The Mechanism of Interaction of Sulfur Dioxide with Unsaturated Systems. Rates of Reaction and the Function of Orbital Symmetry in Sulfolene Dissociation

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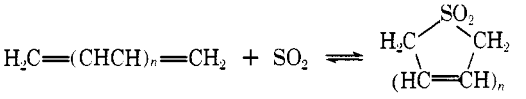
Abstract: The synthesis of a bicyclic 1,6-adduct of sulfur dioxide with cyclooctatriene is described. From rates of decomposition, activation energies (enthalpy and entropy) for fragmentation of the following substances were obtained ($\Delta G^{\ddagger}$, kcal/mol): *cis*-2,5-dimethylsulfolene (26.5); *trans*-2,5-dimethylsulfolene (30.3); episulfone (27.8); dihydrothiepin dioxide (29.7); 9-thiabicyclonona-2,7-diene dioxide (28.6); 9-thiabicyclonona-2,4-diene dioxide (39.4). Dissociation in the case of the last sulfone occurred at a rate comparable to a degenerate 1,3 rearrangement in 9-thiabicyclonon-2-ene dioxide. Equilibrium constants for certain sulfolene reactions were measured by an NMR method. It is concluded that (other factors being equal) an orbital symmetry allowed "linear" mode of sulfur dioxide release is favored over a "nonlinear" mode or sequential bond rupture by ca. 10 kcal/mol in these systems. Other theoretical and mechanistic aspects of these three-, five-, and seven-membered ring cycloregressions are discussed.

Elsewhere we have examined the scope of sulfone formation from trienes and sulfur dioxide[2] and have considered the stereochemistry of the retroreaction within the series shown (n = 1, 2).[3] In this article we take up the question of mechanism in these reactions (and their lower vinylog, n = 0), with specific consideration of the roles of orbital symmetry conservation.[4] In the case of the five- and seven-membered rings, contrasting steric courses were observed, suggesting that there are allowed concerted reaction paths, suprafacial in the case of the five- and antarafacial in the case of the seven-membered ring with respect to the hydrocarbon component of the reaction. What the preceding stereospecificity studies do not reveal is the true magnitude of these stereochemical preferences. We here attempt to evaluate just how "disallowed" are alternative paths of fragmentation. Our approach has been to examine appropriately constrained systems wherein reactions corresponding to a disfavored mode were forced to occur.[5] By consideration of the chemical behavior of these systems and by comparison of kinetic data, a generalized view emerges regarding reactivity in these sulfones, which hopefully has applicability for other types of concerted reactions as well.

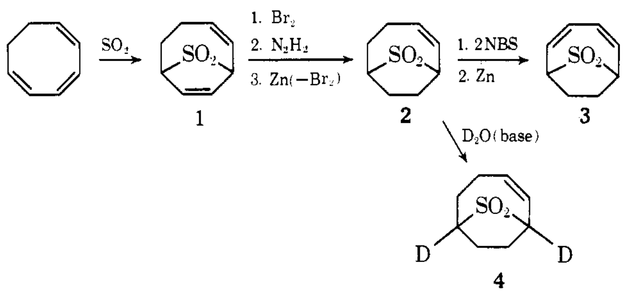


$$H_2C{=}(CHCH)_n{=}CH_2 + SO_2 \rightleftharpoons \overset{SO_2}{H_2C\quad CH_2}\,(HC{=}CH)_n$$

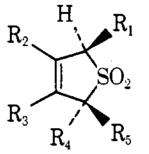
The key substance for our purposes is the formal 1,6 adduct of cyclooctatriene and sulfur dioxide (**3**), prepared indirectly as described subsequently.[5] Its thermolysis behavior (products and kinetics) was examined in detail. In order to place the latter in perspective, and to obtain other requisite knowledge about these sulfone fragmentations, additional and comparable data were collected for dimethylsulfolenes, for episulfone, for dihydrothiepin dioxide, and for bicyclic sulfones critically related to **3**. These results are to be discussed with respect to the probable chemical courses of the pyrolyses of the compounds described.

Results

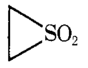
Synthesis. The sulfones utilized in this study were prepared by literature procedures or by further transformation of sulfolenes (e.g., **1** → **2** → **3**, **4**).[5] For previously undescribed substances, details may be found in the Experimental Section.



Fragmentation of Sulfones. Kinetic Parameters. For the purpose of quantitatively evaluating how structural features affect the energetics of various paths of fragmentation described in the preceding article, recourse was made to kinetic studies. In Table I we have listed pertinent rate and activation energy parameters for the dissociation of sulfolenes and related substances, the structures of which are given below or previously. The first examples (**5–9**) were determined by Grummitt, Ardis, and Fick.[6] The other entries represent measurements obtained in this work for compounds which have been elsewhere described (**10–13**, **1**, **3**).



5, $R_1, R_2, R_3, R_4, R_5 = H$
6, $R_1, R_3, R_4, R_5 = H$; $R_2 = CH_3$
7, $R_2, R_3, R_4, R_5 = H$; $R_1 = CH_3$
8, $R_2, R_4, R_5 = H$; $R_1, R_3 = CH_3$
9, $R_1, R_4, R_5 = H$; $R_2, R_3 = CH_3$
10, $R_2, R_3, R_4 = H$; $R_1, R_5 = CH_3$
11, $R_2, R_3, R_5 = H$; $R_1, R_4 = CH_3$



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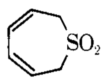

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Grummitt's method was employed; it involves measurement of sulfur dioxide released as a function of time from a molten sample of an appropriate sulfone.[6] The latter procedure was miniaturized on a millimolar scale. We have obtained results for the decomposition of sulfolene itself (**5**) in satisfactory agreement with literature values[6] and therefore believe that a direct comparison between the two sets of numbers is valid.

