References and Notes

(1) Part XXX of the series dealing with Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. Part XXIX is L. A. Paquette, R. A. Boggs, W. B. Farnham, and R. S. Beckley, *J. Amer. Chem. Soc.*, **97**, 1112 (1975).
(2) National Institutes of Health Postdoctoral Fellow, 1972.
(3) (a) L. A. Paquette, R. S. Beckley, and W. B. Farnham, *J. Amer. Chem. Soc.*, **97**, 1089 (1975); (b) L. A. Paquette and R. S. Beckley, *J. Amer. Chem. Soc.*, **97**, 1084 (1975); (c) L. A. Paquette, R. S. Beckley, D. Truesdell, and Clardy, *Tetrahedron Lett.*, *4913 (1972)*.
(4) W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **93**, 7345 (1971).
(5) L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Amer. Chem. Soc.*, **97**, 1101 (1975).
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(7) (a) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); (b) *ibid.*, **92**, 6366 (1970).
(8) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. II, Academic Press, New York, N.Y., 1971, Chapter III.
(9) For a thorough discussion of this concept, consult ref 3a.
(10) G. F. Koser, *Chem. Commun.*, 388 (1971).
(11) Dauben and Kielbania[3] have advanced the suggestion that rearrangement proceeds *via* bidentate interaction of the strained hydrocarbon system with the transition metal complex. We view Ag(I) catalysis to be the result of edge argentation without subsequent oxidative addition.[3a]
(12) A similar interpretation of the Rh(I)-promoted isomerization of 1,4-biscarbomethoxycubane has been advanced without proof by H. Hogeveen and B. J. Nusse, *Tetrahedron Lett.*, 3667 (1973).

9-Thia[4.2.1]nonabicyclic System. Synthesis and Selected Transformations

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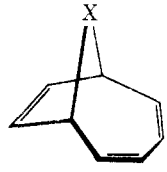
Abstract: The preparation of C_8H_8S, $C_8H_{10}S$, and $C_8H_{12}S$ 9-thia[4.2.1]bicycles and the stereoisomeric pairs of the corresponding sulfoxides is described. The synthetic design necessitated the development and subsequent use of three highly selective reactions: (i) oxidation of the 9-thia[4.2.1]bicycle with *m*-chloroperbenzoic acid to yield a single isomeric sulfoxide which, regardless of degree of saturation, incorporates the SO group invariably syn to the C_2 bridge; (ii) exclusive catalytic hydrogenation of the π appendage located anti to the SO dipole with marked affinity for ethylene over butadiene; and (iii) high-yield regiospecific diimide reduction of the π segment positioned syn to the SO function. Under conditions of thermal activation, C_8H_8SO sulfoxides **2** and **4** and their dihydro counterparts **5** and **7** interconvert, while the tetrahydro analogs **8** and **11** fail to do so. Mechanistically, all the evidence accumulated thus far from a measurement of activation constants suggests that directional transposition of the SO dipole results from scission of the C–SO bond bridging the molecule. Moreover, examination of specifically tagged **4**, namely **18**, in this connection established that the **4** $\rightleftharpoons$ **2** process is attended by bridge migration. Attention is also drawn to the absence of by-products in the **2** $\rightleftharpoons$ **4** and **5** $\rightleftharpoons$ **7** interconversions which is clearly indicative of strong interaction between the reactive sites, sulfinyl radical (S=O) and monoallylic or diallylic carbon center, of the species intermediating the isomerizations.

Because of their inherent rigidity and well-defined shape, 9-heterobicyclo[4.2.1]trienes (**1**; X = heteroatom) are ideally structured as models for the purpose of assessing (i) the practical merits of nonbonded π interaction and, ultimately, of such intriguing concepts as bicycloconjugation and bicycloaromaticity and (ii) the scope and limitations of the influence exerted by orbital symmetry on the course of pericyclic (sigmatropic, cheletropic, electrocyclic, etc.)[1] transformations. Thus far, our recorded work in the area has dealt chiefly with photoinduced bond relocations[2,3] and dimerization,[4] thermal cheletropy,[5] reagent chemistry,[6] and photoelectron spectroscopy[7] of the nitrogen member of the family.[8] Recently, we also briefly touched upon the sulfur analog (**1**; X = S, SO), describing its preparation[9] and photoinduced response.[10] In an effort to probe the π electronics of this intriguing thiabicycle by photoelectron spectroscopy[11] and also to further assess its pericyclic response, we recently prepared a variety of key derivatives and are now offering a full account of the synthetic aspect of this work. In part, the present report also deals with mechanism, its chief emphasis along these lines residing on the inversion of the rigidly held sulfoxide bridge.



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Synthesis and Characterization

Synthetic entry into the general 9-thiabicyclo[4.2.1]nona-2,4,7-triene skeleton was gained by the addition of SO, thermally generated from ethylene sulfoxide, to cyclooctatetraene at 110°.[12] The white crystalline sulfoxide thus prepared (nmr, Figure 1a) was shown to constitute a single stereoisomer, **2**, by conversion to its invertomer **4**. This was accomplished efficiently (*ca.* 40% overall yield) in two steps, (i) careful $LiAlH_4$ reduction of **2** to the corresponding sulfide **3** (nmr, Figure 1b) and (ii) oxidation of **3** with *m*-chloroperbenzoic acid (MCPBA) at *ca.* −40° to produce sulfoxide **4** contaminated with only *ca.* 5% (nmr) of stereoisomer **2**. Compound **4** was effectively separated from its stereoisomeric contaminant by means of column chromatography at *ca.* −15° (nmr, Figure 1c). Chemically, the [4.2.1] frame of **4** was established by its conversion to sulfide **3** on treatment with $LiAlH_4$, while the stereoisomeric relationship between the two sulfoxides was confirmed by the conversion of **2** to **4** on exposure to trimethyloxonium fluoroborate. The specific stereochemical assignments shown in **2** and **4** were made on the basis of nmr spectral information. Specifically, brief comparison of the nmr spectra depicted in Figures 1a and 1c reveals that the "ethylene" protons are displaced to higher field and the "butadiene" hydrogens to lower field on going from **4** to **2**. Bearing in mind the well-documented deshielding effect experienced by protons positioned syn to the SO group,[13-15] it is readily seen that the observed chemical shifts are best accommodated by the stereochemical assignments shown in **2** and **4**.

