

Preparation and Fragmentation of the 3-Thiabicyclo[3.1.0]hexane 3,3-Dioxide Ring System. A Synthesis of 1,4-Dienes¹

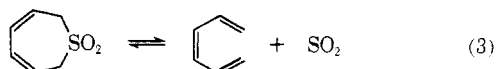
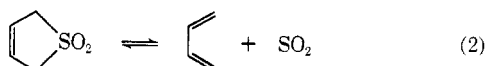
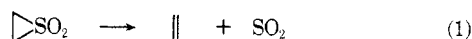
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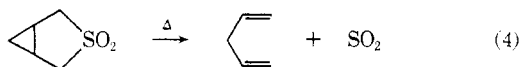
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Abstract: Sulfolane-pyrazolines were obtained by 1,3 addition of diazomethane to variously substituted sulfolenes. Photochemical excision of nitrogen afforded the 3-thiabicyclo[3.1.0]hexane 3,3-dioxide ring system. Pyrolysis of the latter gave sulfur dioxide and a homoconjugated diene. Epoxysulfolanes analogously yielded divinyl ethers. Evidence of stereochemistry and kinetic data indicate a concerted mechanism for the fragmentation.

The cheletropic² interactions of sulfur dioxide with unsaturated hydrocarbons (eq 1–3) represent a valuable series of reactions for examining orbital sym-



metry concepts.^{2,3} At the same time such reactions have great synthetic utility for the preparation of sulfones on the one hand,⁴ and for the stereospecific and stereoselective synthesis and manipulation of alkenes⁵ and polyenes^{8,4,6} on the other. In this paper we have extended our studies of cycloeliminations in this area to the fragmentation of the 3-thiabicyclo[3.1.0]hexane 3,3-dioxide ring system (eq 4). This is a logical ex-



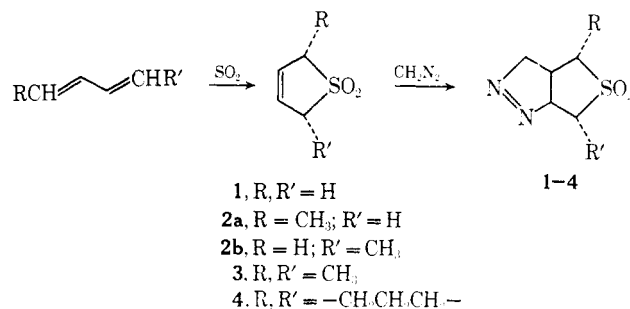
tension of sulfolene decomposition (eq 2), since participation of a cyclopropyl ring in electrocyclic transformations is well documented.^{2,7} The reaction (eq 4), which is surprisingly facile, we find to be mechanistically concerted by tests of stereospecificity. Furthermore, the synthetic sequences we have developed appear to be of value in the preparation of homoconjugated dienes.

In work concurrent with ours, Berson and Olin have examined analogous azo compound decomposi-

tions and have reached similar conclusions.⁸ Certain of our reactions also bear a formal analogy to previously reported decarbonylations,⁹ as discussed later.

Preparation of Intermediates. Sulfolenes are routinely synthesized by reaction between dienes and sulfur dioxide^{4a} (eq 2). Several attempts at direct introduction of a methylene group by addition of a carbenoid species to the double bond of the sulfolene ring led to unsatisfactory results. Since this could be attributed to electron deficiency of the double bond arising from the strong electron-withdrawing effect of the sulfone group, recourse was made to a cycloaddition which was less dependent upon electrophilicity in the attacking reagent (Scheme I).

Scheme I. Synthesis of Sulfolane-Pyrazolines



In spite of assertions to the contrary,¹⁰ 1,3 cycloaddition of diazomethane to sulfolene gave acceptable yields of a 1:1 adduct, **1**, which bears the systematic name 3a,4,6,6a-tetrahydro-3H-thieno[3,4-c]pyrazole 5,5-dioxide. The reaction giving the sulfolane-pyrazoline is slow; it requires several weeks at 0–5°. Formulation of the product as a 1-pyrazoline is unequivocal on the basis of spectroscopic evidence (nmr discussion below and Experimental Section) and subsequent chem-

(1) Previously reported in preliminary form: W. L. Mock, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P-20.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966); (c) W. L. Mock, *ibid.*, **91**, 5682 (1969); (d) *ibid.*, **92**, 3807 (1970).

(4) (a) S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York and London, 1967, pp 13–45; (b) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967).

(5) F. G. Bordwell in "Organosulfur Chemistry," M. J. Janssen, Ed., Wiley, New York, N. Y., 1968, pp 271–284; L. A. Paquette in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 121–156.

(6) E. J. Corey, N. H. Andersen, R. M. Carlson, J. Paust, E. Vedejs, I. Vlittas, and R. E. K. Winter, *J. Amer. Chem. Soc.*, **90**, 3245 (1968); P. Dowd, *ibid.*, **92**, 1066 (1970).

(7) E. Vogel, *Angew. Chem.*, **74**, 829 (1962).

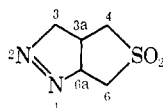
(8) (a) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969); (b) *ibid.*, **92**, 1087 (1970); see also (c) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *ibid.*, **91**, 3382 (1969); E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969); (d) M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969); (e) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 4695 (1969), and references cited therein.

(9) (a) B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Amer. Chem. Soc.*, **89**, 5964 (1967); (b) see also R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, 5231 (1969); R. G. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 988 (1970), and references cited therein.

(10) H. J. Backer, N. Dost, and J. Knotnerus, *Recl. Trav. Chim. Pays-Bas*, **68**, 237 (1949).

ical transformation. In somewhat slower reactions, pyrazolines (**2**, **3**) were obtained from 2-methylsulfolene (piperylene sulfone) and *cis*-2,5-dimethylsulfolene (*trans,trans*-hexadiene sulfone). Diazomethane added relatively rapidly to 2,5-trimethylenesulfolene (cycloheptadiene sulfone) giving a tricyclic compound (**4**). The pyrazolines **1–4** were isolated as crystalline solids. No adduct could be obtained from 3-methylsulfolene (isoprene sulfone), 2,4-dimethylsulfolene, or *trans*-2,5-dimethylsulfolene (each recovered unchanged). In view of the latter result it is reasonable to formulate the addition as proceeding to the less-hindered face of the ring in the cases of the alkylated sulfolenes. The resulting structures **2–4** may confidently be regarded as *cis*-fused sulfolane-pyrazolines in which substituents occupy an *exo* position. This conclusion is also corroborated by subsequent chemical transformations as well as nmr spectroscopy. In the case of 2-methylsulfolene, two isomeric 1-pyrazolines (**2a** and **2b**) could be anticipated and were actually separated by fractional crystallization. Structures could be assigned on the basis of nmr as shown immediately below, although the relative location of the methyl group was of no consequence since the source of isomerism disappeared with the next step.