A systematic consideration of the parameters reported in

Table I. Parameters for the Dissociation of Various Sulfones (as Measured by Rate of Release of Sulfur Dioxide)

Sulfone	Relative rate[a]	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)[b]	$\Delta H^{\ddagger}$, kcal/mol[c]	$\Delta S^{\ddagger}$, eu[d]
Sulfolene[e] (**5**)	1.0	30.1 (125)	33.6	+8.9
3-Methylsulfolene[e] (**6**)	0.49	30.6 (131)	34.6	+9.9
2-Methylsulfolene[e] (**7**)	5.0	28.5 (105)	24.7	−10.1
2,4-Dimethylsulfolene[e] (**8**)	3.6	29.0 (111)	32.3	+8.6
3,4-Dimethylsulfolene[e] (**9**)	0.1	31.9 (148)	35.4	+8.6
cis-2,5-Dimethylsulfolene[f] (**10**)	57.0	26.5 (93)	24.7	−5.0
trans-2,5-Dimethylsulfolene[f] (**11**)	0.62	30.3 (141)	28.9	−3.3
Episulfone[f] (thiirane dioxide, **12**)	15.0	27.8 (93)	28.5	+1.9
2,7-Dihydrothiepin dioxide[f] (**13**)	1.2	29.7 (128)	29.8	+0.2
9,Thiabicyclonona-2,7-diene dioxide (**1**)	5.9	28.6 (108)	29.3	+1.9
9-Thiabicyclonona-2,4-diene dioxide (**3**)	0.0001[g]	39.4 (256)	32.0 (?)[h]	−14.0 (?)[h]

[a] Interpolated or extrapolated to 125° except as noted. [b] Free energy of activation (±1 kcal/mol) for median of temperature range examined (see Experimental Section). [c] Enthalpy of activation (±2 kcal/mol, R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961)). [d] Entropy of activation (±5 eu, footnote *c*). [e] Data of Grummitt, Ardis, and Fick, ref 6. [f] Preparation: 10, 11, ref 3; 12, G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, 90, 2106 (1957); **13**, ref 2. [g] This is a gross estimate based upon a comparison with 1 at 180°, at which temperature it is felt that errors of extrapolation are least. [h] See text for specification of the significance which can be attached to these numbers.

Table I is presented in the Discussion section. In view of the anomalous behavior of **3**, especial attention was directed to the products of its decomposition.[7] In addition to sulfur dioxide (>80% of theory), the major hydrocarbon product was indeed cyclooctatriene (see Experimental Section). However, there were traces of other products of similar volatility (GLC analysis) and a residual tar was produced in the reaction vessel. The latter is atypical, since the decompositions were generally clean. In the cases of the other sulfones in Table I, **5–11** are known to give the appropriate diene, **12** gives ethylene, **13** gives *cis*-hexatriene, and **1** gives 1,3,5-cyclooctatriene (plus in each case sulfur dioxide).

Some comment on the quality of the data in Table I is in order. In general there was no trouble in obtaining reproducible, cleanly first-order (to greater than 90% completion) runs, which in turn gave linear log k vs. $1/T$ plots ("worst" correlation coefficient was >0.997, for **1**). However, consideration of probable systematic errors, having to do with the ex situ measurement of sulfur dioxide, volatility of several sulfones, potential reversibility of the eliminations, and minor side reactions, suggests that error limits in excess of statistical deviation should be estimated. For this reason duplicate runs were not routinely taken.[8] For most of the sulfones (**1**, **10–13**) we claim $\Delta G^{\ddagger}$, ±1 kcal/mol; $\Delta H^{\ddagger}$, ±2 kcal/mol; $\Delta S^{\ddagger}$, ±5 eu. For the critical substance **3**, experimental complications were compounded by isothermal control problems at the elevated temperatures and by the apparently more complex nature of decomposition (see Discussion). In this case the free energy of activation ($\Delta G^{\ddagger}$) is the only parameter in which any measure of confidence can be placed.[7,9]

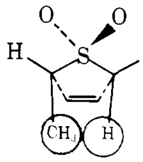
The degenerate isomerization of **4** (producing label scrambling) was detected at elevated temperatures by NMR. Consideration of the operational complexities in the determination of this reaction is given in the Experimental Section. An approximate rate constant of 0.003 min^{-1} is quoted for the process at 310°.

Thermodynamic Considerations. A limited number of equilibration studies were conducted by an NMR method. When heated to 100° for several days in dilute sulfur dioxide solution (sealed NMR tube), both the *cis*- and *trans*-2,5-dimethylsulfolenes (**10** and **11**) were interconverted to the same mixture containing a slight excess of the cis isomer. By integration the equilibrium constant for the isomerization was calculated as $K_{\text{cis/trans}} = 1.5$. We think it likely that hexadienes, formed in small concentration by dissociation of the sulfolenes, are the active isomerizing intermediates. This suggestion follows from the actual observance of *trans,trans*-hexadiene in equilibrium with **10** when the latter was heated with 2–3 molar excess of sulfur dioxide. An equilibrium constant for the cycloaddition was determined by NMR integration over the range 92.8–131° (see Experimental Section) and from this was computed the enthalpy of formation of **10** from hexadiene and sulfur dioxide, $-\Delta H° = 20.0$ kcal/mol. The latter may be compared with the heat of formation which has been recorded[10] for sulfolene itself (**5**), $-\Delta H° = 26.6$ kcal/mol (determined in similar fashion).[11] The same NMR technique was applied to **1** and **11**; however, $\Delta H°$ values were not computable. At 100°, it appeared that **11** was ca. 0.2 times as greatly dissociated as **10**, whereas, **1** was ca. 8.3 times *more* dissociated than **10** under otherwise similar conditions. The latter observation (on **1**) is significant to the ensuing Discussion section. If **10** is accepted as a model for a disubstituted sulfolene, then there can be no more that 1–2 kcal/mol of incremental ring strain associated with the bicyclic system of **1**.[12]

Discussion

The central and fundamental observation is the refractory nature of the bicyclic sulfone **3** and the allied stability of **4** in comparison with the ready decomposition of **1**. In order to place the semiquantitative determination of activation energy parameters for these bicyclic molecules in perspective, the thermolysis behavior of sulfolenes (**5–11**) and the three- and seven-membered ring sulfones (**12**, **13**) will be considered first. The overall remarkable similarity in the relative rates of dissociation of these varied species near 125° should be noted (Table I).