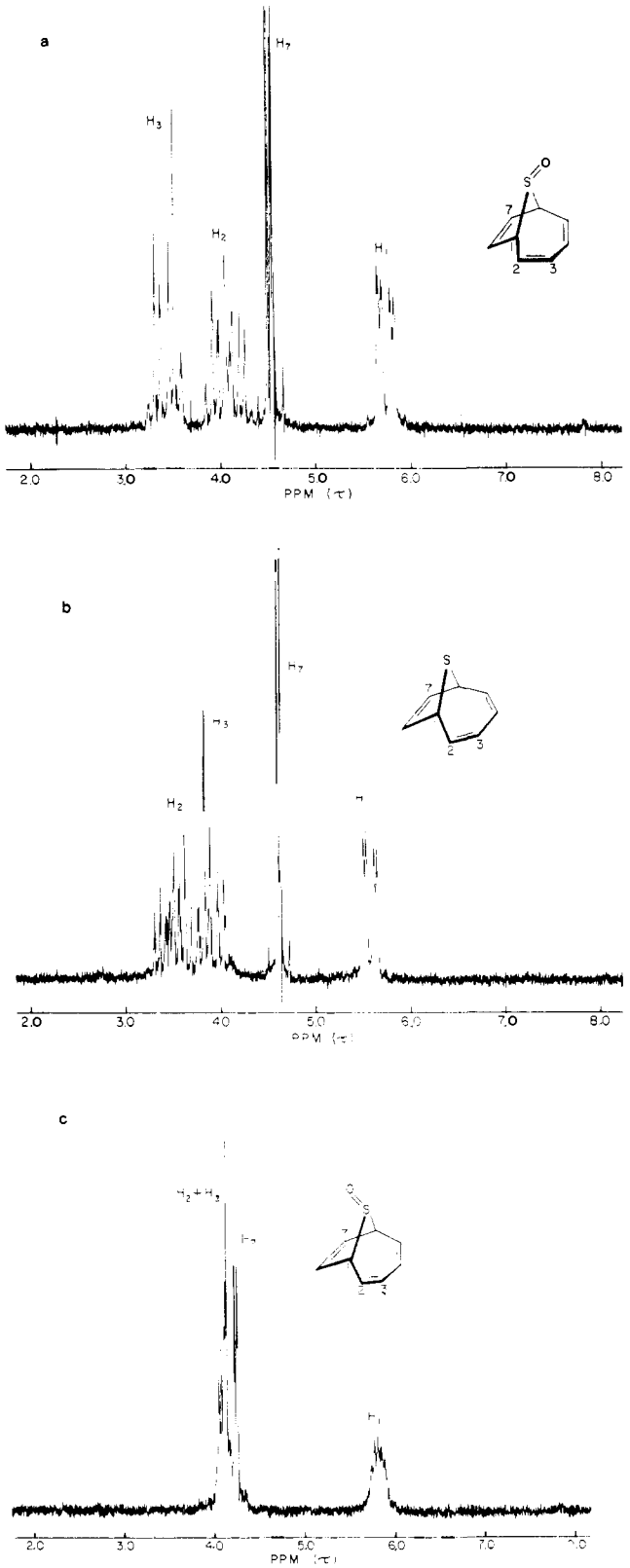


Figure 1. Proton nmr spectra (60 MHz; $CDCl_3$) of (a) 9-thiabicyclo-[4.2.1]nona-2,4,7-triene *syn*-9-oxide; (b)9-thiabicyclo[4.2.1]nona-2,4,7-triene; (c) 9-thiabicyclo[4.2.1]nona-2,4,7-triene *anti*-9-oxide.

In addition, these assignments receive strong support from the results of LIS (lanthanide induced shift) nmr studies depicted graphically in Figures 2 and 3. It is seen that the anticipated linear correlation between chemical shift and molar proportion of added "shift" reagent does obtain for each pair of equivalent protons and, most important, that

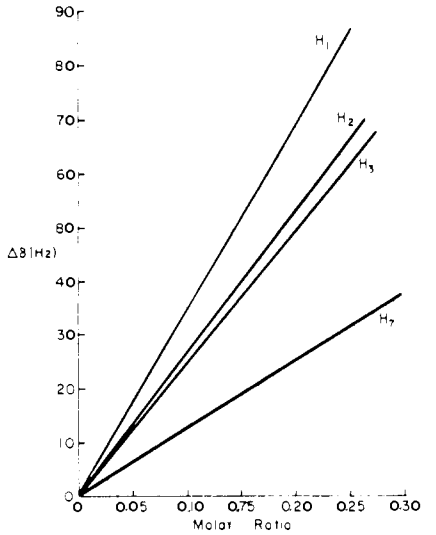


Figure 2. Plot of *downfield* chemical shift *vs.* molar ratio of $Eu(fod)_3$-d_{27} to 9-thiabicyclo[4.2.1]nona-2,4,7-triene *syn*-9-oxide (**2**).

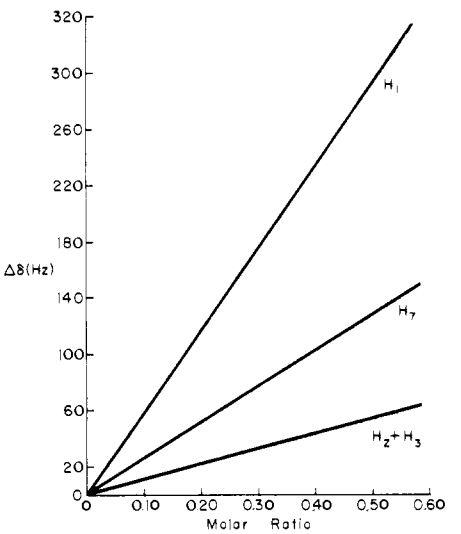


Figure 3. Plot of *downfield* chemical shift *vs.* molar ratio of $Eu(fod)_3$-d_{27} to 9-thiabicyclo[4.2.1]nona-2,4,7-triene *anti*-9-oxide (**4**).

among "olefinic" hydrogens, it is the pair bound to the ethylene bridge of **4** and the two pairs associated with the butadiene appendage of **2** which are most perturbed by the reagent believed to be associated with the negative end of the $(\delta^+)S\text{–}O(\delta^-)$ dipole. The stereochemical assignments shown in **2** and **4** are thus deemed secure.