Although the nmr spectra of the sulfolane-pyrazolines **1–4** are complex, proton assignments may be made with reasonable confidence by noting similarities and differences within the series. It appears that the azo linkage has a consistently strong deshielding effect upon protons (and methyl groups) α and β to it. In **1** the 3-position methylene group appears as a two-



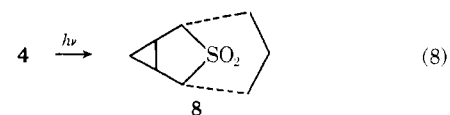
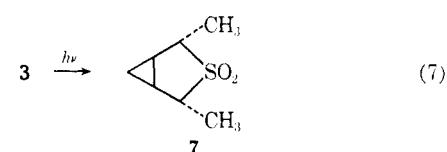
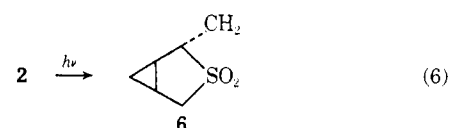
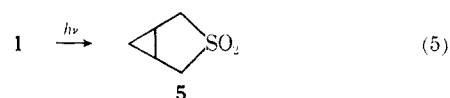
proton multiplet centered at δ 4.65 ppm and the bridge-head methine at the 6a position occurs as a broader single proton multiplet at δ 5.2 ppm (CD_3CN solution).¹¹ In general these same absorptions are distinguishable in the spectra of **2–4**, although they tend to overlap (and in fact appear to be coincident in **3**). There also appears consistently to be absorption in the region of δ 2.5 ppm where the 3a-position (bridge-head) proton could be expected to occur.¹¹ The remaining protons of the sulfolane-pyrazolines **1–4** may be assigned chemical shifts on the reasonable assumption that the 6 position should be more deshielded than the 4 position. In **2a** the methyl group falls at δ 1.35 ppm whereas in **2b** it is found at δ 1.7 ppm (CDCl_3 , doublets, $J = 7$ Hz). The methyls in **3** occur at similar values. The adjacent methinyl protons (4,6 positions) may plausibly be assigned to signals 1–1.5-ppm downfield from the methyl doublets (*ca.* δ 2.5–3.0 and 3.4–3.7 ppm, respectively, in **2–4**). The 6-position proton in **2a** is especially well resolved. It appears approximately as the AB portion of an ABX spectrum, wherein (from relative intensities) X must be the proton at the 6a position. Incidentally, this observation corroborates the relative structural assignments of **2a** and **2b**. Analysis of the AB subspectrum gives the following parameters: $\delta H^{6\text{-endo}} = 3.47$, $H^{6\text{-exo}} = 3.83$ ppm; $J_{\text{gem}} = (-)14.5$, $J_{6a,6\text{-endo}} = 6.0$, $J_{6a,6\text{-exo}} = 9.5$ Hz.

(11) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970).

It is assumed that the larger vicinal coupling represents an eclipsed interaction ($\phi = 0$), and accordingly the 6-*exo*-position proton is the more deshielded. In **1** and **2b** the 4 position is unsubstituted and appears to occur as a broad multiplet δ *ca.* 3 ppm. The trimethylene bridge in **4** falls in the range δ 1.5–2.5 ppm.

Elimination of molecular nitrogen from the pyrazolines was then required to secure the 3-thiabicyclo[3.1.0]hexane 3,3-dioxide ring system. Two well-precedented methods, pyrolysis and photolysis were considered. The former would seem to be unsuitable for preparation of the bicyclic sulfones since it was subsequently found that loss of sulfur dioxide from the intermediates **5–7** was more facile upon pyrolysis than loss of nitrogen under similar circumstances from the sulfolane-pyrazolines. If one's objective were the preparation of 1,4 dienes (see next section), it is conceivable that the two steps might be preparatively carried out simultaneously by thermolysis. However, since the first step (*e.g.*, **1** \rightarrow **5**) may be carried out selectively by the latter (photochemical) method, allowing isolation and purification of the intermediates (**5–8**), it is likely that photolysis is to be preferred in most situations. Because we were interested in the details of the sulfur dioxide elimination step, we adopted the photochemical procedure.

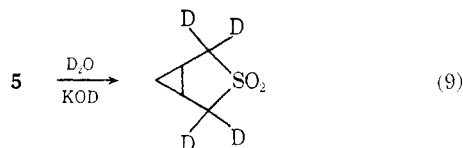
Irradiation of the pyrazolines **1–4** in acetonitrile solution with ultraviolet light of wavelength (300–360 $m\mu$) corresponding to the azo $n \rightarrow \pi^*$ transitions (λ_{max} 318–320 $m\mu$, ϵ 410–460) gave in each case a cyclopropane (**5–8**) with loss of nitrogen (eq 5–8). These examples of the 3-thiabicyclo[3.1.0]hexane 3,3-dioxide



ring system were all obtained as crystalline solids, generally in satisfactory yield. Only in the case of **1** \rightarrow **5** (eq 5) were the side products investigated. Examination of the reaction mixture revealed only isoprene sulfone and 3-methylene sulfolene in addition to the desired bicyclic material. Production of these from



an intermediate diradical (or excited cyclopropane) is regarded as unexceptional.¹¹ By way of confirmation of structure, **5** gave a tetradeuterio derivative when treated with basic deuterium oxide (eq 9).



The nmr spectra of the bi- and tricyclic sulfones 5–8 are of interest in that assignments of chemical shifts (as in 1–4) and coupling constants within the ring system are feasible. The analysis is confirmed by the effects of the varying positions of the substituents in 6–8. An approximate analysis, yielding values recorded in Table I, has been made with corrections for

Table I. Analysis of Nmr Spectra of 3-Thiabicyclo[3.1.0]hexane 3,3-Dioxide Ring System

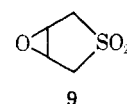
Chemical shift, ppm, from TMS (± 0.03) (no. of protons)	Proton assignment	Coupling constants, Hz (± 0.5)
0.65 (1)	H ^A	$J_{A,B} = -6.3^a$
1.23 (1)	H ^B	$J_{A,C} = 7.9^a$
1.72 (2)	H ^C	$J_{B,C} = 4.8^a$
2.80 (2)	H ^D	$J_{C,D} = \sim 0$
3.43 (2)	H ^E	$J_{C,E} = 7$
		$J_{D,E} = (-)14^b$

^a As calculated to fit observed spectra (see text).¹² ^b Assumed negative.

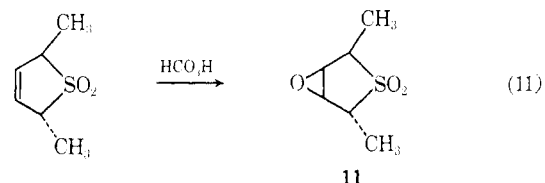
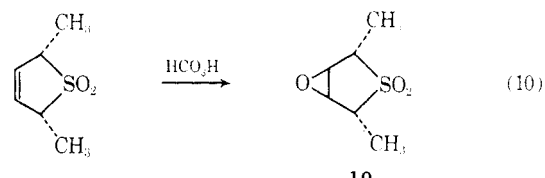
gross second-order effects, but with neglect of small coupling constants (< 1 Hz).¹² Of the five groups of resonances observed, the highest field absorption (δ 0.65, 1.23 ppm), obviously due to cyclopropyl hydrogens, were assigned to H^A and H^B, respectively. The relative deshielding of H^B must be associated with the presence of the five-membered ring and/or the sulfone functionality; the rather inflexible, fused ring system holds the proton over the ring and in proximity to an oxygen atom. The assignments do not rest upon the foregoing presumptions, but rather are derived from mutual coupling constants determined for α -deuterated 5 (eq 9). It has been established in cyclopropyl compounds that J_{gem} is negative and that J_{vic} (positive) is greater for *cis* coupling than for *trans*.¹³ The signal arising from H^A (Table I) is an approximate quartet whereas that from H^B is an irregular sextet in α -deuterated 5. A satisfactory fit to the observed spectrum was obtained with the coupling constants reported in Table I.¹² Since H^A exhibits the larger vicinal coupling ($J_{A,C} = 7.9$ vs. $J_{B,C} = 4.8$ Hz), H^A must be *cis* to H^C. The value of the geminal coupling ($J_{A,B} = -6.3$ Hz) is in line with precedent.¹³ The spectra of 6–8 are consistent with the assignment, although in 8 the signal from H^A appears as a sextet indicating some conformational shift induced by the