General, 5–11, 13. There are several features of sulfolene reactivity which may be derived from our data plus that in the literature.[13] The substituent effects of appended methyl groups, first studied quantitatively by Grummitt, Ardis, and Fick[6] (data reproduced in Table I, entries **5–9**), is substantiated by the rates of decomposition of *cis*-2,5-dimethylsulfolene (**10**) and *trans*-2,5-dimethylsulfolene (**11**). As previously noted alkylation in the β position (on the double bond) apparently stabilizes sulfolenes (compare **6**, **9**), whereas α substitution has a destabilizing effect (**5**, $\Delta G^{\ddagger} = 30.1$; **7**, $\Delta G^{\ddagger} = 28.5$; **10**, $\Delta G^{\ddagger} = 26.5$ kcal/mol). This trend has also been noted elsewhere for the dihydrothiepin system.[2] A steric influence on the transition state is revealed in the approximate 100-fold acceleration in decomposition of cis isomer **10** relative to the trans isomer **11**. This reactivity difference in fact forms the basis of the convenient separation of the stereoisomers.[3] It was shown that this observation cannot be ascribed to a significant ground state destabilization of **10** (e.g., due to methyl–methyl steric repulsions absent in **11**) since at equilibrium **10** predominates slightly; $K_{10/11} = 1.5$. The fact that the rate differential may be traced to the enthalpy of activation (**11–10**, $\Delta\Delta H^{\ddagger} = 4.2$ kcal/mol) supports attribution of the effect to methyl–hydrogen compression in the transition state for decomposition of **11**.[14] Consistent with this is the absence of *cis,cis*-hexadiene in the pyrolysate from **10**; here potential methyl–methyl repulsions direct the reaction to the alternative transition state leading to *trans,trans*-hexadiene exclusively. Such effects have been noted previously. Only *trans*-piperylene is obtained from 2-methylsulfolene (**7**),[15] and 2,4-dimethylsulfolene (**8**) is reported to behave similarly.[16] However, 2,3-dimethylsulfolene has been reported as yielding a 97:3 mixture of dienes, in which the minor isomer corresponds to the disfavored mode here described.[16] It would appear that product (diene) stability may have some influence on the transition state, since in this case the slight energy increment inherent in a trans double bond (vs. cis) is likely unavailable.

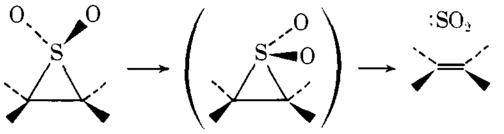


Additionally worthy of note is our observation that the overall exothermicity of sulfolene formation may in favorable cases be determined by NMR examination of reaction mixtures. Previously, a gravimetric technique was used to derive an enthalpy of formation of sulfolene itself (**5**), $-\Delta H° = 26.6$ kcal/mol (from butadiene and sulfur dioxide).[10] Detection of *trans,trans*-hexadiene in the presence of **10** and a slight excess of sulfur dioxide at a series of temperatures (≥90°) allows a similar calculation of the enthalpy of formation of **10** from the components ($C_6H_{10} + SO_2$): $-\Delta H° = 20.0$ kcal/mol. We make the reservation that these values should only be quoted in the context of the system in which they were determined.[11,17] A similar (single) NMR observation on **11** allows the conclusion that its formation is more exothermic than in the case of **10** by ca. 1 kcal/mol, which is qualitatively in accord with expectations from comparative diene stabilities.[18] The fact that these dissociations can be directly observed by the NMR method means that for α,α'-disubstituted sulfolenes the free energy of reaction ($\Delta G°$) is near zero (±2 kcal/mol). From the trend exhibited it may be surmised that more highly α-substituted sulfolenes will in general not be isolable, in accord with experience.[13,16]

In summary, for the sulfolene formation the overall energetics are such that the cycloaddition is exothermic in most cases by ca. 20–25 kcal/mol, but this apparently is counterbalanced by the normal entropy factor in bimolecular reactions. Alkyl substituents apparently impose a consistently small perturbation on ground state equilibrium. The influence of steric factors on transition state structure is likewise interpretable in terms of the geometry of a concerted process (see following).

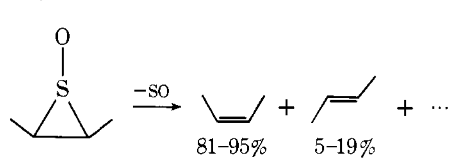
The dimethyldihydrothiepin dioxides described in the preceding article[3] were not available in sufficient quantities for kinetic studies; however, rates of decomposition of the parent seven-membered ring **13** were determined (Table I). Although the activation parameters apply to elimination (**13**, $\Delta G^{\ddagger} = 29.7$; **5**, $\Delta G^{\ddagger} = 30.1$ kcal/mol), it may reasonably be inferred that 1,6-addition also is kinetically about as feasible as 1,4-addition in the absence of steric constraints (as manifested, e.g., in **3**). This is borne out by synthetic studies where the two processes were shown to be competitive.[2] It is likely that in any given triene case fairly subtle factors will dictate which path is favored. For decomposition the slightly less positive entropy of activation (**5–13**, $\Delta\Delta S^{\ddagger} = 8.7$ eu) for **13** is reasonable, considering that in the larger ring there should be more vibrational and rotational degrees of freedom to be aligned in the transition state of a synchronous reaction. This is compensated by an enthalpy effect (**5–13**, $\Delta\Delta H^{\ddagger} = 3.8$ kcal/mol), perhaps associated with angle strain or other steric factors. The two transition states are geometrically sufficiently unrelated as not to reward further speculation along these lines.[3] For the purposes of this article, the relevant point established is that 1,6-extrusion of sulfur dioxide in an *unconstrained* situation proceeds at the same rate as 1,4-extrusion.

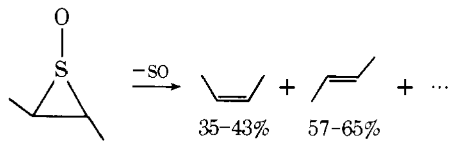
Three-Membered Rings, 12. Thiirane 1,1-dioxide (episulfone) is the smallest member of a vinylogous series (**13, 5, 12**). Considerable information has accrued in the literature regarding fragmentation of its derivatives to sulfur dioxide and olefins. Briefly, the following is known. The decomposition is stereospecific and is cleanly suprafacial with respect to the incipient olefin in all cases examined to date.[19-21] On the theoretical side, Woodward and Hoffmann[4] have described a "nonlinear" reaction path which meets symmetry restrictions for a concerted decomposition, thus accommodating the observed stereospecificity. The geometrical course of this process involves deforming the sulfone as shown prior to scission of carbon–sulfur bonds. This path brings the pertinent sulfur localized molecular orbitals into operation in an antarafacial fashion, thus fulfilling the requirements for a $[_{\pi}2_s + _{\sigma}2_a]$ (allowed) cycloregression.



