. The general procedure was modified by running the reaction and work-up at or below room temperature to take into account the sensitivity of **6** to heat; prolonged exposure to temperatures greater than 50° causes elimination of the elements of sulfur monoxide. The ^1H nmr spectrum of **6** shows ($CDCl_3$) δ 3.11 (d, 1 H, J = 12 Hz, methine H), 1.87 (d, 1 H, J = 12 Hz, methine H), 1.28 (s, 9 H, *t*-Bu), 0.92 (s, 9 H, *t*-Bu); ir (KBr) 1062 cm^{-1} (S→O). *Anal.* Calcd for $C_{10}H_{20}OS$: C, 63.77; H, 10.71; S, 17.03. Found: C, 63.84; H, 10.68; S, 16.94.

Attempts to make *trans*-2,3-di-*tert*-butylthiirane *S*-dioxide by the methods described in the attempted synthesis of the cis isomer also failed, due in part to the thermal lability of **7** when heated. In all cases either **7** or, at higher reaction temperatures (*ca.* 60°), *trans*-di-*tert*-butylethylene was recovered.

Preparation of *cis*-2,3-di-*tert*-butyl-*S*-methylthiironium fluorosulfonate (13) was carried out in a nitrogen swept, flame-dried flask equipped with a magnetic stirrer and rubber septum. A solution of **4** (*ca.* 1.0 g) was made in 10 ml of carbon tetrachloride and was cooled in a 15° water bath. Methyl fluorosulfonate (Aldrich Chemical Co., bp 92–94°; 1.2–2.0 equiv) was added neat, dropwise, through the rubber septum. A white solid formed within 1 hr; the mixture was decanted under nitrogen into a Büchner funnel and was washed with 300 ml of carbon tetrachloride to remove excess methyl fluorosulfonate and fluorosulfonic acid. Drying in a vacuum desiccator gave **13** as a white, water-sensitive, powdery solid which decomposed to a black tar after 4 hr at room temperature; it could be stored under nitrogen at −30° for about 1 day: nmr ($CDCl_3$) δ 4.40 (s, 2 H, methine H), 2.80 (s, 3 H, SCH_3), 1.32 (s, 18 H, *t*-Bu). The instability of the product precluded the determination of melting point, ir spectra, or elemental analysis.

Alternatively, the reaction could be run in the same manner as described above using methylene chloride as a solvent; a clear, homogeneous solution results which can be used in further reactions without purification in those cases where small amounts of methyl fluorosulfonate or fluorosulfonic acid are not objectionable.

Thiirane **5** was treated with methyl fluorosulfonate in an attempt to isolate the *S*-methylsulfonium salt. When **5** was stirred for 1 hr under conditions identical with those of the synthesis of **13**, a brown tar was obtained with a complex nmr spectrum indicative of decomposition of the reactant. When this reaction was repeated at −70° and followed by nmr spectroscopy, no change took place within 3 hr; warming to room temperature over a period of 4 hr produced no change until decomposition of the starting material commenced at 0°. Addition of methanol at 0° gave no isolable product.

Similarly, cyclohexene sulfide, prepared by the method of van Tamelen,[39] or tetramethylthiirane[7] decomposed in the presence of methyl fluorosulfonate at temperatures greater than 0°, giving tars with very complex nmr spectra; addition of methanol to the partially decomposed substrate gave no characterizable products.

Diisopropylmethylsulfonium fluorosulfonate was prepared by adding methyl fluorosulfonate dropwise to a *ca.* 10% solution of isopropyl sulfide (prepared according to McAllan[40]) in $CDCl_3$ with

(36) M. S. Newman, *J. Amer. Chem. Soc.*, **72**, 4783 (1960).

(37) S. Hünig and O. Boes, *Justus Liebigs Ann. Chem.*, **579**, 23 (1953).

(38) A. H. Alberts, H. Wynberg, and J. Strating, *Syn. Commun.*, in press.

(39) E. E. van Tamelen, *J. Amer. Chem. Soc.*, **73**, 3444 (1951); *Org. Syn.*, **32**, 39 (1952).

(40) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, **73**, 3627 (1951).