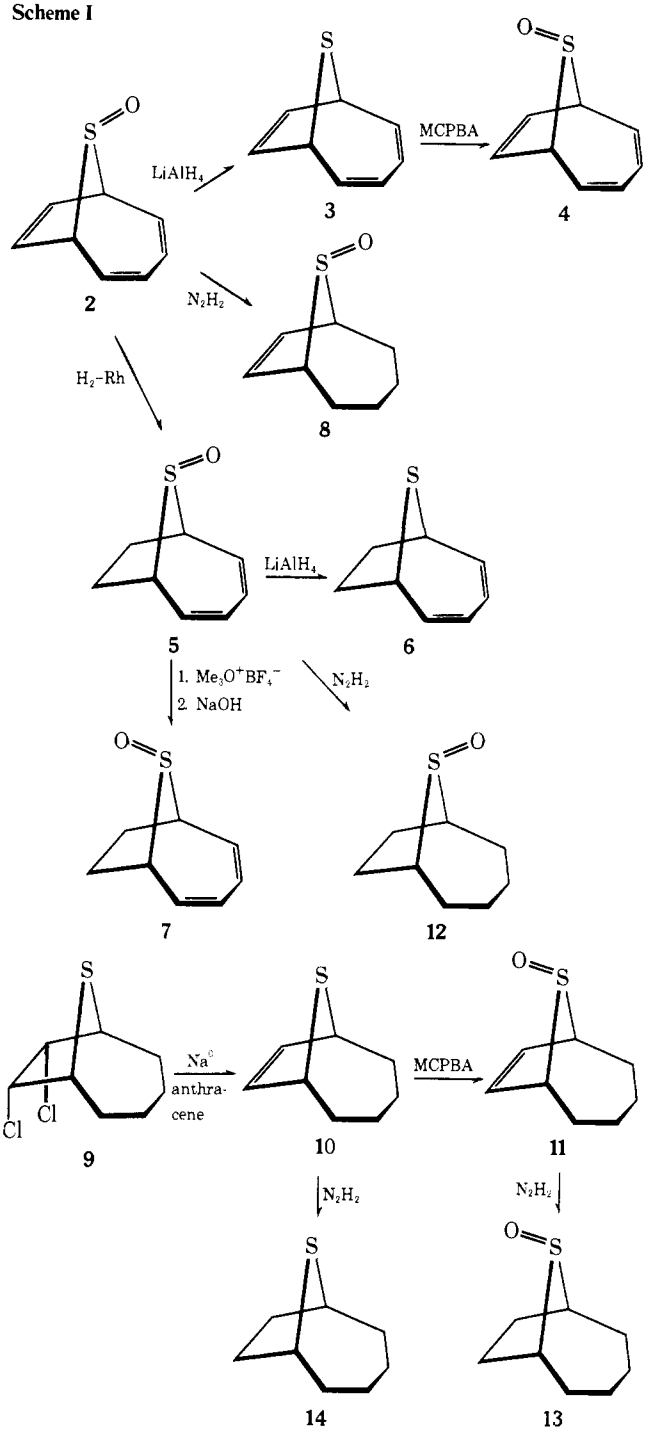
Effort in this project was next directed at selectively saturating each of the three available thiabicyclotrienes (**2, 3, 4**). Attention along these lines was first concentrated on the selective reduction of the ethylene bridge under such conditions of controlled catalytic hydrogenation as were previously shown to be successful in work dealing with a nitrogen member of the family (**1**; X = NCN).[8] Indeed, prolonged exposure of **2** to hydrogen (60 psi) in the presence of 5% Rh/C yielded the desired diene **5** in *ca.* 62% yield. Perhaps the single most significant spectral characteristic of **5** is the olefinic portion of its nmr spectrum which consists of the same well-resolved butadiene pattern as does the spectrum of **2**, but unlike the latter it lacks the sharp 2-H resonance of the olefinic bridge. Sulfoxide **5** was then converted to sulfide **6** on careful treatment with $LiAlH_4$ and into its stereoisomer **7** on successive exposure to trimethyloxonium fluoroborate and sodium hydroxide. Sulfoxide **7** was also

prepared in *ca.* 40% yield on diimide reduction of its dehydro counterpart **4** but failed to materialize to any significant extent on exposure of this triene (**4**) to conditions of catalytic hydrogenation (60 psi; Rh/C) which proved successful in the conversion of **2** to **5.** Spectrally, the stereochemical disposition of the SO bridge in **7** is clearly indicated by the poor resolution of the butadiene portion of its nmr spectrum which strongly resembles that of its dehydro progenitor **4** but sharply contrasts the highly resolved appearance of this group of resonances in the spectra of **2** and **5.**

Selective saturation of the butadiene portion of **2** was conveniently accomplished in *ca.* 50% yield on diimide reduction. The tetrahydro derivative **8** obtained in this fashion was shown to be spectrally identical with a sample obtained in other work from the thermal cycloaddition of SO to 1,3-cyclooctadiene.[16] By contrast, all attempts designed to afford the stereoisomer of **8,** *i.e.*, **11,** by the selective saturation of triene **4** proved unsatisfactory.[17] Instead, **11** was prepared by an alternate, highly stereoselective (<5% **8** by nmr) sequence which afforded sulfide **10** as well. This entailed dechlorination of dichloro sulfide **9**[18] into the novel unsaturated derivative **10** on treatment with sodium anthracene in THF, followed by oxidation of **10** with MCPBA at *ca.* −40°. Significantly, the stereochemical assignments shown in **8** and **11** are fully consistent with the results of LIS nmr studies revealing the expected trend whereby the "shift" reagent affects primarily the butane bridge of **8** and the ethylene bridge of **11.**

Finally, the perhydro derivatives **12, 13,** and **14** were conveniently prepared on diimide reduction of the respective dehydro analogs **5, 11,** and **10.**

Scheme I



Mechanistic Implications

The rigid frame of the π heterobicycles examined in the present account serves as an effective probe for the assessment of stereoelectronic preferences attending the functionalization of double bonds. The three recurring key reactions employed in the present study (Scheme I) are (i) peracid oxidation, (ii) diimide reduction, and (iii) catalytic hydrogenation, and in this section we shall briefly comment on their mechanistic implications.

Low-temperature oxidation of the sulfide bridge with MCPBA was invariably employed in the present work as a means of introducing the sulfoxide function syn to the ethylene bridge, *e.g.*, conversions **3** to **4** (*ca.* 95% stereoselective) and **10** to **11** (essentially stereospecific). In order to further probe into the selectivity of the peracid oxidation in this system, we also examined its course in the case of sulfides **6** and **14,** *i.e.*, two members incorporating a saturated two-carbon bridge. Again, the reaction proved to be highly stereoselective in the same direction, with **6** yielding a mixture of sulfoxides consisting (nmr) of *ca.* 92% **7** and 8% **5,** and **14** affording *ca.* 95% **13** and 5% **12** (nmr). Mechanistically, the peracid oxidation of sulfides to sulfoxides is known to operate chiefly under kinetic control (otherwise known as steric-approach control)[19-21] insofar as the product formed in each case need not be the more stable of possible stereoisomers. The situation in the present case is no exception inasmuch as the sulfoxides formed are not, for the most part, the thermally most stable isomers (*vide infra*). In light of this information, the pronounced stereoselectivity of peracid oxidation observed here is clearly indicative of strongly preferred approach by the oxidant from the side of the two-carbon bridge. Moreover, judging from the fact that the stereoselectivity observed in the oxidation of **3** and **10** persists on passing to **6** and **14** where the two-carbon segment is saturated and only the four-carbon bridge (in the case of **6**) incorporates elements of unsaturation, it is clear that the directive influence is not exerted from possible stabilizing complexation between peracid and π system but rather from the steric situation developed by the approach of the oxidant. Surprisingly then, the sulfur bridge of the [4.2.1]bicycle appears to be more accessible to the approaching peracid from the side of what might, at first glance, be construed to be the smaller cavity, *i.e.*, the five-membered segment as opposed to the seven-membered portion defined by the four-carbon bridge. In fact, this stereoselectivity emerges all the more remarkable in the case of **6** where saturation of the two-carbon bridge ought to clearly increase its effective size relative to that of the ethylenic counterpart in **3.** Some insight into the cause of the highly stereoselective peracid oxidation of **3, 6, 10,** and **13** is gained from brief examination of a "Dreiding" molecular model of **3** which reveals a distinct "tilt" of the sulfur bridge toward the butadiene segment, generating a C–C–S angle of *ca.* 140° on the side of the ethylene and *ca.* 110° on