trimethylene bridge. The remaining high-field resonances in 5, two equivalent protons at δ 1.72 ppm, are assigned to H^C. They are extensively coupled in all sulfones, although in α -deuterated 5 they are simplified to a broadened quartet. Absorptions at δ 2.80 and 3.43 ppm are assigned to H^D and H^E, respectively. These protons were exchanged for deuterium in basic deuterium oxide (eq 9). It appears that H^D is coupled only to H^E ($|J_{D,E}| = 14$ Hz). As seen most clearly in 6, H^E shows a reciprocal coupling ($|J_{D,E}| = 14$ Hz) as well as a smaller coupling to H^C ($J_{C,E} = 7$ Hz). The latter value is reasonable for eclipsed vicinal hydrogen; this observation and the apparent lack of resolvable coupling between H^C and H^D is the basis for the relative assignments of H^D and H^E. Finally, most of the resonances in the series 5–8 are broadened, indicating either unaccounted-for second-order effects or neglected small coupling constants, some of which may be long range (through four bonds).

Epoxysulfolane (9) has been prepared by performic acid oxidation of sulfolene.¹⁴ As subsequently described, this was found to fragment to sulfur dioxide

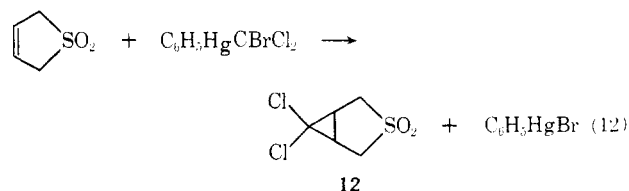


and divinyl ether. Consequently, we adapted the epoxidation procedure to *cis*- and *trans*-2,5-dimethylsulfolene (eq 10, 11), the latter of which, it will be recalled, failed to react with diazomethane. In each case a crystalline epoxide (10, 11) was isolated, together



with a *trans*-diol in the case of 10. Separation and purification was easily effected by column chromatography. Again, structural assignments were corroborated by nmr spectroscopy (see Experimental Section) and subsequent chemical transformation.

Various attempted carbenoid additions to the double bond of the sulfolene ring succeeded only in the case of dichlorocarbene generated from phenyl(bromodichloromethyl)mercury (eq 12). The product, 6,6-dichloro-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (12),



(12) We thank Dr. S. M. Castellano for assistance with this analysis.

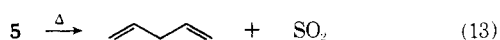
(13) R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron, Suppl.*, No. 7, 355 (1966); S. Meiboom and L. C. Snyder, *J. Amer. Chem. Soc.*, **89**, 1038 (1967).

(14) W. R. Sorenson, *J. Org. Chem.*, **24**, 1769 (1959).

could be obtained only with low conversion of sulfolene. The method of adduct formation is necessarily limited in scope since sulfolenes dissociate slowly to dienes and sulfur dioxide under conditions sufficiently vigorous to produce addition by dichlorocarbene. However, since methods are available for hydrodechlorination¹⁵ of species such as **12**, this represents a feasible alternative entry into the 3-thiabicyclo[3.1.0]hexane 3,3-dioxide ring system and its subsequent transformation products. Our investigation was limited to the decomposition of **12** itself.

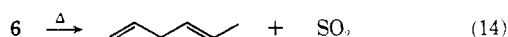
Fragmentation of Sulfones. The decomposition of the bicyclic and tricyclic sulfones **5–12** will be discussed with the primary objective of elucidating mechanistic details. We shall examine stereochemical behavior and relative rates for this purpose. Synthetic applicability, which should be apparent, will be emphasized subsequently.

Compared with other saturated sulfones, 3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**5**) showed a relative thermal instability. It rapidly and cleanly yielded sulfur dioxide and 1,4-pentadiene (eq 13) when heated 10–20° above its melting point (110°). Identities of the reaction products were established by comparison with authentic materials; in particular, it was shown

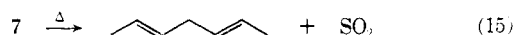


that less than 0.5% of *cis*- or *trans*-piperylene was formed. Kinetic data, reduced to activation energy parameters characteristic for this decomposition, will be described after consideration of the stereochemical course of the reaction as revealed by the substituted derivatives of **5**.

Decomposition of *exo*-2-methyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**6**) gave only sulfur dioxide and *trans*-1,4-hexadiene (eq 14). Presence of the *cis* isomer was excluded (<0.5%) by glpc comparison with an



authentic commercial mixture of the dienes. This evidence indicates that the reaction is highly stereoselective; there is strong inference that it is stereospecific as well. The latter conclusion is substantiated by the results of the decomposition of *exo,exo*-2,4-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**7**). Only *trans,trans*-2,5-heptadiene was detected as the hydrocarbon product (eq 15). Although the stereoisomeric heptadienes were not available, through the courtesy

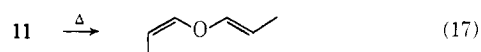
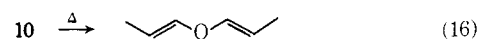


of Professor J. Berson spectral and glpc data were provided which excluded the presence of either of the *cis*-heptadiene geometrical isomers in the pyrolysate of **7**. The correlation of stereochemistry between sulfone and diene requires that the reaction proceed suprafacially (*i.e.*, in disrotatory fashion—see later).² However this does not constitute proof of concertedness since a dimethylsulfone stereoisomeric to **7** was not available for comparative purposes.

Recourse to the readily available epoxysulfolanes **10** and **11** provided the desired proof of stereospecificity.

(15) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963); P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960); L. F. Feiser and D. H. Sachs, *J. Org. Chem.*, **29**, 1113 (1964).

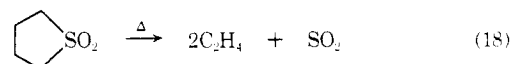
Decomposition of the parent **9** is less facile than is decomposition of **1**. However, at 250° liberation of sulfur dioxide is noted. Although the pyrolysate is complex in the neat liquid, vapor-phase cracking at 280° gave almost exclusively sulfur dioxide and divinyl ether, identified by comparison with authentic material. Cracking of the epoxides **10** and **11** could not be carried out preparatively under the same conditions. However, injection of small quantities into the inlet (maintained at 300–350°) of a gas chromatograph with subsequent glpc analysis gave clean decomposition results. Each stereoisomer, **10** and **11**, gave a single dipropenyl ether, with less than 1% crossover product under conditions of a rigorously cleaned injection port and closely controlled flow rate and temperature (eq 16, 17). The identifications as *trans,trans*-dipropenyl ether and *cis,trans*-dipropenyl ether, respectively, were assigned by glpc comparison with an authentic mixture of the isomeric propenyl ethers produced by isomerization



of diallyl ether with iron pentacarbonyl and ultraviolet irradiation.¹⁶ It follows that the sulfone fragmentations occur suprafacially (with disrotation) in each case.

The preceding evidence we feel is sufficient to establish the stereospecificity of the sulfone fragmentation step beyond reasonable doubt. It must be noted, however, that on the basis of what has been presented so far one may not exclude rigorously a two-step mechanism with an intermediate (sequential carbon–sulfur bond rupture) in which loss of sulfur dioxide is faster than bond rotation within the intermediate. Furthermore, a fraction of a per cent of cross-product, while preparatively insignificant and capable of eluding detection, would be thermodynamically significant in that it could indicate nonsynchronous bond rupture, or at least that a nonstereospecific path requires at most a few kilocalories more of activation energy. One should note the experimental restriction that the upper limit on detectable stereospecificity is determined by the stereochemical integrity of the sample submitted to pyrolysis. We regard that kinetic evidence is capable of providing support for an alternative, concerted mechanism. In the latter case orbital symmetry considerations are applicable, and for an allowed transformation (as are the examples here cited) the transition state for a single step reaction *may* be stabilized relative to a process involving sequential bond rupture. We shall compare the thermal stabilities of **5**, **8**, sulfolene, and sulfolane.