In the case of phenyl-substituted thiirane dioxides, rates of dissociation have been observed, leading to activation energies on the order of 17.5–18.5 kcal/mol. The near identity of rates of decomposition of monophenyl, *cis*-diphenyl, and *trans*-diphenyl episulfones (inference: only one aryl group provides conjugative stabilization in the transition state) and rate acceleration accompanying increasing ionizing power of the medium (inference: dipolar diradical mechanism) has led to a preference for sequential bond rupture as opposed to a concerted process.[19g]

Of obvious relevance is the steric course of episulfoxide decomposition. Only partial stereospecificity is observed; the reaction has been interpreted as proceeding through a short lived zwitterionic intermediate in which internal rotation partially occurs.[22,23]

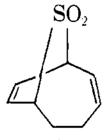




While the evidence seems clear in the case of sulfur monoxide extrusion, for the stereoexplicit thiirane dioxide elimination a mechanistic dichotomy remains. It is this interpretational ambiguity which we address in the present article: an apparently stereospecific cycloreversion is disallowed by the normally favored linear cheletropic process; is the resulting path nonlinear concerted or does a nonconcerted (two step, sequential bond rupture) mechanism intervene? Furthermore, should the latter prove to be the case, could not the sequential process *in fact* operate in the case of the *linear allowed* processes as well?[24]

We have measured the activation parameters for episulfone itself (**12**, Table I). Surprisingly, thiirane 1,1-dioxide proved to have the same order of stability as the sulfolenes, in contrast to what would have been anticipated from literature citations of its derivatives.[19] In particular, comparison of the activation parameters of **12**, $\Delta H^{\ddagger} = 28.5$ kcal/mol, vs. phenyl episulfone,[19g] $E_a = 17.5$ ($CHCl_3$), 18.5 (CH_3OH) kcal/mol, tends to substantiate a strong perturbation of the fragmentation mechanism for episulfone by an appended aryl group. Accordingly, while a two-step mechanism may occur with episulfones bearing potential stabilizing substituents,[19] the nonlinear concerted[4] path may not be excluded for the parent. Rate studies of thiirane dioxides are inherently ambiguous because of the effects of ring strain.[25] In the case of **12** there is certainly a destabilization due to bond angle deformation which would tend to accelerate fragmentation relative to sulfolenes (**5–11**). Apparently a counterbalancing stabilization, which we attribute to orbital symmetry constraints, neutralizes any potential rate acceleration. Since the magnitude of the expected destabilization cannot be known, no quantitative conclusion may be drawn about the importance of the symmetry constaint in **12**, and mechanistic interpretation must rely on indirect evidence in analogous systems, as follows.

Thiabicyclononenes, 1, 3, 4. What is required to answer the questions raised in the previous section is a system which, as in the case of episulfones, would be forced to undergo cycloelimination in an unfavorable direction (based upon stereochemical preferences previously described[3]). However, it must have appropriate model systems such that comparisons can be drawn and factors other than stereoelectronic may be accounted for. A suitable set of molecules appeared to be the sulfones formally derived from cyclooctatriene and sulfur dioxide. The kinetic and thermodynamic data as regards compounds **1** and **3** (Table I) provide some idea of the magnitude of the stereobias manifested in these sulfur dioxide eliminations, which we believe may be attributed to orbital symmetry factors. The pertinent observation is that **3** undergoes fragmentation some 60,000 times more slowly than does **1**.



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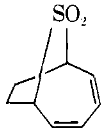

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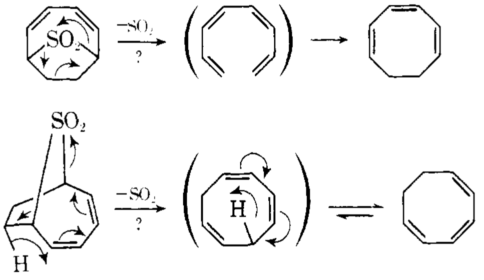
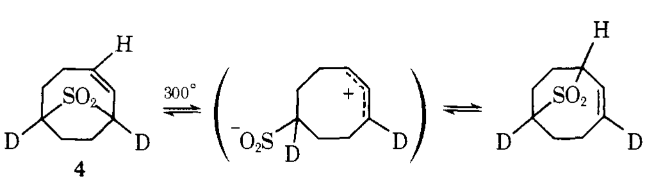
It will be observed that **1** is a sulfolene, the product of an (allowed) suprafacial 1,4-addition. Dissociation of **1** proceeded cleanly at apparent first-order rates in the temperature range 100–120°. From the temperature dependence of the rate the activation parameters recorded in Table I were obtained ($\Delta H^{\ddagger} = 29.3$ kcal/mol, $\Delta S^{\ddagger} = 1.9$ eu). It will be observed that they are typical for sulfolene decompositions (compare **5–11**). We therefore infer that **1** is a suitable reference model for an allowed cycloregression. Equilibrium studies previously cited demonstrated no more than ca. 2 kcal/mol of incremental ring strain in this system; however, even this is not manifested in a lowering of $\Delta H^{\ddagger}$ relative to **10** or **11**. Potential conjugation from the additional double bond in **1** might be expected to induce some nonsynchrony in the order of bond rupture (cf. phenyl episulfone); however, it can only be said that this is not revealed in the kinetics.

By way of comparison **3** is formally a 1,6-adduct, which due to the steric constraints of the bicyclic system may also undergo only suprafacial elimination with respect to the hydrocarbon (triene) moiety instead of the antarafacial path apparently preferred by **13**.[3] The sulfone **3** was completely stable at 120° and required considerably higher temperatures for measurable rates of fragmentation. As described in the Results section, elimination proceeded less cleanly than customary, although the major products appeared to be sulfur dioxide and cyclooctatriene. A set of activation parameters (Table I) was similarly obtained, albeit under forcing conditions. It will be observed that there is a 11 kcal/mol differential (10 kcal/mol at an extrapolated common temperature, 180°) in free energy of activation between **1** and **3**. Our conclusion will be that *this may be taken as a measure* (*minimal*) *of the magnitude of orbital symmetry constraints in these cycloregressions.* The striking feature of the activation parameters (Table I) is the negative entropy of activation for **3** ($\Delta S^{\ddagger} = -14$ eu), which appears to account largely for the reactivity difference compared to the sulfolenes ($\Delta S^{\ddagger} = +1.9$ for **1**). However, as noted in the Results section, it is not at all certain that any significance can be attached to this number because of experimental complications (also, see later). Several reaction mechanisms are compatible with the information available on the decomposition of **3**. In addition to a nonlinear $[_{\pi}6_s + {}_{\omega}2_a]$ concerted path or a nonconcerted sequential bond scission alternative as hypothesized in the case of derivatives of **12**, other, more subtle concerted processes could afford the same products. For example, each of the transformations shown below is symmetry allowed with linear departure of sulfur dioxide. In each case an intermediate is formed (*cis,cis*-octatetraene or 1,3,6-cyclooctatriene) which under the conditions prevailing in the pyrolysis of **3** would be transformed into 1,3,5-cyclooctatriene.[26]