1% TMS in an nmr tube until formation of the salt was complete as determined by the nmr spectrum. The reaction at room temperature is rapid, exothermic, and quantitative, giving a clear, colorless, stable solution: nmr ($CDCl_3$) δ 3.86 [septet, 2 H, J = 7 Hz, $CH(CH_3)_2$], 2.84 (s, 3 H, SCH_3), 1.66 [d, 6 H, J = 2 Hz, $CH(CH_3)_2$], 1.51 [d, 6 H, J = 2 Hz, $CH(CH_3)_2$].[30]

Diethylmethylsulfonium fluorosulfonate was formed in the same way as described above: nmr ($CDCl_3$) δ 3.35 (q, 4 H, J = 7 Hz, CH_2CH_3), 2.92 (s, 3 H, SCH_3), 1.48 (t, 6 H, J = 7 Hz, CH_2CH_3).

Protonated sulfides were prepared by adding dropwise the sulfide, neat or dissolved in methylene chloride, to a tenfold (weight) excess of fluorosulfonic acid in a flame-dried, magnetically stirred flask equipped with a rupper septum and cooled to −50°. No polymerization of **4** and **5** occurs providing that the solution is stirred vigorously during addition. Stirring was continued at this temperature for 30 min; the product was transferred to an nmr tube which was sealed to exclude moisture and was stored at −60° until used. Spectra were calibrated with TMS; the probe temperature was determined from the chemical shifts of methanol; the region δ 0–18 was scanned and all peaks except fluorosulfonic acid (δ 13.92) are reported.

The protonated species were quenched by adding dropwise at −70° a cold solution of the ion in fluorosulfonic acid to a vigorously stirred solution of sodium methoxide in methanol. Work-up gave the starting sulfide in at least 80% yield.

Reactions of 13 were carried out in a flame-dried, nitrogen-swept, magnetically stirred flask equipped with a rubber septum. Although none of the reactions were noticeably exothermic, a 15° water bath was used to stabilize the temperature. To **13**, either in the form of the isolated product redissolved in *ca.* 10 ml of methylene chloride or as the crude product of the reaction run in methylene chloride, was added in one portion the reagent dissolved, if necessary, in a suitable solvent. After stirring for 2–4 hr, the mixture was diluted with 30 ml of methylene chloride and was washed twice with 50-ml portions of water. The organic layer was dried with anhydrous sodium sulfate and the solvent was removed. Yields were determined (unless noted) by weight of the crude product and the per cent composition of each component in it as calculated from peak areas on the glc; peak areas have not been corrected for variations in detector response from one compound to another. A number of minor products with short glc retention times including *cis*- and *trans*-di-*tert*-butylethylene, **4**, and methyl disulfide were observed in all reactions. All glc peaks with a retention time greater than **4** are reported; nmr analysis of the crude reaction mixture demonstrated in all cases that all major products were detected by glc. Although use of the unpurified **13** gave superior yields due, in part, to the susceptibility of **13** to attack by traces of atmospheric moisture or decomposition during the isolation procedures, it was necessary in some cases to isolate the crystalline salt to eliminate the possibly undesirable presence of methyl fluorosulfonate or fluorosulfonic acid in the subsequent reaction. In no instance did isolation of **13** give results not obtainable using unpurified solutions.

Water, 3 ml, was added to the unpurified sulfonium salt solution formed from 1.5 g (8.7 mmol) of **4**. Work-up afforded 1.45 g of a colorless semisolid; recrystallization from ether–pentane gave 1.3 g (6.4 mmol, 73% yield) of 1,2-di-*tert*-3-thiabutan-1-ol (**20**), a colorless solid: mp 84–85°; nmr ($CDCl_3$) δ 3.42 (s,[41] 1 H, methine H), 2.36 (s, 1 H, methine H), 2.19 (s, 3 H, SCH_3), 2.17 (position varies, disappears in the presence of D_2O, s, 1 H, OH), 1.02 (s, 9 H, *t*-Bu), 0.96 (s, 9 H, *t*-Bu); ir (KBr) 3445 cm^{-1} (sharp, OH); mass spectrum *m/e* 204 (calcd for $C_{11}H_{24}OS$, 204). The same product was obtained when water was added to isolated **13** redissolved in methylene chloride. *Anal.* Calcd for $C_{11}H_{24}OS$: C, 64.64: H, 11.84; S, 15.69. Found: C, 64.60; H, 11.92; S, 15.75.

One equivalent of *m*-chloroperbenzoic acid oxidized **20** to the sulfoxide **25**, a colorless solid: mp 97.5–99°; ir (KBr) 3410 (OH), 1081 cm^{-1} (S→O). *Anal.* Calcd for $C_{11}H_{24}O_2S$: C, 59.95; H, 10.98; S, 14.55. Found: C, 59.62; H, 10.83; S, 14.50.