The decomposition of **5** yielding 1,4-pentadiene (eq 13) has formal analogy to both the fragmentation of sulfolane to sulfur dioxide and 2 equiv of ethylene (eq 18) and the fragmentation of sulfolene to sulfur



dioxide and butadiene (eq 2). This is merely a restatement of the recognized, unsaturated partial char-

(16) P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965).

Table II. Comparative Rates and Activation Energy Parameters for Dissociation of Sulfones

Sulfone	Rate sec ⁻¹	ΔG^\ddagger , kcal mol ⁻¹ ^b	ΔH^\ddagger , kcal mol ⁻¹ ^c	ΔS^\ddagger , eu ^d
Sulfolene ^a	$k = 2.64 \times 10^{-4}$ (124.7°)	30.1	33.6 ± 0.5	8.9 ± 1.2
5	$k = 2.64 \times 10^{-4}$ (125.4°)	30.1	29.7 ± 0.5	-1.0 ± 1.2
Sulfolane	$k = 2.3 \times 10^{-6}$ (256°)			
8	$k < 5 \times 10^{-6}$ (275°)			

^a Values for sulfolene from ref 17. ^b Free energy of activation. ^c Enthalpy of activation. ^d Entropy of activation.

acter of small rings, which suggests that, mechanistically, the dissociation of **5** might be intermediate between that of eq 2 and eq 18 considered as extremes. The relationships may be established quantitatively by kinetic evidence, as presented in Table II. Reaction rates were determined in the appropriate temperature ranges by measurement of sulfur dioxide evolved from the molten sulfones as a function of time.¹⁷

The decomposition behavior of **5** is quite similar to that of sulfolene,¹⁷ suggesting a much closer mechanistic parallel than to the fragmentation of sulfolane. The rates noted for **5** and for sulfolene (Table II) are identical near 125°. As for interpreting the small differences between them in enthalpy and entropy of activation, we would only suggest that, assuming a mechanistic similarity, **5** is less dissociated in the transition state ($\Delta\Delta S^\ddagger = -10$ eu) but that some release of cyclopropyl ring strain is felt ($\Delta\Delta H^\ddagger = -4$ kcal mol⁻¹, also see later). However, it is doubtful that the systems are sufficiently alike to justify this analysis. For sulfolane comparable quantitative data are not available; however, it has been reported as stable to 240° with decomposition at the boiling point (285°).¹⁸ With our apparatus we have measured the rate of sulfur dioxide release from sulfolane as 2.3×10^{-6} sec⁻¹ at 256°. Derivation of activation parameters for this compound was not practical (see Experimental Section). An extrapolation of the rate of decomposition of **5** to this temperature may be carried out, since the latter has been studied over the temperature range 117–145°. Although the calculated rate so obtained should be regarded with caution due to the large temperature increment, the rate differential between **5** and sulfolane is estimated as greater than 10⁵. This would suggest a $\Delta\Delta G^\ddagger$ in the neighborhood of 12–16 kcal mol⁻¹ at intermediate temperatures for sulfolane decomposition relative to **5** or sulfolene.

A product study of the cracking of sulfolanes in a flow system at 490–500° has been reported.¹⁹ The major products were olefins as expected from eq 18. However, there was also reported 9–19% of "saturated hydrocarbon" in the pyrolysate. We suggest that this may be indicative of a nonconcerted reaction mechanism involving, perhaps, radical intermediates.²⁰ There is no evidence regarding stereospecificity in the production of olefins in the latter fragmentation. The reactions in eq 1–3 all exhibit complete stereospecificity as regards the hydrocarbon products.^{3,5}

The evidence regarding rate acceleration in **5**, then, suggests coupling of cyclopropane ring opening with

carbon–sulfur bond rupture in the transition state. Since this involves release of some ring strain, the coincidental relative rates of **5** and sulfolene are reasonable (Table II).

The relative stability of **8** remains to be commented upon; it provides final confirmation that the fragmentation of the bicyclic sulfones must indeed proceed concertedly through a transition state with specific stereochemical requirements. The tricyclic sulfone **8** is quite stable at the decomposition temperatures of **5**. In fact, it appears to possess greater thermal stability than sulfolane itself. Upon being rapidly heated above 300°, **8** distills without decomposition. A quantity of the material maintained at 275° failed to release a detectable amount of sulfur dioxide over a period of 2 hr (although the sample did show degradation), thus establishing an upper limit upon its rate of fragmentation (Table II). Decomposition of **8** in an intensely heated injection port (350°) of a gas chromatograph gave a very low conversion to what appears to be a C₈ species of hydrocarbon. The only information obtained regarding its structure was that it had a retention time (Carbowax column) less than that of 1,5-cyclooctadiene and about equal to that of 1,3-cyclooctadiene. The yield even at this temperature was so low as to preclude isolation. Considering the severity of the conditions, it could be questioned whether this was a primary reaction product, and the problem would be exacerbated by going to yet higher temperatures (which we could not achieve). In view of a possibility of multiple reaction paths and in the absence of a product study, we restrict our discussion to the relative stability of **8** compared to **5**.

From the nominal decomposition temperatures given in Table II (**5**, ca. 125° vs. **8**, >275°), it follows that there is some factor, amounting to at least 15 kcal mol⁻¹ in free energy of activation ($\Delta\Delta G^\ddagger$), which destabilizes the transition state(s) for decomposition of **8** (whatever the mechanism) relative to **5**.²¹ The most important consideration is steric; the hypothetical fragmentation of **8** in manner directly analogous to **7** and **10** or **11** would produce the impossibly strained *trans,trans*-1,4-cycloheptadiene. We feel that this "product forbiddenness" is reflected in the transition state.

The stereochemical and kinetic results for **8** as well as the other sulfones may be summarized with reference to Scheme II in which two disrotatory reaction courses are depicted. The essential difference between them is whether the molecular distortion leading to the transition state, envisaged as folding of the five-mem-

(17) O. Grunmitt, A. E. Ardis, and J. Fick, *J. Amer. Chem. Soc.*, **72**, 5167 (1950).

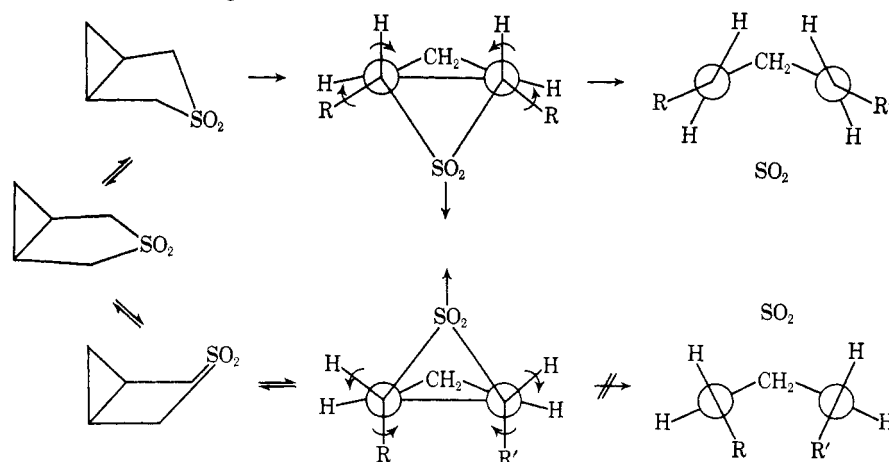
(18) H. Webber, *Res. Develop. Ind.*, No. 10, 47 (1962).