Of the mechanistic possibilities listed, for our purposes the most relevant to the question of the sulfolene transition state is the nonconcerted process in which the carbon–sulfur bonds would be broken sequentially to yield sulfur dioxide and 1,3,5-cyclooctatriene directly. The disguised symmetry of the synthetic intermediate **2** uniquely offers opportunity for an independent estimate of the rate of such a reaction. In order to be able to make measurement, a label was introduced by deuterium exchange, giving **4**. When the latter



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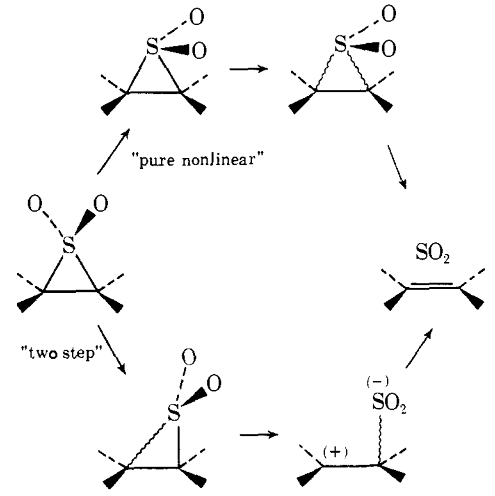
substance was heated in diphenyl ether solution (>300°), reappearance of a signal from the bridgehead position (as in **2**) was noted by proton NMR examination. For reasons given in the Experimental Section, only an estimated first-order reaction rate constant may be stated: $k = 0.003$ min^{-1} at 310°. Derivation of activation parameters was not feasible. The interpretation given is as depicted; it was confirmed by recovery of thermolyzed **4** that deuterium scrambling had occurred. Formulation of the isomerization as proceeding through a diradical or zwitterionic intermediate is not essential. An equivalent, $[_\pi 2_s + {}_\sigma 2_a]$ concerted sigmatropic migration may also be entertained. The distinction is not important to our argument; the key feature in the rearrangement is that only a single carbon-sulfur bond participates.

An estimate of the rate of decomposition of **3** at this temperature (310°) may be obtained by extrapolation. Comparison of rate constants, with a correction for the statistical factor to two potentially rupturable carbon-sulfur bonds in **3**, reveals that **3** undergoes reaction only 100 ± 50 times more rapidly than does **4**. Reaction by a mechanism analogous to that presented for **4** (two-step) should indeed proceed more rapidly for **3** (relative to **4**) due to the additional double bond extending conjugation in the intermediate from **3**.[27] The conclusion to be drawn is that *sequential rupture of carbon-sulfur bonds in* **3** (i.e., a two-step mechanism, therefore symmetry allowed) *is compatible with the observed energy barrier to its decomposition.*[28] Therefore, it is not necessary to invoke a nonlinear (or other concerted) pathway to explain the fragmentation of **3**.

Mechanistic Conclusion. From this work we should like to draw two major observations regarding cycloeliminations of sulfur dioxide from these cyclic sulfones. It has been emphasized that for the sulfur dioxide extrusions which are disallowed in the linear mode (**12**, **3**), a clear choice as to whether a concerted nonlinear or a two-step process in fact occurs cannot be drawn on the basis of experiment. The negative entropy of activation noted for **3** offers a potential clue which we have not hitherto considered. To the extent that it suggests a constrained transition state, a concerted formulation would be preferred over an intermediate having additional degrees of rotational freedom. However, we have previously expressed the belief that the rate data for **3** are too doubtful to support such an interpretation. Furthermore, the entropy component in the case of phenyl episulfone, for which independent evidence suggests sequential bond scission, is of the same negative magnitude.[19g,29] What we suggest is that for the linearly disallowed cases (**3**, **12**, and derivatives) a particular characteristic transition state may not prevail, but rather a continuum of reaction paths may be available. This follows from a critical examination of the nonlinear fragmentation mode, exemplified for **12**. The point to be established is that *the molecular distortion leading to the nonlinear reaction path readily accommodates itself to sequential bond rupture.* This is seen with reference to the diagram (⁓ indicates bond rupture), wherein it may be seen that the physical distinction between paths idealized as "nonlinear" and "two step" (sequential) is slight indeed.[30] The motion of the sulfonyl group in the nonlinear mode depicted inherently differentiates between the carbon-sulfur bonds; nonsynchrony in their order of rupture is almost an expected consequence. In this light it tends to become unprofitable to attempt to classify these "disallowed" reactions as either nonlinear concerted or two step; these very likely are an unreal distinction in this case.[30] Our suggestion is that in any given case the configuration of the transition state may respond strongly within this continuum to perturbing substituents.

The ambiguity which clouds the actual mechanism of the linearly disallowed reactions should not obscure what we regard as the more significant conclusion deriving from this work. The inertness of **3** tells more about sulfolene dissociation $[_\pi 4_s + {}_\sigma 2_s]$ than about the symmetry restricted mechanisms. The pertinent observation is that *there is no synchronous bond rupture pathway available to the eight-electron system of* **3** *which is within 10 kcal/mol in activation energy* ($\Delta\Delta G^\ddagger$) *compared to the concerted mechanism available to the six-electron system of the sulfolenes.* Presumably sulfolenes (and **13**) *could* avail themselves of a sequential bond scission process. An especially suitable model for this was provided in **4**. Clearly this would be a relatively unfavorable sequence. Therefore, our inference is that a (near) *synchronous* (simultaneous) *bond scission transition state represents a saddle point on the energy hypersurface for the allowed sulfolene* $[_\pi 4_s + {}_\sigma 2_s]$ *reaction.*[31] Progressively less symmetrical transition states must be of higher energy, tending toward that of **4**. Several qualifications must be attached to this rather sweeping generalization. Substituents will of course perturb the mechanism (e.g., perhaps shift the saddle point to one side). Furthermore, the principle of least motion[32] might tend to disfavor a process in which both bonds break to exactly the same extent (with attendant readjustments of bond distances and atomic hydridizations elsewhere) in the activated complex. Consequently, we use the term "near" synchronous, and it is therefore still meaningful to speak of "diradical" or "dipolar" character in the sulfolene reaction. In fact the (small) effect of substituents and of solvents of high dielectric constant on the reaction has previously led to the formulation of a polar mechanism of addition.[33] We should only like to observe that a rate acceleration brought about by a polar solvent does not necessarily imply a nonsynchronous mechanism. It can equally well be accommodated by a synchronous mechanism with a variable amount of charge transfer.