The sulfone **26** was formed by oxidation of **20** with 2 equiv of *m*-chloroperbenzoic acid. Recrystallization from ether–pentane gave white crystals: mp 101–102°; ir (KBr) 3520 (weak, OH), 1305, 1136 cm^{-1} (S→O). *Anal.* Calcd for $C_{11}H_{24}O_3S$: C, 55.89; H, 10.23; S, 13.57. Found: C, 55.86; H, 10.09; S, 13.57.

Methanol, 5 ml, was added to the crude sulfonium salt solution formed from 0.5 g of **4** (2.9 mmol). Work-up gave 0.48 g (2.5 mmol, 86% yield) of essentially pure (greater than 96% by glc) 1,2-di-*tert*-butyl-1-methoxy-3-thiabutane (**21**), a colorless liquid. The analytically pure sample was isolated by preparative glc: ir (pure) 1110 cm^{-1} (C–O); mass spectrum *m/e* 218 (calcd for $C_{12}H_{26}OS$, 218). The same product was isolated when methanol was added to purified **13**. *Anal.* Calcd for $C_{12}H_{26}OS$: C, 65.99; H, 12.00; S, 14.68. Found: C, 65.99; H, 11.99; S, 14.72.

Oxidation with 1 equiv of *m*-chloroperbenzoic acid gave the sulfoxide **27**, a white, crystalline solid: mp 94–95°; ir (KBr) 1115 (C–O), 1058 cm^{-1} (S→O). *Anal.* Calcd for $C_{12}H_{26}O_2S$: C, 61.49; H, 11.18; S, 13.68. Found: C, 61.25; H, 10.96; S, 13.79.

The sulfoxide **27** was oxidized to the sulfone **28** with 1 equiv of *m*-chloroperbenzoic acid, resulting in crystals: mp 97–98°; ir (KBr) 1310, 1160 (SO_2), 1112 cm^{-1} (C–O). *Anal.* Calcd for $C_{12}H_{26}O_3S$: C, 57.56; H, 10.47; S, 12.81. Found: C, 57.69; H, 10.39; S, 12.88.

Lithium fluoride, 0.50 g (19 mmol), partially dissolved in 10 ml of acetonitrile was added to the unpurified solution of **13** made from 0.50 g (2.9 mmol) of **4**. Work-up afforded 0.53 g of a colorless, semicrystalline mass. Glc analysis indicated a single product, 1-acetamido-1,2-di-*tert*-butyl-3-thiabutane (**24**), with a purity of greater than 90% (0.48 g of unisolated **24**, 1.9 mmol, 65% yield). Column chromatography eluting with 2:1 acetone–chloroform followed by drying and three recrystallizations from 30–60° petroleum ether gave the analytical sample, a white solid: mp 62–63°; ir (KBr) 3410 (NH), 1680 (C=O), 1500 cm^{-1} (NH). *Anal.* Calcd for $C_{13}H_{27}NOS$: C, 63.62; H, 11.09; N, 5.71; S, 13.07. Found: C, 63.77; H, 11.11; N, 5.56; S, 13.07.

When the same reaction was run in nitromethane, an inert solvent, a black tar resulted after work-up. Only *cis*- and *trans*-di-*tert*-butylethylene could be identified by nmr and glc analysis of the complex mixture; no other characterizable products could be isolated.

Lithium chloride, 0.50 g (12 mmol), partially dissolved in 10 ml of acetonitrile, when added to unpurified **13** formed from 0.50 g (2.9 mmol) of **4** gave 0.71 g of a colorless liquid upon work-up. Glc analysis showed three products: the ubiquitous **20** (3% yield), **24** (5%), and 1-chloro-1,2-di-*tert*-butyl 3-thiabutane (**22**) (80%). The analytical sample was isolated by preparative glc: ir (pure) 2970, 1485, 1380 cm^{-1}. *Anal.* Calcd for $C_{11}H_{23}ClS$: C, 59.29; H, 10.42; Cl, 15.91; S, 14.39. Found: C, 59.33; H, 10.42; Cl, 15.57; S, 14.65.

Lithium bromide, 0.50 g (5.8 mmol), completely dissolved in 10 ml of acetonitrile was added to the unpurified **13** solution made from 0.92 g (5.3 mmol) of **4**. A faintly yellow liquid (1.3 g) was recovered after work-up; glc analysis indicated a mixture of **20** (1% yield), **24** (59%), and 1-bromo-1,2-di-*tert*-butyl-3-thiabutane (**23**); products were identified by retention times and spectral properties of samples isolated by preparative glc. **23** was a clear, colorless liquid: ir (pure) 2980, 1491, 1378 cm^{-1}. Addition of lithium bromide partially dissolved in diethyl ether to **13** gave **23** in 69% yield.