the side of the butadiene, thus resulting in better steric access of the sulfur atom from the side of the C_2 bridge. Moreover, inspection of a "Dreiding" molecular model of **6** reveals that the steric interference introduced by the $-CH_2CH_2-$ bridge does not appear to be serious, the distance between the sulfur atom and each of the exo protons of the bridge amounting to *ca.* 3 Å. Our results bearing on the oxidative formation of [4.2.1] sulfoxides are thus entirely consistent with earlier mechanistic interpretations,[19-21] namely that conversion of a sulfide into a sulfoxide under the influence of MCPBA is kinetically controlled, occurring along the path of least steric congestion. The synthetic usefulness of the observed stereoselectivity is, of course, self evident.

High stereoselectivity also proved to be the key to the successful partial saturation of trienes **2** and **4**. In the first place, it is seen that diimide reduction of the π system invariably operates on the side syn to the SO function, the conversions **2** → **8**, **4** → **7**, **5** → **12**, and **11** → **13** occurring cleanly and in good yield. Obviously, the reducing agent here operates under the directive influence of the negative portion of the SO dipole, presumably through some type of active complex. Secondly, it is noted that while catalytic hydrogenation distinctly favors ethylene over butadiene, it is effectively inhibited by the presence of a syn SO group; compare, for example, the ready conversion of **2** to **5** with the resistance of **4** to respond under similar or even more vigorous conditions.[17] The SO dipole of the [4.2.1] system thus appears to offer stereoelectronic interference to the catalytic hydrogenation of a syn π ribbon.

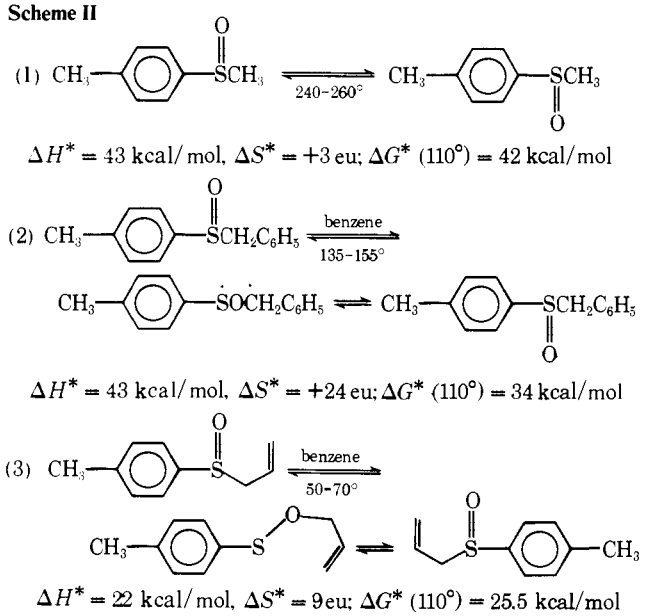
The two methods of selective saturation employed in the present study, *i.e.*, diimide reduction and catalytic hydrogenation, are thus seen to effectively complement one another by their differing steric demands.

Sulfoxide Inversion

Mechanistically, the well-defined geometry of the 9-thia-[4.2.1]bicyclic skeleton is well suited for the purpose of examining the various tortional constraints imposed on the inversion process of the SO function and also for assessing any possible preference this group might display for alignment with one or the other carbocyclic bridge.

The operational details of SO stereomutation have in recent years been subjected to extensive scrutiny,[22-24] and there exists now convincing evidence for the operation of all three mechanistic alternatives shown in Scheme II.[25] Of

Scheme II



$\Delta H^* = 43$ kcal/mol, $\Delta S^* = +3$ eu; ΔG^* (110°) = 42 kcal/mol

$\Delta H^* = 43$ kcal/mol, $\Delta S^* = +24$ eu; ΔG^* (110°) = 34 kcal/mol

$\Delta H^* = 22$ kcal/mol, $\Delta S^* = 9$ eu; ΔG^* (110°) = 25.5 kcal/mol

Table I. Activation Constants for the Thermolysis of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene, -2,4-diene, and -7-ene 9-Oxides

Reactant	T, °C	Solvent	Rate constant $\times 10^4$, sec^{-1}	ΔG^*, kcal/mol
4[a]	110.7	Benzene-d_6	1.28 ± 0.04	29.5
	121.4	Benzene-d_6	2.64 ± 0.18	29.7
	141.3	Benzene-d_6	20.5 ± 0.6	29.6
	139.8	Acetonitrile-d_3	8.21 ± 0.9	30.2
18	111.0	Benzene-d_6	1.06 ± 0.07	29.6
	140.5	Benzene-d_6	16.0 ± 1	29.7
7	141.4	Benzene-d_6	0.75 ± 0.04	32.3
5	141.4	Benzene-d_6	2.8 ± 0.08	31.2
	139.8	Acetonitrile-d_3	0.83 ± 0.08	32.0
8	179.0	Benzene-d_6	2.06 ± 0.15	34.5
11	194.0	Benzene-d_6	<0.03	>39.5

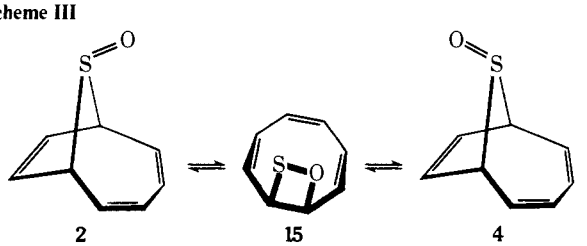
[a] $\Delta H^* = 27.8$ kcal/mol; $\Delta S^* = -4$ eu.

these, sequence 1 entails simple inversion about the SO tetrahedron and is seen to require a significantly higher activation energy than either 2 or 3. Process 2 relates to sulfoxides incorporating substituents capable of converting into stabilized radical fragments. It involves a rupture-recombination sequence of the C-S link and is associated with detectably lower activation energies than (1) chiefly as a result of a highly positive ΔS^* term. Finally, the third mechanistic alternative (3) involves the intermediacy of a sulfenate and is specifically reserved for sulfoxides carrying allylic substituents. It is by far the least energetically demanding of the three, primarily because of a drastically reduced ΔH^* term resulting from the cyclic nature of the transition state interconverting the sulfenate with the two epimeric sulfoxides.