(19) T. E. Bezmenova, V. S. Gutyr, and N. M. Kamakin, *Ukr. Khim. Zh.*, **30**, 948 (1964); *Chem. Abstr.*, **62**, 2752 (1965).

(20) We would direct attention to the more fully studied cyclic azo compounds: P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968), and references cited.

(21) An even more apt comparison is between **5**, **8**, and their corresponding sulfolenes. As previously noted, **5** shows no retardation of rate of decomposition relative to sulfolene. Cycloheptadiene sulfone, the precursor of **8**, decomposes vigorously at 106° ($k = 4.5 \times 10^{-3}$ sec⁻¹), whereas a comparable rate of decomposition of **8** would probably require a temperature in excess of 400°.

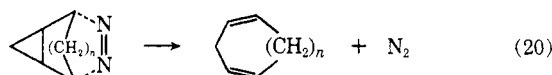
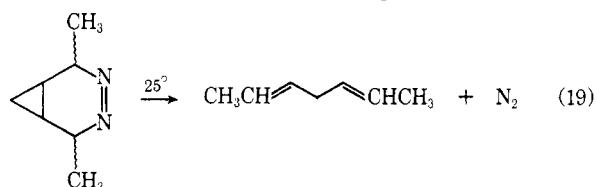
Scheme II. Transition State for Sulfone Fragmentations



bered ring as pictured, involves sulfur dioxide departure syn or anti to the three-membered ring. The bicyclic sulfones (**5–7**, **9–11**) in this study are free to adopt the geometry illustrated in the upper portion of Scheme II. The stereochemical evidence indicates that they do so; the sulfones in each case correlate with diene products required by this model. Since **8** is constrained to transition states corresponding to the geometry of the lower reaction course of Scheme II, its stability is comprehended, as very poor overlap would be obtained in the incipient double bonds. The possibility exists that in its eventual decomposition, one or the other of the nonbridge cyclopropane bonds of **8** ruptures concertedly with carbon–sulfur bond breaking, leading to a reactive intermediate which can give a variety of products.

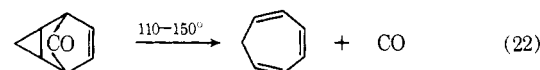
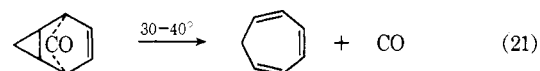
Regardless of the actual fate of **8**, the kinetic evidence suggests a substantial destabilization of any accessible decomposition transition state compared to **5**. We attribute this to the unattainability of optimal geometry as shown in Scheme II. The inference is that the decomposition of **5** is a fully concerted $2 + 2 + 2$ retrogression² with synchronous rupture of three σ bonds. Only thusly may the strain energy of the three-membered ring be usefully coupled with sulfur dioxide departure to produce the observed facile reactions.

In conjunction with the mechanism just discussed, we must mention studies of certain azo and polycyclic carbonyl compounds, which indicate the generality of cyclopropane participation of the sort which we have described. Of most direct pertinence are the following systems wherein molecular nitrogen is the departing group in place of sulfur dioxide⁸ (eq 19, 20). As in our study, complete stereospecificity was observed with respect to correlation of the azo compounds with homo-



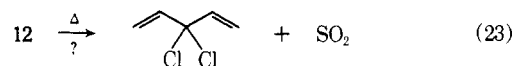
conjugated diene product. In the cases of the tricyclic systems (eq 20, $n = 1$ or 2), no large rate retardation

was observed; however, nitrogen departure in these compounds is anti to the three-membered ring in contrast to **8**. The mechanistic interpretations of these very facile reactions parallel ours;^{8a} furthermore, study of excited state processes may be carried out with this system.^{8b,e} As might be expected,² carbon monoxide can take the place of sulfur dioxide or nitrogen in analogous eliminations.⁹ We shall mention only the following pair of ketones. The endo isomer (eq 21) was observed to decarbonylate with greater ease than the exo isomer (eq 22). Cyclopropyl participation

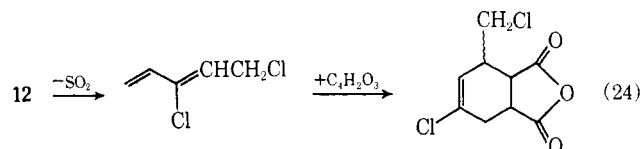


is an attractive explanation for the rate differential;^{9a} again, carbon monoxide departure anti to the three-membered ring is that which is favored.^{2,2}

On the basis of the preceding, the anticipated initial product of the decomposition of the dichlorocarbene adduct of sulfone (**12**) would be divinylidichloromethane (eq 23), which is a species bearing unusual func-



tionality. In actuality, the isolated product exhibited methylene protons in its nmr spectrum (at δ 4.2 ppm), indicating it to be a dichloropiperylene (eq 24). The

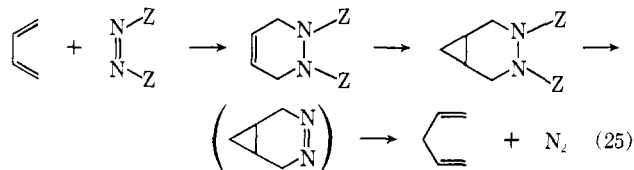


diene was characterized as its Diels–Alder adduct with maleic anhydride. Isomerization of the homoconjugated product (eq 23) to the observed diene could reasonably be facile under the conditions of the pyrolysis, although the possibility may not be excluded that the conjugated diene (eq 24) is formed directly

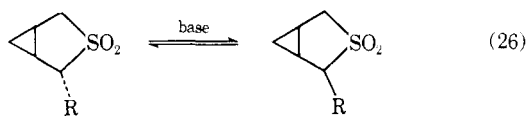
(22) The relative rate differential between this pair of reactions may approach that between **5** and **8** although the absolute rates are considerably faster; in both decarbonylations there is also a double bond situated for cooperative participation.

from **12** without the intermediacy of divinylchloromethane.

Synthetic Utility. It is clear that the sequence of operations—sulfolene formation (eq 2), diazomethane addition (Scheme I), photolysis (eq 5–7), and pyrolysis (eq 13–15)—potentially constitutes a general synthesis of 1,4 dienes. More specifically, since the sulfolene precursor is a conjugated diene, what one has at hand is a method of inserting a methylene (or oxide) function between two double bonds. In this regard the method is complementary to that of Berson⁸ involving the introduction of an azo linkage and its elimination as molecular nitrogen (eq 25). The final step (N_2 elimina-



tion) of the latter process is found to occur spontaneously at low temperatures (25°).⁸ In certain circumstances this should be advantageous. On the other hand, the decomposition temperatures (ca. 150°) of our sulfones are not so high as to prove a serious obstacle in general. The yields in our study were not great; however they can probably be improved, e.g., by using a higher proportion of diazomethane in the cycloaddition (Scheme I). We have previously noted the possibility of hydrodechlorination¹⁵ of **12**. There are additional features of the intermediates we have described, which merit emphasis. The sulfones are generally crystalline, which allows easy purification, and they are stable for storage. The sulfone functionality is relatively inert, permitting chemical modification of other sites of a molecule by a variety of reagents (oxidation, reduction, acid, etc.): the fairly reactive 1,4-diene functionality may then be produced as needed. Not the least significant feature of the synthetic sequence is its stereospecificity, which has been adequately commented upon. However, an additional possibility for steric control exists by virtue of the anion-stabilizing effects of the sulfone group. While not examined experimentally, base-catalyzed epimerization (eq 26) has the potential of circumventing the stereoselective bias



toward *trans*-alkene introduced at the diazomethane addition step. The observation of exchange of proton by deuterium in **5** (eq 9) may be taken as affirmation of the feasibility of this isomerization. Incidentally, tetradeuterio-**5** provides a source of 1,1,5,5-tetradeuterio-1,4-pentadiene.