Summary

The sulfolene reaction is concluded to be mechanistically concerted, proceeding through a transition state with near synchronous formation (or rupture) of carbon-sulfur bonds. Activation energies for 1,4- and 1,6-eliminations are similar. The preferred stereochemical course in the former (1,4) is suprafacial and in the latter (1,6) is antarafacial with respect to the hydrocarbon component. Suprafacial 1,2- or 1,6-elimination is relatively disallowed; this is attributed to orbital symmetry constraints. In these cases a clear distinction cannot be drawn between highly nonsynchronous (two step) or concerted nonlinear reaction paths, and it is suggested that there may be variability between individual cases in this respect and with regard to the position of the transition states along the reaction coordinate.[29]

Experimental Section

General. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were taken in capillary tubes and were corrected. Infrared spectra (ir) were obtained with a Perkin-Elmer spectrophotometer, Infracord Model; ultraviolet spectra (uv) with Cary spectrophotometer, Model 14; nuclear magnetic resonance spectra (NMR) with a Hitachi Perkin-Elmer Model R-20 instrument; mass spectra with an Atlas Model MS-9 instrument.

Preparation of 2 and 4. To a solution of 8.7 g (0.051 mol) of cyclooctatriene sulfone[2] (**1**) in 25 ml of chloroform was added dropwise a solution of 8.5 g of bromine in 20 ml of carbon tetrachloride. Heat was evolved and toward the end of the reaction crystalline material separated. After several hours additional carbon tetrachloride was added, the mixture was chilled to 0°, and 13.7 g of precipitate was collected. Recrystallization from tetrahydrofuran-hexane gave 11.0 g (65%) of 2,3-dibromo-9-thiabicyclo[4.2.1]non-7-ene 9,9-dioxide: mp 196-197° dec; NMR ($CDCl_3$) δ 1.5-3.5 (m, 4, CH_2), 3.5-5 (m, 4, CH), and 6.5 ppm (m, 2, sulfolene olefin CH).

Anal. Calcd for $C_8H_{10}Br_2O_2S$: C, 29.11; H, 3.05. Found: C, 29.24; H, 3.07.

To a mechanically stirred slurry of 78 g (0.4 mol) of freshly prepared potassium azodiformate in 200 ml of tetrahydrofuran and 50 ml of methanol containing 6.0 g (0.018 mol) of the dibromide was added dropwise 40 g of acetic acid in 80 ml of methanol at 25° over 6 hr. The resulting white slurry was vacuum filtered and the collected precipitate was washed twice with tetrahydrofuran. The combined filtrates (containing some suspended solids) were evaporated under reduced pressure to a paste. The residue was treated with 400 ml of cold water whereupon the salts dissolved and the organic products precipitated and were collected. Analysis (NMR) indicated only partial reduction; the mixed sulfones were inseparable (by crystallization or chromatography) and were therefore both debrominated together. The precipitate from the preceding step was slurried with 60 ml of acetic acid and 2 g of zinc powder was added with swirling. Heat evolution was immediate and the solid passed into solution. After the mixture had cooled, excess zinc was removed by suction filtration and was washed with acetone. The combined filtrates were evaporated to small volume under reduced pressure and the residual oil was dissolved in chloroform and extracted in turn with dilute hydrochloric acid and 10% sodium carbonate solutions. The dried organic extracts were evaporated to dryness under reduced pressure. The resulting solid mixture of sulfones (**1** and **2**) was heated to 150° and held at that temperature for 20 min while decomposition of **1** proceeded (SO_2 evolution). The solid material obtained upon cooling was recrystallized from benzene-hexane to give 1.69 g (55%) of 9-thiabicyclo[4.2.1]non-2-ene 9,9-dioxide (**2**): mp 148.5-152.5° (range unaltered by intensive purification); ir (KBr) 1284 and 1110 cm^{-1}; NMR ($CDCl_3$) δ 1.5-3.0 (m, 8, CH_2), 3.0-3.7 (m, 2, CH), and 5.6-6.3 ppm (m, 2, olefin CH).

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.80; H, 7.03. Found: C, 55.74; H, 7.01.

Bromination of **2** (excess Br_2 in CCl_4) regenerated a dibromide, probably identical with the intermediate, mp 217-218°. For **4**, exchange of bridgehead protons for deuterium was carried out by heating for several hours at 100° a mixture of **2**, dioxane, D_2O, and *t*-BuOK in a sealed tube. Recovered **4** was >87% $C_8H_{10}D_2O_2S$ and <3% $C_8H_9D_3O_2S$ by mass spectral analysis.

Preparation of 3. To a solution of 1.0 g (0.0058 mol) of **2** in 30 ml of carbon tetrachloride was added 2.5 g of *N*-bromosuccinimide. The mixture was simultaneously heated to reflux and irradiated from below with a sun lamp for 1 hr at which time a starch-iodide test was negative and succinimide had collected on the surface of the solution. The filtered solution was concentrated and submitted to column chromatography on 60 g of silicic acid with carbon tetrachloride-chloroform gradient elution. Promptly eluted (compared to by-products) were fractions containing, after recrystallization from benzene-hexane, 0.74 g (39%) of 2,5-dibromo-9-thiabicyclo[4.2.1]non-3-ene 9,9-dioxide: mp 143-143.5°; NMR ($CDCl_3$) δ 2.4-2.55 (m, 4, CH_2), 3.5-3.8 (m, 2, CH), 5.1 (d, 2, J = 4 Hz, CHBr), and 5.7 ppm (s, 2, olefin CH).

Anal. Calcd for $C_8H_{10}Br_2O_2S$: C, 29.11; H, 3.05. Found: C, 28.91; H, 3.15.

With lesser amounts of *N*-bromosuccinimide there could be obtained upon column chromatography mixed monobromides, mp 120-125° (more slowly eluted than the dibromide). These were not further investigated.