Sulfoxide inversion within the 9-thiabicyclo[4.2.1] frame ought to manifest itself as geometrical isomerization resulting from directional transposition of the SO dipole. We find this thermal transformation to obtain readily among pairs **2,4** and **5,7** and to fail altogether with **8,11.** We shall now elaborate on the mechanistic implications of these findings.

When heated above 100°, in benzene, **4** readily and cleanly isomerizes to a mixture consisting (nmr) of *ca.* 90% **2** and 10% **4.** The loss of reactant was monitored by nmr spectroscopy in benzene-d_6 at three different temperatures, yielding the activation parameters collected in Table I. Obviously, the isomerization here requires the input of significantly less energy ($\Delta G^* = 29.5$ kcal/mol at 110.7°) than that normally quoted for process 1 under the same conditions, *i.e.*, 42 kcal/mol for the first stereomutation of Scheme II. And since direct inversion about sulfur is normally associated with a widening of the C-S-C angle, *i.e.*, a motion undoubtedly to be resisted by the rigidly held bridge of a 9-hetero[4.2.1]bicycle, we interpret the relatively mild activation required in **4** ⇌ **2** to be inconsistent with unassisted inversion as exemplified by process 1. Interconversion between **4** and **2** is also formally accountable through a process similar to that depicted in (3), *i.e.*, as in Scheme III.

Scheme III



2 **15** **4**

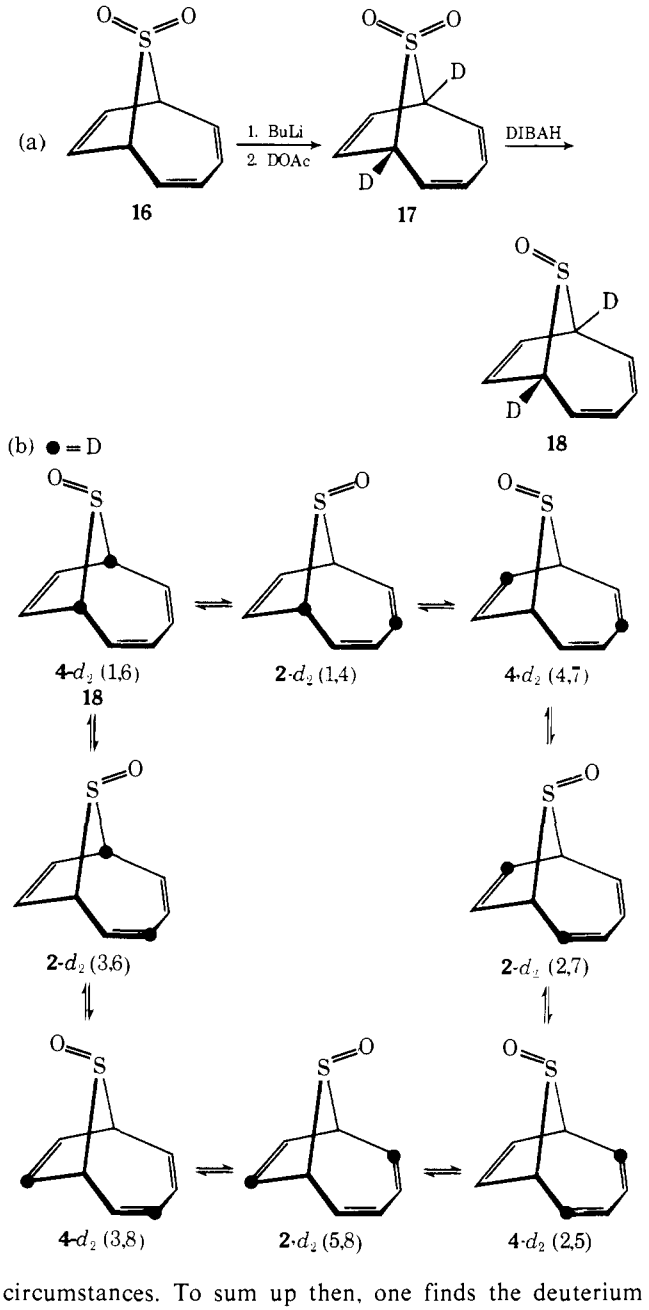
Here too, however, the structural characteristics of the sulfoxides **2** and **4** make the process unlikely insofar as their interconversion by this mechanism necessitates the genera-

tion of a rather strained [6.2.0] bicyclic sulfinate (**15**) as a common intermediate. Our provisional rejection of this mechanistic possibility receives added, albeit indirect, support from the related interconversion observed among the partially saturated analogs **5** and **7** (*vide infra*) which obviously are structurally incapable of stereoisomerization by the cyclic process 3, *i.e.*, one analogous to that of Scheme *III*.

The **4** ⇌ **2** isomerization is clearly energetically compatible with the C–S bond cleavage–recombination process shown in (2), known to be worth *ca.* 34 kcal/mol at 110°. Here too, however, closer examination reveals certain inconsistencies. In particular, the observed ΔS^* term is small and *negative* (−4 eu), whereas that controlling process 2 is, for obvious reasons, large and *positive*. In fact, the entropy change associated with the **4** to **2** interconversion is indicative of a somewhat ordered transition state, *i.e.*, one possibly involving concerted bond migration. Now, in the specific case of **2** and **4**, there also exists the formal possibility that interconversion is effected as a result of $[_\sigma 2_s + {}_\pi 2_s]^1$ bridge migration. Of course, such a process is disallowed by orbital symmetry and may be deemed unattractive on this basis. On the other hand, the symmetry-allowed alternative, $[_\sigma 2_a + {}_\pi 2_s]$, is expected to be ineffectual in this connection, the prediction here being that the migration will merely serve to convert each isomer (**2** or **4**) into itself. In order to test the possibility of bridge migration in the **2** ⇌ **4** process, it was of course necessary to assess the thermal fate of specifically tagged **4** such as **18**. In brief, it is easily seen from the full sequence of $[_\sigma 2_s + {}_\pi 2_s]$ bridge transpositions depicted in Scheme IVb that **18** should yield entirely scrambled **2**-d_2 and **4**-d_2 (0.75 H per carbon). By contrast, SO inversion occurring without the benefit of bridge migration is predicted to fully preserve the deuterium label at the bridgehead positions of **2**-d_2 and **4**-d_2.