Similarly to the decomposition of **5**–**7**, epoxysulfolene pyrolysis has the potential of offering a general, stereospecific synthesis of dialkenyl ethers. Existing methods are inadequate in this regard.^{16,23} However, our experimental efforts suggest that there are disappointing

complications. The high temperature required for sulfur dioxide elimination and the instability of the enol ether product to the conditions, particularly in the presence of a Lewis acid (SO_2) apparently render the reaction less satisfactory than in the case of the hydrocarbon sulfones, **5**–**7**. For the epoxides, the requirement for successful ether formation appears to be vapor-phase cracking under carefully controlled conditions involving minimal contact time. Whether a generally applicable procedure could be so devised is uncertain. We suggest that the lesser stability of the azo compounds studied by Berson indicates that a more satisfactory synthesis, obviating the difficulties of epoxysulfolene pyrolysis, might be found with molecular nitrogen as a leaving group in place of sulfur dioxide.

Experimental Section

General. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn., or Micro-Tech Laboratories, Skokie, Ill. Melting points were taken in capillary tubes and were corrected. The ir spectra were obtained with a Perkin-Elmer spectrophotometer, Model 21; the uv spectra with a Cary spectrophotometer, Model 14; the nmr spectra with a Varian A-60 or Hitachi Perkin-Elmer Model R-20 instrument.

Diazomethane Cycloaddition to Sulfolenes. Preparation of 1. A solution of 0.357–0.5 mol of diazomethane in 1.0 l. of diethyl ether was prepared and to this was added 10.3 g (0.087 mol) of 2,5-dihydrothiophene 1,1-dioxide (sulfolene) in 100 ml of methylene chloride. The resulting solution was allowed to stand in a refrigerator (5–15°) for 1 week, whereby crystalline material and some polymethylene had precipitated. More product could be obtained by allowing the solution to continue to stand at 5°. The precipitate was recrystallized from 200 ml of hot ethanol to give 4.9 g (35%) of 3a,4,6,6a-tetrahydro-3H-thieno[3,4-c]pyrazole 5,5-dioxide (**1**): mp 128–129°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.7 (s), 8.65 (s), 9.0 (s) (sulfone), and 6.45 (w) μ (azo); uv $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 318.5 m μ (ϵ 415); nmr (CD_3CN), see text.

Anal. Calcd for $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 37.50; H, 5.04; N, 17.50. Found: C, 37.78; H, 5.01; N, 17.39.

Preparation of 2a and 2b. According to the general directions for **1**, from 0.176 mol of diazomethane and 11.7 g (0.089 mol) of 2-methyl-2,5-dihydrothiophene 1,1-dioxide (piperylene sulfone) there was obtained after 2 months an ether-insoluble oil (6.5 g) containing a mixture of 1- and 2-pyrazolines. Separation was effected by column chromatography on 50 g of neutral silicic acid with chloroform eluent. This gave as the first fraction after some unreacted methylsulfolene 0.94 g (6%) of a mixture of 1-pyrazolines, **2a** and **2b**. Presumably isomerization to 2-pyrazoline could have been suppressed by more frequent work-up of the oily product as formed. Fractional crystallization from ethanol gave 250 mg of the less soluble isomer, *exo*-6-methyl-3a,4,6,6a-tetrahydro-3H-thieno[3,4-c]pyrazole 5,5-dioxide (**2b**): mp 159–161°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.7 (s), 8.75 (s) (sulfone), and 6.45 (w) μ (azo); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 319 m μ (ϵ 419); nmr (CD_3CN) (distinguishes **2a** from **2b**), see text.

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2\text{S}$: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.63; H, 5.71; N, 16.27.

Repeated recrystallization from benzene of the residues of the ethanolic mother liquors from **2b** gave 50 mg of the second isomer, *exo*-4-methyl-3a,4,6,6a-tetrahydro-3H-thieno[3,4-c]pyrazole 5,5-dioxide (**2a**, obtained in a purity estimated >95% by nmr): mp 113–114.5°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.65 (s), 8.8 (s) (sulfone), and 6.45 (w) μ (azo); nmr (CDCl_3) (distinguishes **2a** from **2b**), see text.

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2\text{S}$: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.53; H, 5.71; N, 16.25.

Preparation of 3. According to the general directions for **1** and **2**, from 0.036 mol of diazomethane and 1.33 g (0.009 mol) of *cis*-2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide^{23,24} after 2 months there was obtained upon column chromatography (as for **2**) a 50% recovery of dimethylsulfolene and 335 mg (19.5%) of *exo,exo*-4,6-dimethyl-3a,4,6,6a-tetrahydro-3H-thieno[3,4-c]pyrazole 5,5-dioxide (**3**): mp 152–153° (from ethanol); ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.65 (s), 8.6 (s) (sulfone),

(23) B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **25**, 2187 (1960); L. Brandsma and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **81**, 33 (1962); C. C. Price and W. H. Snyder, *Tetrahedron Lett.*, 69 (1962); L. W. McTeer, U. S. Patent 3,256,344, *Chem. Abstr.*, **65**, 8762 (1966).

(24) Details of the preparation of the hexadiene sulfones will be reported subsequently.

and 6.43 (w) μ (azo); uv $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 319 m μ (ϵ 412); nmr (CDCl_3), see text.

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 44.68; H, 6.43; N, 14.88. Found: C, 44.80; H, 6.40; N, 15.05.

Preparation of 4. According to the general directions for 1, from 0.076 mol of diazomethane and 5.0 g (0.032 mol) of 8-thiabicyclo[3.2.1]oct-6-ene 8,8-dioxide (cycloheptadiene sulfone)²⁵ after 1 month there was obtained 4.5 g (70%) of *exo*-4,6-propano-3a,4,6,6a-tetrahydro-3*H*-thieno[3,4-*c*]pyrazole 5,5-dioxide (4): mp 154–155° (from ethanol); ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.75 (s), 8.55 (s), 9.0 (s), 9.15 (s) (sulfone), and 6.45 (w) μ (azo); uv $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 318.5 m μ (CDCl_3), see text.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 47.99; H, 6.04; N, 13.99. Found: C, 48.13; H, 6.01; N, 14.08.

Photolysis of Pyrazolines. Preparation of 5. A solution of 1.0 g (6.2 mmol) of the sulfolane-pyrazoline 1 in 120 ml of acetonitrile in a Pyrex flask was irradiated with a bank of 12 "black-light" (360 m μ) ultraviolet lamps (Rayonet photochemical reactor) for 24 hr, at the end of which time the ultraviolet absorption of 1 had disappeared. Evaporation of the solvent left a residue which was recrystallized from benzene-hexane and then from 200 ml of hexane to give 0.46 g (56%) of 3-thiabicyclo[3.1.0]hexane 3,3-dioxide (5): mp 110–111°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.75 (s) and 8.85 (s) μ (sulfone); nmr (CDCl_3), see text (Table I). The product sublimed at 100° (0.1 mm). Examination (nmr) of the mother liquors from the recrystallizations of 5 revealed the presence of isoprene sulfone and 3-methylene sulfolane (neither actually isolated).