Table II. Kinetic Data for Table I

Substance ($\Delta \log k/\Delta T^{-1}$)	Temp, °C	Rate, min^{-1}
10	81.8	0.02164
(5552)	86.1	0.03515
	92.0	0.0633
	96.1	0.0926
	98.1	0.1132
	102.5	0.1541
11	125.1	0.01206
(6506)	130.6	0.02045
	137.1	0.03664
	145.7	0.0823
	149.2	0.1062
	155.7	0.1715
12	77.8	0.00196
(6395)	85.9	0.00516
	96.0	0.0154
	100.8	0.0255
	105.9	0.0450
13	120.7	0.01477
(6696)	124.9	0.0230
	130.4	0.0387
	137.1	0.0714
1	99.8	0.00876
(6561)	101.4	0.0106
	105.8	0.0149
	107.3	0.0196
	109.9	0.0269
	114.6	0.0406
	120.4	0.072
3	236.9	0.0133
(7193)	256.0	0.0383
	276.5	0.138

A mixture of 685 mg (2.1 mmol) of the latter dibromide and 0.3 g of zinc in 10 ml of acetic acid was swirled until liberation of heat was no longer noticed. Excess zinc was removed by suction filtration and the filtrate was concentrated under reduced pressure. The residue was taken up in chloroform and extracted in turn with dilute hydrochloric acid and 10% sodium carbonate solutions. After drying and evaporation of solvent, the residue was submitted to column chromatography on 15 g of silicic acid with chloroform eluent. Chromatographic fractions which yielded solid upon removal of solvent were combined and recrystallized from benzene-hexane. Final purification required sublimation at 100° (0.1 mm) to give 200 mg (57%) of 9-thiabicyclo[4.2.1]nona-2,4-diene (**3**): mp 101.5-102°; ir (KBr) 1294 and 1110 cm^{-1}; uv$_{max}$ (95% C_2H_5OH) 268.5 nm (ϵ 3600); NMR ($CDCl_3$) δ 2.5-2.8 (m, 4, CH_2), 3.2-3.9 (m, 2, CH), and 5.4-6.5 ppm (m, 4, olefin CH).

Anal. Calcd for $C_8H_{10}O_2S$: C, 56.46; H, 5.92. Found: C, 56.24; H, 5.75.

Rates of Decomposition. The kinetic method (modification of that of ref 6) for following the fragmentation of sulfones **1**, **3**, and **10-13** was described briefly in the Results section. The individual runs from which the values presented in Table I were computed are given in Table II. The substances which were submitted to thermolysis have all been described in this series of articles or elsewhere (see Table I). In general, ca. 1 mmol of the appropriate substance plus a few milligrams of *tert*-butylcatechol polymerization inhibitor was heated in the neat molten state to the desired decomposition temperature in the presence of a few carborundum chips to aid ebulition. In those cases in which the melting point of the substance exceeded the required temperature of pyrolysis, a few drops of sulfolane were added to secure liquefication. The reaction vessel (volume, ca. 1 ml) was heated by bathing in the refluxing vapors of pure solvents of appropriate boiling points. A constant temperature of ±0.2° (usually ±0.1°) could easily be maintained (exception: **3**, see text). Decomposition gases (SO_2) released from the molten sulfones emerged from a small orifice in the top of the pyrolysis vessel and were immediately entrained in an inert gas (argon) sweep and conducted via valve system (such that uninterrupted flushing could be maintained) through a glass frit into a standard quantity of 0.1 *N* sodium hydroxide solution containing

Table III

Temp, °C	K_n	Temp, °C	K_n
92.8	9.17	120.9	1.046
100.0	4.76	126.2	0.830
110.3	2.55	131.0	0.656
114.8	1.59		

sufficient hydrogen peroxide to oxidize all of the sulfite to sulfate plus a few drops of ethanol to facilitate gas dispersion. The standard base solution was replaced at measured time intervals. Sulfur dioxide production was determined by back-titration of these solutions with 0.1 *N* hydrochloric acid to the Methyl Orange indicator end point. Generally, five to seven "points" were taken for each run and an infinity titer was obtained by decomposing residual sulfone at elevated temperature after several half-lives. Good linear first-order plots were routinely obtained and rate constants were obtained graphically.

Comparison of Pyrolysis Products of 1 and 3. Similar results were obtained whether **1** was injected directly into the heated (200°) injection port of a GLC instrument or whether it was heated as a neat liquid with the decomposition products (swept away by argon) being subsequently collected in a cold (−80°) trap and analyzed by GLC. Since **3** was too stable for the former (injection port themolysis) technique, the latter method was used for product comparison. The decomposition of **3** was carried out near its boiling point (>300°) by rapid heating with a hot air blower in order to secure fast removal of the products from the melt. GLC analysis was by a tris(2-cyanoethoxy)propane column maintained at 85°. In both cases there was one major peak of relatively long retention time which was identified as 1,3,5-cyclooctatriene. There was also observed a lesser peak (relative intensity ca. 0.3) with a retention time 0.50 that of cyclooctatriene. This must be the valence tautomer bicyclo[4.2.0]octa-2,4-diene. There was "filling in" between these peaks (raised baseline) which was taken to indicate on-column equilibration between them, as is known to be the case in the temperature range examined. The quantity of the minor valence tautomer and the extent of equilibration could be diminished in the case of **1** by the direct injection technique with careful manipulation of injection port and column temperatures. In the case of **3** there were also several small additional peaks in the GLC trace (relative retention times 0.38, 0.42, and 0.63) which in total intensity were less than 0.05 of the major products. These were not identified nor were numerous other very small peaks which were visible at very low attenuation. Congruence of the major products of both **1** and **3** was established by coinjection.

Determination of Heat of Formation for 10. A mixture of 6.94 mmol of sulfur dioxide and 2.586 mmol of **10** was sealed in an NMR tube and suspended sequentially in the vapors of refluxing pure solvents at the temperatures listed in Table III. After allowing for equilibration to be obtained, the tube was immediately chilled in an ice water bath and the NMR integral intensity ratio for the methyl groups in **10** vs. *trans,trans*-hexadiene was measured. A mole fraction equilibrium constant, K_n, was then computed at each temperature, following Drake, Stowe, and Partansky:[10] $K_n = (\Sigma n)(n_{10})/(n_{C_6H_{10}})(n_{SO_2})$, where n = number of millimoles of the various species indicated. At least-squares fit ($r > 0.98$) of ln K_n vs. T^{-1} gave a value of 20.0 kcal/mol for the enthalpy of formation of **10** from hexadiene and sulfur dioxide.