The desired dideuterio derivative of **4**, *i.e.*, **18**, was prepared by the following sequence of steps (Scheme IVa): (i) the known[26] sulfone **16** was converted to its dideuterio counterpart, shown in **17** (>95% bridgehead deuterated), on successive exposure to *n*-butyllithium in THF and acetic acid-*O*-*d*,[27] and (ii) the tagged sulfone **17** was selectively reduced to **18** [white crystals, mp 90–91°; ν_{SO} (KBr) 1030 cm^{-1}; nmr (60 MHz, $CDCl_3$) singlets at τ 4.10 (4 H) and 4.23 (2 H); *m/e* 154 (P^+; 69%)] (>95% bridge-deuterated by nmr) on treatment with diisobutylaluminum hydride in dichloromethane.[28] Finally, thermal exposure of **18** in benzene at 140° generates the expected two-component mixture displaying nmr multiplets at τ 3.6–4.0 ($H_3 + H_4$ of **2**-d_2), 4.3–4.8 ($H_2 + H_5$ of **2**-d_2 and $H_2 + H_5$, $H_3 + H_4$, and $H_7 + H_8$ of **4**-d_2), 5.2–5.4 ($H_7 + H_8$ of **2**-d_2), and 6.2–6.7 ($H_1 + H_6$ of **2**-d_2 and **4**-d_2) in a time (34–154 min) invariant (within *ca.* 5%) area ratio of 1.00:1.53:1.01:1.15, respectively. The thermolysis mixture thus appears to consist of *ca.* 87% **2**-d_2 and 13% **4**-d_2 with *very nearly statistical distribution of the label.* Careful processing of the two-component mixture at *ca.* −15° on alumina afforded pure **2**-d_2 [white crystals, mp 120–121°; nmr (60 MHz; $CDCl_3$) τ 3.3–3.5 (m, $H_3 + H_4$), 3.9–4.3 (m, $H_2 + H_5$), 4.55 (m, $H_7 + H_8$), and 5.6–5.9 (m, $H_1 + H_6$) in an area ratio of 1.00:1.05:1.05:0.99; *m/e* 154 (P^+; 48%)]. Owing to its small proportion in the thermolysis mixture, the minor isomer, **4**-d_2, could not be obtained pure in sufficient quantity to allow for similar nmr scrutiny. Nonetheless, the known label distribution in pure **2**-d_2 allows one to partially estimate the deuterium distribution in **4**-d_2 as well. Briefly, one finds from the nmr data of the **2**-d_2 + **4**-d_2 thermolysate, given above, the proportion of H_1 to $H_2 + H_3 + H_7$ to be 15/53 = 0.29 as compared with 0.33 predicted from the sequence of Scheme IVb, a marginally good match under the

Scheme IV



circumstances. To sum up then, one finds the deuterium distribution in **2**-d_2 and **4**-d_2 to be consistently accommodated by the sequence of shifts depicted in Scheme IVb. In other words, the obvious conclusion is that *the thermal interconversion between* **2** *and* **4** *very likely materializes from suprafacial 1,3 migration of the SO bridge.*[29]

A further, albeit less conspicuous identifying feature of the sequence shown in Scheme IVb is that deuterium incorporation in the ethylene bridge of newly formed **2**-d_2 ought to be gradual rather than immediate insofar as the isomer bearing the label on the C_2 bridge, **2**-d_2 (2,7), is seen to be preceded by one, **2**-d_2 (1,4), incorporating a fully protiated ethylene function. In practice, the notion of gradual isotopic enrichment of positions 7 and 8 in **2**-d_2 receives credence from the fact that attempted evaluation of the rate of the **18** to **2**-d_2 conversion by monitoring the appearance of the ethylene bridge of **2**-d_2 by nmr, yields ever decreasing values ranging, at 140.5°, from 1.88×10^{-3} sec^{-1}, after 2-min reaction, to 0.66×10^{-3} sec^{-1}, after 34-min reaction. Obviously, the decrease in measured rate is only apparent, resulting from progressively increasing isotopic enrichment of the chosen frame of reference, *i.e.*, the ethylene bridge.

To conclude this segment of mechanistic interpretation, we make note that the rate of the **4** → **2** process shows only insignificant solvent dependence, *e.g.*, $k_{141.3°} = 2.05 \pm 0.06 \times 10^{-3}$ sec^{-1} in benzene and $k_{139.8°} = 0.82 \pm 0.09 \times 10^{-3}$ sec^{-1} in acetonitrile, thus suggesting that C–S bond cleavage is largely homolytic in nature.

Turning now to the stereoisomeric dienes **5** and **7**, we note that here too each component of the pair undergoes thermal equilibration to a clean mixture of the two isomers. Thermolysis of either **5** or **7** in benzene at 141.4° thus generates a 20:80 mixture (nmr) of the two components with $k_{5\rightarrow7} = 2.8 \pm 0.1 \times 10^{-4}$ sec^{-1}, and $k_{7\rightarrow5} = 0.75 \pm 0.04 \times 10^{-4}$ sec^{-1}. In light of the discussion of mechanistic alternatives presented earlier in this section, it is evident that the interconversion between **5** and **7** is best and perhaps uniquely accommodated by the mechanism depicted in (2); it obviously cannot materialize sigmatropically, nor can it proceed through the cyclic process of mechanism 3. Moreover, the relatively low activation energy associated with this process is clearly reflective of the allylic nature of the SO bridge, pointing to (2) rather than unassisted inversion as the preferred mode of equilibration.

The situation with the tetrahydro counterparts, **8** and **11**, is fundamentally different, in that both are stable to prolonged heating (28 hr) at 140°, *i.e.*, a temperature known to activate rapid stereoisomerization among pairs **2,4** and **5,7**. Moreover, while **8** does respond to more forcing thermal conditions (175°), it does not isomerize to **11** but undergoes more complex rearrangement and/or fragmentation instead.[30] In sharp contrast, the stereoisomer **11** was found to be thermally stable to prolonged heating (*ca.* 9 hr) at a temperature as high as 194°, thus suggesting that SO stereomutation in this system is associated with a ΔG^* term in excess of 39 kcal/mol.

To conclude, we might ask why are isomeric pairs **5,7** and **8,11** associated with significantly different activation energies for stereoisomerization in spite of the fact that the key C–SO link is in both cases singly allylic. The activation energy here is certainly not reflective of the type of C–S bond ruptured, as required by the unqualified adoption of mechanism 2, but appears to be controlled by rather significant secondary effects. We believe these effects to be stereoelectronic in nature and specifically associated with the preferential "tilt" of the sulfur bridge toward the C_4 moiety of the molecule, invoked earlier to rationalize the stereoselectivity of peracid oxidation in the corresponding sulfides. In brief, inspection of appropriate "Dreiding" models reveals the angle between the key C–S bond and the nodal plane of the π system to be *ca.* 100° for **5** and **7** and *ca.* 140° for **8** and **11**. Operationally, this obviously means that only in the **5,7** pair, where the hetero bridge is very nearly orthogonal to the π appendage, will the incipient carbon radical, generated from scission of the C–S link, fully benefit from allylic stabilization without major realignment. In other words, we offer the suggestion that the relatively high-energy input necessary to activate the stereoisomerization **8** ⇌ **11** results primarily from the steric inability of this pair to effectively utilize the stabilizing influence of its π system on the scission of the C–S bond.