Anal. Calcd for $\text{C}_6\text{H}_8\text{SO}_2$: C, 45.45; H, 6.10. Found: C, 45.33; H, 6.11.

Preparation of 6. Since the purified isomers 2a and 2b were not available in quantity, a mixture of both was used to prepare 6. A solution containing 0.43 g (2.5 mmol) of 2a and 2b in 100 ml of acetonitrile was irradiated for 12 hr in the manner of the photolysis of 1. The residue obtained by removal of solvent was purified by column chromatography on 15 g of neutral silicic acid with carbon tetrachloride-chloroform gradient elution. The materials from the fractions containing the desired product were combined and recrystallized from hexane. There was obtained 111 mg (30.5%) of *exo*-2-methyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (6): mp 44–45°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.75 (s) and 8.9 (s) μ (sulfone); nmr (CDCl_3) δ 1.4 ppm (d, 3, J = 7 Hz, CH_3), other protons similar to 5 and 7, see text.

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{SO}_2$: C, 49.31; H, 6.90. Found: C, 49.30; H, 6.60.

Preparation of 7. A solution of 226 mg (1.2 mmol) of 3 in 100 ml of acetonitrile was irradiated for 5.5 hr in the manner of the photolysis of 1. Evaporation of the solvent left a residue which was recrystallized from hexane to give 104 mg (54%) of *exo*,*exo*-2,4-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide: mp 72–72.5°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.7 (s) and 8.9 (s) μ (sulfone); nmr (CDCl_3) δ 1.5 (d, 6, J = 7 Hz, 2CH_3), 2.7 ppm (broad q, 2, J = 7 Hz, 2CHSO_2), other protons similar to 5, see text.

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{SO}_2$: C, 52.49; H, 7.55. Found: C, 52.32; H, 7.44.

Preparation of 8. A solution of 403 mg (2 mmol) of 4 in 110 ml of acetonitrile was irradiated for 28 hr in the manner of the photolysis of 1. The residue obtained by removal of solvent was submitted to column chromatography on 15 g of neutral silicic acid with chloroform elution. Effective further purification required recrystallization from hexane and sublimation at 100° (0.1 mm). There was obtained 91 mg (26.5%) of *exo*-9-thiatricyclo[3.3.1.0^{4,6}]nonane 9,9-dioxide (8): mp 165–170° (range unchanged after intensive purification); ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.8 (s) and 8.95 (s) μ (sulfone); nmr (CDCl_3) complex but with similarities to 5, see text.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{SO}_2$: C, 55.80; H, 7.03. Found: C, 55.75; H, 6.97.

Isotopic Exchange of 5. To a solution of 110 mg of 5 in 2 ml of dioxane and 2 ml of deuterium oxide was added ca. 250 mg of commercial potassium *tert*-butoxide. The resulting two phase solution was stirred and refluxed for several hours. After cooling and acidification the sulfone was extracted with chloroform. Recrystallization of the residue obtained from the extracts gave 86 mg of deuterated 5, mp 110–111°. From the integral of the nmr spectrum it was estimated that there was 6% (total) residual proton in the positions adjacent to the sulfonyl function.

Epoxidation of Sulfolenes. Epoxysulfolane (9) may be produced by performic acid oxidation of sulfolene.¹⁴ Similar reaction conditions (as follows) afforded epoxides from *cis*- and *trans*-2,5-dimethylsulfolenes.^{3,24}

Preparation of 10. A solution of 5 ml of 98% formic acid and 0.7 ml of 30% hydrogen peroxide plus 0.68 g (4.65 mmol) of *cis*-2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide was allowed to stand for 3 days (initially at 0°, mostly at room temperature). Solvent was removed under vacuum and the residue was dried by repeatedly dissolving in benzene-ethanol and evaporating under vacuum until a clear benzene solution could be obtained. Removal of solvent left a residual mixture which was resolved by column chromatography on 15 g of neutral silicic acid. Elution with a carbon tetrachloride-chloroform gradient gave three fractions. First eluted was 0.17 g of unreacted dimethyl sulfolene. The second in order of elution was the desired epoxide. The third appeared to be the corresponding trans diol.

Upon recrystallization from hexane the second fraction gave 0.10 g (17%, based on sulfolene consumed) of *exo*,*exo*-2,4-dimethyl-6-oxa-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (10): mp 55.5–56.0°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.7 (s), 8.9 (s), (sulfone), 11.2 (m), 11.9 (m), and 12.3 (m) μ (epoxide ?); nmr (CCl_4) δ 1.42 (d, 6, J = 7.5 Hz, 2CH_3), 3.08 (q, 2, J = 7.5 Hz, identical CHSO_2), 3.39 ppm (s, 2, identical CH -epoxide).

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}_3\text{S}$: C, 44.44; H, 6.22. Found: C, 45.22, 45.30; H, 6.22, 6.09.

The third fraction from the chromatography was examined only briefly. After recrystallization from benzene-hexane it gave 0.19 g of material, mp 101–102.5°. It was assigned structure *trans*-3,4-dihydroxy-*cis*-2,5-dimethyltetrahydrothiophene 1,1-dioxide on the basis of ir data (hydroxyl and sulfone) and its nmr (CCl_4) δ 1.39 (d, 3, J = 7.0 Hz, CH_3), 1.45 (d, 3, J = 7.0 Hz, CH_3), and 2.8–3.8 ppm (m, ~6, ring and hydroxyl protons) as well as mechanistic precedent.

Preparation of 11. The procedure for the epoxidation of the *cis* isomer was followed. A solution of 55 ml of 97% formic acid and 15.5 g of 30% (0.104 mol) *trans*-2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide was allowed to stand for 3 days with subsequent removal of solvent. Chromatography on 80 g of silicic acid (as for 10) gave two fractions. First eluted was 5.65 g of unreacted dimethyl sulfolene. This was followed by 6.7 g (72%) based on sulfolene consumed) of *endo*,*exo*-2,4-dimethyl-6-oxa-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (11), mp 78–80° after recrystallization from benzene-hexane: ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.7 (s), 8.9 (s) (sulfone), 11.0 (m), 11.85 (m), and 12.2 (m) μ (epoxide ?); nmr (CDCl_3) δ 3.46 (d, 3, J = 6.5 Hz, CH_3), 3.47 (d, 3, J = 8 Hz, CH_3), 3–4 ppm (m, 4, ring protons). As expected the nmr spectrum of 11 was similar to but more complex than that of 10. No diol was observed in the products of this oxidation.

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}_3\text{S}$: C, 44.44; H, 6.22. Found: C, 45.23, 45.07; H, 6.18, 6.19.

Dichlorocarbene Addition to Sulfolene. A mixture of 9.8 g (0.083 mol) of sulfolene and 25 g (0.057 mol) of phenyl(bromodichloromethyl)mercury in 100 ml of dry benzene was heated at 65–70° under argon with magnetic stirring for 48 hr. Solvent was removed under vacuum and the residue was repeatedly extracted with hot chloroform. The extracts were treated with gaseous hydrogen sulfide. The coagulated precipitate was removed by filtration. Evaporation of solvent and recrystallization of the residue from 120 ml of hot ethanol (two crops) yielded 2.62 g (23%) of 6,6-dichloro-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (12). From the filtrate was recovered 5.3 g of sulfolene. For analysis the product was sublimed at 100° (0.1 mm) and recrystallized from ethanol. It decomposed without melting at 160–180°. By rapid heating a temperature of 205° could be obtained without melting; ir $\lambda_{\text{max}}^{\text{KBr}}$ 7.65 (s) and 8.85 (s) μ (sulfone).