A similar analysis for **11** and **1** was not undertaken, since the NMR spectra were less suitable for quantitative work. However, the following values for the equilibrium constant were estimated at 100°: for **11**, K_n = 24; for **1**, K_n = 0.57.

Isomerization of 4. Label scrambling was accomplished by sealing dilute solutions of **4** in diphenyl ether solution in NMR tubes which were then suspended in refluxing solvents at the desired temperatures. Unfortunately, the reaction was not clean (side reactions produced tars). Furthermore, the spectral properties of the substance do not facilitate accurate rate determination (by NMR). The bridgehead resonances in **2** are inherently broad, due to coupling to adjacent protons. Obscuring resonances accumulate in the course of the isomerization (side reactions). Most importantly, the reaction is reversible and proceeds toward an equilibrium in which there is only 50% incorporation of proton at one of the bridgeheads. Consequently, the critical detection of percentage conversion must be made in the early part of the reaction; measurement of small quantities by the NMR integral method is difficult. Hence, derivation of activation parameters for **4** is out of the question. Isomerization only commenced to be detectable after 60 hr at 283°. Qualitative observations suggested a half-life of ca. 200 min at 310–315°, whence an estimated rate constant of 0.003 min^{-1} is given for that temperature. Isomerized material was recovered and purified to confirm its chemical identity with **2**. (The new resonances which had appeared were indeed due thereto.)

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(7) In our preliminary communication (ref 5) we gave values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for 1 and 3 which differ from those in Table I. The former numbers were based upon a subjective weighting of kinetic runs, which we no longer wish to sustain. The present analysis utilizes a least-squares fitting of the data.

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(9) Similar difficulties may have been encountered in the previous study by this technique (ref 6). It should be noted that data for some of the substances (7, **8**, **9**) were collected only over a 10° range and that the derived parameters (e.g., for 7) may be suspect ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$). See also O. Grummitt and H. Leaver, *J. Am. Chem. Soc.*, 74, 1595 (1952).

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(11) A gravimetric technique was employed for the latter measurement (ref 10); the results perhaps should be questioned since corresponding rate studies by the same method gave results which diverge seriously from titrimetric values (ref 6), and since a companion determination of the enthalpy of formation of piperylene sulfone (7) yielded $-\Delta H^{\circ}$ = 14.9 kcal/mol. It is our intuitive expectation that the value for 7 should fall between that for **5** and **10**. The authors (ref 10) acknowledge severe experimental difficulties, which appear to be less critical for **5**, however.

(12) It is obvious that a fairly large uncertainty must be attached to this number (and the ΔH° values), since what is observed is actually a $\Delta\Delta G^{\circ}$ value in which differences in diene stabilities, solvation, etc., have been incorporated. (A ring strain energy of 8.9 kcal/mol has been identified in cyclooctatriene; S. W. Benson, F. G. Cruikshank, D. M. Golden, C. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).) The mixtures used in these determinations (see Experimental Section) are far from representing a standard state; in fact they are a heterophase system comprised of variable amounts of sulfone, diene, and sulfur dioxide (gas and liquid) at differing pressures.

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(28) It is well to bear in mind the premises underlying this conclusion: that **1**, **3**, and **4** have "equivalent" ground state energies (i.e., none is uniquely activated toward reaction by ring strain nor deactivated by conjugative stabilization, etc.), that the reactivity differences observed are not due to some unrecognized factor such as intramolecular nonbonded interactions (which for example we believe leads to the relatively refractory nature of the adduct between 1,3-cyclooctadiene and sulfur dioxide, ref 2). Consideration has been given to these points, and while it is felt that none is of a magnitude to vitiate our conclusions, an uncertainty amounting to several kilocalories per mole should be attached to activation energy comparisons between these sulfones.

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Augmented Silicon–Carbon Bond Strengths via d–σ Hyperconjugation[1]

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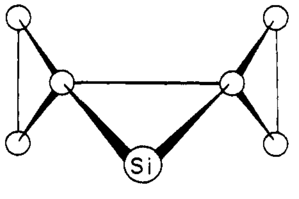
Abstract: The potentially interesting silacyclopropanes continue to be elusive, as only three stable members of this class of compounds have been reported to date; interestingly, all three are derivatives of 7-siladispiro[2.0.2.1]heptane. Molecular orbital calculations have been carried out on various derivatives of silacyclopropane and 7-siladispiro[2.0.2.1]heptane, together with their carbon analogs. The results suggest that d–σ hyperconjugation may contribute substantially to the strengthening of the silicon–carbon ring bonds in the siladispiroheptane. A similar hyperconjugative interaction should also operate to augment the total silicon–carbon bond strength in the yet unknown cyclopropylidenesilanes.

Ando et al., have recently claimed the formation of 1,1-dimethyl-2-phenylsilacyclopropane, which rearranges to form a benzosilacyclopentene[2] (thus adding one more chapter to the continuing account of unsuccessful attempts to synthesize stable silacyclopropanes).[3] To date, three derivatives of 7-siladispiro[2.0.2.1]heptane (**1**) are the only stable, isolable silacyclopropanes to have been reported.[4] This suggests that there may be some special stability associated with these spirocyclopropyl compounds.[5,6] In particular, we will consider here the possibility of augmented silicon–carbon bond strengths via d–σ hyperconjugation.



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The interaction of carbon pπ units with acceptor orbitals on silicon has been adduced to explain numerous observations in organosilicon chemistry.[7] The identity of the acceptor orbitals is not altogether well defined; they are most generally considered to be the Si 3d orbitals, but they may be the hyperconjugating σ^* orbitals of the Si–R bonds. Part of the difficulty in distinguishing between the extremes of hyperconjugation and d-orbital participation is that both orbital sets present π-conjugating orbitals of the same local symmetry. The work presented here assumes a set of low-lying silicon 3d orbitals[8] and traces its consequences.

The cyclopropane unit has proved itself as an excellent, conformationally specific donating group relative to vicinal electron-deficient centers.[9] The theoretical basis of this conjugative behavior is well understood.[10] The highest occupied molecular orbitals of cyclopropane are a degenerate set, the Walsh orbitals. Composed almost entirely of peripheral C 2p orbitals, this set endows cyclopropane with good conjugative properties.

Preparatory to a consideration of the siladispiroheptanes, we wish to compare the cyclopropane σ (Walsh) orbitals with the ethylene π orbital in terms of their respective potentials for conjugative interaction with the vacant 3d orbitals of silicon. Any interaction will be governed by symme-