Experimental Section[31]

Preparation of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene *syn*-9-Oxide (2). To a boiling solution of freshly distilled cyclooctatetraene (57.4 g, 0.59 mol) in toluene (348 ml) was added, under nitrogen with constant stirring and over a period of 1 hr, a solution of ethylene sulfoxide[14] (30 g, 0.395 mol) in toluene (29 ml), and the resulting mixture was maintained at the reflux temperature until it acquired a deep red color (*ca.* 5 hr). The clear, dark solution was then decanted free of tar and concentrated first at the water aspirator at *ca.* 45° and then at ambient temperature (*ca.* 0.5 mm) to yield a dark residue which crystallized on cooling to 0°. One recrystallization of this material from carbon tetrachloride followed by sublimation [60–80° (*ca.* 0.01 mm)] produced pure **2** (9.1 g, 15%) as white crystals: mp 122–123°; ir (KBr) prominent maxima at 1075 (SO), 860, 742, and 683 cm^{-1}; uv (CH_3CN) max 220 nm (ϵ 4100), 278 (2600); nmr ($CDCl_3$) τ 3.40 (2 H, dt, J = 12.5, 3.0 Hz), 3.8–4.3 (2 H, m), 4.50 (2 H, d, J = 2.7 Hz), 5.75 (2 H, dd, J = 2.7, 8.0 Hz); mass spectrum, parent ion at *m/e* 152, base peak at *m/e* 104.

Anal. Calcd for C_8H_8SO: C, 63.14; H, 5.26; S, 21.07; O, 10.52. Found: C, 62.99; H, 5.18; S, 21.12; O, 10.87.

Preparation of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene (3). To a suspension of lithium aluminum hydride (3 g, 0.079 mol) in *dry* ethyl ether (200 ml) was added, under nitrogen with constant stirring and over a period of 2.5 hr, a solution of sulfoxide **2** (4 g, 0.026 mol) in *dry* ethyl ether (800 ml) and the resulting mixture was warmed to a gentle reflux for 15 min. It was then cooled to 0°, treated dropwise with saturated aqueous ammonium chloride, and filtered, and the filtrate was washed with water (4 × 100 ml) and dried over calcium sulfate. Concentration at the water aspirator afforded a malodorous yellow oil (3.3 g) which was placed on a column (540 × 14 mm) wet-packed (petroleum ether) with activity III Woelm neutral alumina and maintained at *ca.* −15°. Elution with petroleum ether (500 ml) afforded **3** (2.7 g, 76%) as an air-sensitive colorless and odorless liquid: ir (neat) prominent bands at 2900, 1380, 1310, 942, 850, 798, and 726 cm^{-1}; uv (C_6H_{14}) max 260 nm (ϵ 4000); nmr (acetone-d_6) τ 3.3–3.7 (2 H, m), 3.96 (2 H, dt, J = 12.5, 3.5 Hz), 4.60 (2 H, d, J = 2.0 Hz), 5.56 (2 H, dd, J = 2.0, 7.0 Hz); mass spectrum, parent ion at *m/e* 136, base peak at *m/e* 31.

Preparation of Thiabicyclo[4.2.1]nona-2,4,7-triene *anti*-9-Oxide (4). To a stirring solution of sulfide **3** (2.72 g, 0.02 mol) in methylene chloride (350 ml) was added, under nitrogen at *ca.* −35° and over a period of 1 hr, a solution of *m*-chloroperbenzoic acid (85% pure, 4.06 g, 0.02 mol) in methylene chloride (75 ml). After the addition was completed, the mixture was allowed to warm to *ca.* −25° and saturated with a stream of ammonia and the resulting precipitate removed by filtration. Concentration of the filtrate at the water aspirator produced a semisolid (2 g) consisting (nmr, $CDCl_3$) of *ca.* 95% **4** and 5% **2**. This was dissolved in the minimum amount of methylene chloride; the solution was applied onto a column (760 × 13 mm) wet-packed (petroleum ether) with activity III Woelm neutral alumina and maintained at *ca.* −15°. Elution was carried out with ethyl ether–tetrahydrofuran (5:2 v/v) to yield **2** (0.05 g) in the first fraction (200 ml), a mixture of *ca.* 70% **4** and 30% **2** (0.05 g) by nmr in the subsequent fraction (120 ml), and pure **4** (1.9 g) in the final fraction (300 ml). One recrystallization of **4** from ethyl ether yielded an analytical sample (1.85 g, 60%) in the form of white crystals: mp 90.5–91.5°; ir (KBr) prominent maxima at 1030 (SO), 854, 803, 742, and 680 cm^{-1}; uv (CH_3CN) max 230 nm (ϵ 4070), 281 (2240); nmr ($CDCl_3$) τ 3.9–4.1 (4 H, m), 4.18 (2 H, dd, J = 1.6, 0.5 Hz), 5.6–5.9 (2 H, m); mass spectrum, parent ion at *m/e* 152, base peak at *m/e* 104.

Anal. Calcd for C_8H_8SO: C, 63.14; H, 5.26; S, 21.07. Found: C, 63.16; H, 5.33; S, 21.27.

Preparation of 9-Thiabicyclo[4.2.1]nona-2,4-diene *syn*-9-Oxide (5). To a prehydrogenated suspension of 5% rhodium on charcoal catalyst (500 mg) in absolute ethanol (10 ml) was added a solution of sulfoxide **2** (250 mg, 1.65 mmol) in absolute ethanol (10 ml), and the mixture was shaken in a "Paar" hydrogenator for 1 hr under 60 psi of hydrogen. The catalyst was then removed by filtration and the filtrate concentrated at the water aspirator to produce a white solid (250 mg) consisting (nmr, $CDCl_3$) of *ca.* 80% **5** and 20% **2**. Exposure of this mixture to the same hydrogenation sequence effected complete conversion to **5**. Recrystallization of this substance from carbon tetrachloride followed by sublimation at 83° (*ca.* 0.01 mm) produced a pure sample of **5** (158 mg, 62%) as white crystals: mp 131.5–132.5°; ir (KBr) prominent bands at 1060 (SO) and 715 cm^{-1}; uv (CH_3CN) max 273 nm (ϵ 3500); nmr ($CDCl_3$) τ 3.59 (2 H, dt, J = 12.5, 3.5 Hz), 3.9–4.3 (2 H, m), 5.8–6.1 (2 H, m), 7.8–8.0 (4 H, m); mass spectrum, parent ion at *m/e* 154, base peak at *m/e* 78.

Anal. Calcd for $C_8H_{10}SO$: C, 62.29; H, 6.55; S, 20.78. Found: C, 62.36; H, 6.47; S, 21.0.