Lithium iodide, 1.0 g (7.5 mmol), was completely dissolved in 10 ml of acetonitrile and added to the unpurified solution of **13** formed from 0.4 g (2.3 mmol) of **4**. The reaction mixture turned an iodine-brown color within 5 min. Work-up afforded 0.50 g of a dark brown liquid. Glc analysis showed that **24** was the major product (68% yield) along with a small amount of **20**.

Tetrabutylammonium iodide, 1.0 g (3.6 mmol), was added, neat, to an unpurified solution of **13** formed from 0.50 g (2.9 mmol) of **4**. The solution turned iodine brown within 3 min. After stirring for 2 hr, the reaction was quenched with methanol. Glc and nmr analysis of the product showed that, in addition to a small amount of *cis*- and *trans*-di-*tert*-butylethylene, **21** was the only product.

Acetonitrile was allowed to react with both crude and purified **13**. In both cases, **20** and **24** were the only products observed by glc which had a retention time greater than **4**; these products were identified by spectral properties of samples isolated by preparative glc.

Phenol, 0.24 g (2.5 mmol), was added, neat, to the unpurified **13** solution formed from 0.40 g (2.3 mmol) of **4**. After 1 hr, 4 ml of methanol was added and the solution was worked up. Glc and nmr analysis indicated that, in addition to some minor products with a very high glc retention time, only **20** and **21** were present; no product corresponding to an addition product of phenol could be

(41) In some samples this peak would appear initially as a broad doublet and then coalesce to a singlet after a few hours at room temperature in $CDCl_3$. This puzzling behavior led to a suspicion that a rearrangement might be taking place but no evidence could be obtained that any compound other than **20** was present. We have no explanation for the nmr behavior.

detected. Similarly, 1,4-dimethoxybenzene gave no product on prolonged stirring with **13**.

Methyllithium, *n*-butyllithium, diisopropyllithium amide, or *n*-butylmercaptan (1–3 equiv) gave products with very complex nmr and glc spectra, indicative of decomposition of reactants when stirred for 3 hr at room temperature with **13**.

Chlorination of 4 was carried out by dissolving 0.75 g (4.35 mmol) of **4** in 50 ml of methylene chloride in a flame-dried, magnetically stirred, nitrogen swept flask. After wrapping the system carefully with towels to exclude all light, the mixture was cooled to −80° and chlorine was bubbled through the solution at the rate of *ca.* 100 ml/min for 20 min. After stirring in the cold for 2 hr, the cooling bath was removed and nitrogen was bubbled through the solution overnight to sweep out the excess chlorine; removal of solvent gave 1.00 g (4.15 mmol, 95% yield) of 1,2-di-*tert*-butyl-2-chloroethylsulfenyl chloride (**9**), with a purity of greater than 95% by glc analysis. The analytical sample, a yellow liquid, was isolated by preparative glc: ir (pure) 2970, 1482, 1380, 913, 820 cm^{-1}. *Anal.* Calcd for $C_{10}H_{20}Cl_2S$: C, 49.38; H, 8.29; Cl, 29.15; S, 13.18. Found: C, 49.43; H, 8.39; Cl, 28.81; S, 13.17.

Stirring of **9** at room temperature with a large excess of saturated sodium bicarbonate solution for 2 hr resulted in only a small amount of product with a glc retention time about twice that of **9** at a column temperature of 150°; this product was not isolable in quantities sufficiently large for analysis; the major portion of **9** was recovered unchanged.

A solution of **9** (0.5 g, 2.1 mmol) in ether (10 ml) was added to a stirred solution of 0.5 g (13 equiv) of lithium aluminum hydride in 20 ml of ether at room temperature. A vigorous reaction was noted during addition. The reaction was quenched by careful dropwise addition of water as soon as all the substrate was added. Acidification with hydrochloric acid followed by extraction with ether, drying, and removal of solvent gave 0.29 g (1.7 mmol, 82% yield) of almost pure (glc) **4**; this product was identified by comparison of ir and nmr spectra with an authentic sample.