Anal. Calcd for $\text{C}_6\text{H}_6\text{Cl}_2\text{O}_2\text{S}$: C, 29.87; H, 3.01. Found: C, 29.29; H, 2.97.

Pyrolysis of Sulfones. The bicyclic sulfones 5–7 all decomposed smoothly and completely (without leaving a residue) when heated to ca. 150° (well above their melting points). Preparative experiments were conducted by heating a quantity of one of the sulfones to this temperature under an inert gas sweep, such that the evolved hydrocarbon was carried into a cold trap. Subsequent analysis of the contents of the trap revealed in each case a single diene product, as indicated by glpc with a 1,2,3-tris(2-cyanoethoxy)propane column and as described in the text. In the case of 5 direct comparison was made with authentic 1,4-pentadiene with respect to glpc retention time (shorter than that of *cis*- or *trans*-piperylene) and congruence of spectra: ir $\lambda_{\text{max}}^{\text{CCl}_4}$ 7.0, 7.1, 10.05, and 10.9 μ

(25) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **22**, 1590 (1957).

(diagnostic for vinyl); nmr δ 2.8 (m, 2), 5.0 (m, 4), and *ca.* 5.7 ppm (m, 2). In the case of **6**, direct comparison was made with an authentic mixture of *cis*- and *trans*-1,4-pentadiene.²⁶ The *cis* isomer (retention time, 1.15 that of the *trans* isomer) was totally absent (<0.5%) in the pyrolysate. The ir spectrum contained absorptions (also in the mixture) at $\lambda_{\text{max}}^{\text{CCl}_4}$ 10.35 (μ , diagnostic for *trans*-olefin), 10.1 and 11.0 μ (diagnostic for vinyl). In the case of **7**, the isomeric heptadienes are known to be separable on the glpc column used.²⁷ The single hydrocarbon component in the pyrolysate possessed ir absorption at $\lambda_{\text{max}}^{\text{CCl}_4}$ 10.35 μ (diagnostic for *trans*-olefin) and gave an nmr spectrum δ 1.55 (m, 6), 2.5 (m, 2), and *ca.* 5.1 ppm (m, 4) identical with that of *trans,trans*-2,5-heptadiene and distinguishably different from that of the *cis,cis* isomer.²⁷ Since **8** distilled without decomposition, the products of its decomposition could not be examined in this way. An alternative, analytical method of studying the decomposition of the sulfones was to inject a small quantity into an intensely heated (upward to 350°) injection port of a gas chromatograph. The products were then detected in conventional fashion as eluted from the column. Only the latter technique was applicable for **8** and substituted epoxysulfolanes **10** and **11**, as described in the text and below.

A third technique for fragmentation was vapor-phase pyrolysis. Epoxysulfolane itself (**9**) could successfully be cracked to sulfur dioxide and divinyl either by sublimation (1–10 mm pressure, inert gas sweep) through a short tube (10 cm) filled with glass beads and maintained at 280°. The pyrolysate was trapped at low temperature and subsequent identification was made by comparison with authentic divinyl ether. Congruence of spectra (ir and nmr) was observed. Neither **10** nor **11** gave an analogous product under these conditions; hence for these sulfones recourse was made to the analytic (glpc) method as previously mentioned. The order of elution (Carbowax column) of an authentic mixture¹⁸ of dipropenyl ethers is: (relative retention time) *cis,cis* (1.0); *cis,trans* (1.24); *trans,trans* (1.62). Peaks corresponding to the latter two were observed from **11** and **10**, respectively, with less than 1% crossover under appropriate conditions, which involved injection of the smallest possible amount in sulfolane solution and carefully adjusting flow rate and temperature in the gas chromatograph (in which all acidic sites were neutralized). The purity of the epoxysulfolanes **10** and **11** cannot be guaranteed (with respect to stereochemical integrity) to a greater degree than 99%.

Decomposition of 12. The fragmentation of the dichlorocarbene adduct of sulfolane was carried out in the fashion of the preparative decomposition of **5**. Analysis by nmr of the trapable material swept out of the reaction zone (at slightly reduced pressure) and collected at low temperature revealed only the conjugated diene²⁸ (eq 24): nmr (CCl₄) δ 4.2 (apparent t, 2, coupling *ca.* 7.5 Hz, indicating either geometrical isomers or long-range coupling) and 6–7.7 ppm (m, 4, complex coupling not recognizable as a simple vinyl group). For characterization this was converted to a maleic anhydride adduct in refluxing toluene (24 hr). After several re-

crystallizations from benzene–hexane there was obtained 4-chloro-6-(chloromethyl)-4-cyclohexene-*cis*-1,2-dicarboxylic anhydride: mp 101–103°; ir $\lambda_{\text{max}}^{\text{KBr}}$ 4.5 (m) and 5.6 (s) μ (anhydride); nmr (CDCl₃) δ 6.16 (sextet, 1, *J* = 5, *J* = 1.5 Hz, olefin), 4.1 (pair of d, 2, *J* = 6 Hz, chloromethyl), 2.7 (m, 2, ring methylene), 3.1 (m, 1), \sim 3.6 (m, 1), and \sim 3.8 ppm (m, 1, ring methines).

Anal. Calcd for C₈H₈Cl₂O₃: C, 45.99; H, 3.43. Found: C, 45.92; H, 3.45.

Rates of Decomposition. The technique used by Grummitt¹⁷ for comparing the stability of sulfolenes was adopted for determining the rate of thermal decomposition of **5**. The analytical method involved collecting in standard base over measured time intervals the sulfur dioxide released from a molten sample of sulfone, oxidizing the sulfite so obtained to sulfate with hydrogen peroxide, and back-titrating with standard acid. The apparatus of Grummitt¹⁷ was miniaturized for operation on a microscale. Our modification has been successfully used to measure rates of decomposition of a number of unsaturated cyclic sulfones with satisfactory results. Good first-order rate plots have been obtained regularly, and we have obtained values for the rate of decomposition of sulfolene itself in satisfactory agreement with those reported by Grummitt.¹⁷ Hence, a comparison of his activation parameters with ours should be valid. The apparatus will be described more fully in conjunction with other studies, and a discussion of experimental complications (which are minimal for **5**) will be deferred until that time. In general, the problem of accuracy is greater than that of precision in the measurement of rates by this technique.

The following first-order constants were measured for the de-

Temp, °C	Rate, sec ⁻¹
117.1 \pm 0.1	1.14×10^{-4}
125.2	2.62×10^{-4}
130.0	4.11×10^{-4}
136.7	7.78×10^{-4}
145.3	15.6×10^{-4}

composition of **5**. From the preceding a value for $\Delta \log k/\Delta T^{-1}$ of 6660 was obtained, from which the activation parameters given in Table II are derived. The same apparatus was used to measure the release of sulfur dioxide from sulfolane. The much higher temperature required to effect decomposition led to experimental difficulties; in addition to less certain external temperature control, sulfolane possesses appreciable volatility in the region of its instability, suggesting that the sample may in part be refluxing to cooler portions of the reaction vessel. For such considerations it was impractical to attempt to secure activation parameters, and we record only an approximate rate constant of 2.3×10^{-8} sec⁻¹ at 256°.

Under similar conditions (275°) no sulfur dioxide evolution at all could be detected from **8**. We therefore give the maximal rate constant shown in Table II. Recovery of **8** from the latter attempted pyrolysis was carried out (>50% yield); the sample did show some degradation (tar formation).

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