Oxidation of **9** to the sulfonyl chloride **10** by stirring for 2 days with 2 equiv of *m*-chloroperbenzoic acid gave, after column chromatography (an aqueous work-up is, of course, not desirable) eluting with chloroform a clear, viscous liquid, 1,2-*tert*-butyl-2-chloroethylsulfonyl chloride (**10**): nmr ($CDCl_3$) δ 4.24 (s, 1 H, methine H), 1.33 (s, 9 H, *t*-Bu), 1.08 (s, 9 H, *t*-Bu); ir (pure) 1373, 1162 cm^{-1} (SO_2Cl). Hydrolysis in water gave the sulfonic acid **11**.

Chlorination of 5 in a manner identical with the chlorination of **4** gave a complex mixture of products upon isolation. Glc analysis indicated one component (*ca.* 15% yield) with a retention time slightly longer than **9**. This product was isolated by preparative glc: nmr ($CDCl_3$) δ 4.37 (q, J = 12 Hz), 3.80 (d, J = 4 Hz), 1.08 (s). Meaningful integrations could not be obtained and the identity of this product is not known. The remainder of the mixture was composed of four products with very long retention times on the glc; these products were isolated, but give complex spectra which elude interpretation.

Reaction of 4 with *tert*-butyl hypochlorite was carried out with **4** (344 mg, 2 mmol) dissolved in 10 ml of methylene chloride contained in a flame-dried three-necked flask equipped with dropping funnel, condenser, and magnetic stirrer. The entire apparatus was protected from light. The solution was cooled to −20° and solution of *tert*-butyl hypochlorite (220 mg, 2 mmol) in 5 ml of methylene chloride was added slowly. The hypochlorite color disappeared rapidly on addition. The solution was warmed to room temperature for 30 min. The solvent was removed leaving 550 mg of an oil; nmr showed the presence of two components. These were separated by preparative glpc (glass SE-30, 200° programmed to 250°). The major isomer was **12**: nmr ($CDCl_3$) δ 1.17 (broad s, splits into two peaks at 100-Hz sweep width, **18**, two *t*-Bu's), 1.23 (s, 9, *t*-Bu), 1.30 (s, 9, *t*-Bu), 3.40 (s, 1, methine H), 4.10 (s, 1, methine H), and 6.00 (s, 1, vinyl H); mass spectrum *m/e* 378 (calcd for $C_{20}H_{39}S_2Cl$ 378), 171, 123, 101, 83, 69, and 57; calcd exact mass 378.21770, found 378.21816.

The second fraction isolated from the glpc had nmr ($CDCl_3$) δ 1.1 (broad absorption) and 2.18 (sharp s). No definite parent peak could be obtained in the mass spectrum. The structure remains unknown.

Reaction of 5 with *tert*-butyl hypochlorite was carried out as described above. After 2 weeks in the refrigerator the *tert*-butyl hypochlorite had nearly completely decomposed but **5** was recovered unchanged.

Ozonolysis of 4 was carried out in 50 ml of methylene chloride at −50°. Ozone (2 g) was passed into the solution. After stirring the dark blue solution for 0.5 hr, the ozone was swept from the solution with oxygen. Removal of solvent gave 0.65 g of a clear, slightly orange oil; nmr and glc analysis indicated a complex product mixture. The presence of an aldehydic component is suggested by nmr (s, δ 9.30) and ir (1700 cm^{-1}) spectra; however, no product could be isolated.

Compound **4** was treated with acetyl chloride at room temperature for 1 hr according to the method of Schwartz,[10] with iron pentacarbonyl[17,42] and with *p*-toluenesulfonyl azide and copper after the method of Cram.[14c] In all cases, work-up gave the starting material **4** as the only isolable product. Prolonged refluxing of **4** in benzene with an equivalent amount of diethyl azodicarboxylate led to no detectable changes. Neither **4** nor **5** was affected when treated with dry HCl gas in methylene chloride solution at room temperature.

No reaction occurred when **6** was refluxed for 3 hr with 1 equiv of acetic anhydride in benzene. No isolable product was obtained when **6** was treated with *N*-sulfinyl-*p*-toluenesulfonamide or *N,N'*-bis(*p*-toluenesulfonyl)sulfur diimide by using the method of Cram.[14c] Decomposition to unidentifiable tars was the fate of **7** treated with methyl fluorosulfonate in an attempt to make a compound analogous to the alkoxysulfonium salts of Johnson.[43]

Reaction of 2 with methanesulfenyl chloride was attempted to see whether the salt **13** was available by this route. Equimolar solutions at ambient temperature failed to react, however, when followed by nmr for about 12 hr. Under the same conditions cyclohexane was rapidly consumed by methanesulfenyl chloride.

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