Preparation of 9-Thiabicyclo[4.2.1]nona-2,4-diene (6). To a sus-

pension of lithium aluminum hydride (1.86 g, 0.049 mol) in dry ethyl ether (100 ml) was added, under nitrogen with constant stirring and over a period of 2.5 hr, a solution of sulfoxide **5** (2.5 g, 0.016 mol) in dry ethyl ether (500 ml), and the resulting mixture was warmed to a gentle reflux for 15 min. It was then cooled in ice, treated dropwise with saturated aqueous ammonium chloride, and filtered, and the filtrate was washed with water and dried over calcium sulfate. Concentration at the water aspirator afforded a malodorous yellow oil (2.06 g) which was applied on a column (760 × 13 mm) wet-packed (petroleum ether) with activity III Woelm neutral alumina and maintained at *ca.* −15°. Elution with petroleum ether (500 ml) afforded **6** (1.57 g, 71%) as a clear colorless liquid: ir (neat) prominent bands at 2870, 1300, 950, 855, and 710 cm^{-1}; uv (CH_3CN) max 261 nm (ϵ 6900); nmr ($CDCl_3$) τ 3.4–3.8 (2 H, m), 4.0–4.4 (2 H, dt, J = 12.5, 3.5 Hz), 5.8–6.2 (2 H, m), 7.7–7.9 (4 H, m); mass spectrum, parent ion at *m/e* 138, base peak at *m/e* 138.

Anal. Calcd for $C_8H_{10}S$: C, 69.51; H, 7.29; S, 23.19. Found: C, 69.32; H, 7.26; S, 23.16.

Preparation of 9-Thiabicyclo[4.2.1]nona-2,4-diene *anti*-9-Oxide (7). Trimethyloxonium fluoroborate (296 mg, 2 mmol) was added to a stirring solution of sulfoxide **5** (280 mg, 1.8 mmol) in methylene chloride (5 ml) under nitrogen at ambient temperature. The mixture was allowed to stir for 90 min, it was then cooled to 0°, ethyl ether (3 ml) was added, and the resulting white precipitate (423 mg) was isolated by filtration, dissolved in water (100 ml) and finally titrated with aqueous sodium hydroxide (33.5 ml, 0.05 *N*) to the phenolphthalein end point. The aqueous solution was then extracted with methylene chloride (4 × 50 ml), and the combined dried (calcium sulfate) extracts were concentrated at the water aspirator to yield a colorless oil (240 mg) which was distilled at 36° (*ca.* 0.01 mm) to yield pure sulfoxide **7** (230 mg, 80%) as a clear oil: ir (neat) prominent maxima at 2880, 1040 (SO), and 723 cm^{-1}; uv (CH_3CN) max 276 nm (ϵ 2580); nmr ($CDCl_3$) τ 4.1–4.3 (4 H, m), 6.0–6.3 (2 H, m), 6.9–7.3 (4 H, m); mass spectrum, parent ion at *m/e* 154, base peak at *m/e* 78.

Anal. Calcd for $C_8H_{10}SO$: C, 62.29; H, 6.55; S, 20.78. Found: C, 62.66; H, 6.64; S, 20.74.

Preparation of 9-Thiabicyclo[4.2.1]non-7-ene *syn*-9-Oxide (8). To a stirring mixture of sulfoxide **2** (2 g, 1.3 mmol) and excess potassium azodicarboxylate[32] (23.6 g, 0.122 mol) in absolute ethanol (200 ml) was added at 0° and over a period of 1 hr glacial acetic acid (7.3 g) in absolute ethanol (7 ml). The reaction mixture remained a bright yellow suspension after stirring for 8 days at *ca.* 0° but turned white on subsequent warming to ambient temperature overnight. The precipitate was removed by filtration and the filtrate concentrated at the water aspirator to afford a pale yellow semisolid (1.4 g) consisting (nmr, $CDCl_3$) of *ca.* 66% **8** and 33% **12**. The mixture was then placed on a column (760 × 13 mm) wet-packed (petroleum ether) with silica gel (*ca.* −15°) and eluted first with petroleum ether–ethyl ether (1:1 v/v; 1.5 ml) to yield **8** (0.8 g, 40%) then with petroleum ether–ethyl ether (2:3 v/v; 800 ml) to afford a mixture (0.6 g) of **8** (30%) and **12** (70%) by nmr ($CDCl_3$). Recrystallization of **8** from petroleum ether followed by sublimation at 30° (*ca.* 0.02 mm) produced a pure sample: mp 183–184°; ir (KBr) 2850, 1065 (SO), 797, and 695 cm^{-1}; uv (C_6H_{14}) max 243 nm (ϵ 132); nmr ($CDCl_3$) τ 4.06 (2 H, d, J = 3.0 Hz), 6.0–6.3 (2 H, m), 7.5–8.5 (8 H, m); mass spectrum, parent ion at *m/e* 156, base peak at *m/e* 79.

Preparation of 9-Thiabicyclo[4.2.1]non-7-ene (10). To a rapidly stirring (mechanical stirrer equipped with glass blade) solution of anthracene (26.8 g, 0.15 mol) in *dry* tetrahydrofuran (250 ml) were added thin strips of sodium metal (3.46 g, 0.15 g-atom) under nitrogen, and stirring at ambient temperature was continued for an additional 24 hr to produce a deep blue mixture. To this was added a solution of 7,8-dichloro-9-thiabicyclo[4.2.1]nonane[18] (10.5 g, 0.05 mol) in dry tetrahydrofuran (50 ml) over a period of 15 min, and stirring was continued for an additional 20 min. Water (*ca.* 2 ml) was then carefully added, the resulting yellow-green suspension filtered free of solid, and the filtrate concentrated at the water aspirator until a precipitate formed. This was removed by filtration and the filtrate concentrated to dryness at the water aspirator to yield a white solid residue (10 g) which was subjected to selective sublimation at 49° (0.01 mm) to produce pure sulfide **10** (4.0 g, 58%) as a white wax: mp 108–109°; ir (KBr) 2820, 1430, 952, 780, and 685 cm^{-1}; uv (C_6H_{14}) max 260 nm (ϵ 135); nmr ($CDCl_3$) τ 4.10 (2 H, d, J = 2.0 Hz), 5.9–6.2 (2 H, m), 8.0–8.7 (8 H, m); mass spectrum, parent ion at *m/e* 140, base peak at *m/e* 97.

Anal. Calcd for $C_8H_{12}S$: C, 68.51; H, 8.62; S, 22.86. Found: C, 68.44; H, 8.56; S, 23.10.

Preparation of 9-Thiabicyclo[4.2.1]non-7-ene *anti*-9-Oxide (11). To a stirring solution of sulfide **10** (5.33 g, 0.038 mol) in methylene chloride (200 ml) was added, under nitrogen at *ca.* −35° and over a period of 1.5 hr, a solution of *m*-chloroperbenzoic acid (85% pure, 9.7 g, 0.0476 mol) in methylene chloride (1 l.). After the addition was completed, the mixture was allowed to warm to *ca.* −25° and saturated with a stream of ammonia, and the resulting precipitate was removed by filtration. Concentration of the filtrate at the water aspirator produced a white solid (6.74 g). This was dissolved in the minimum amount of carbon tetrachloride, and the resulting solution was applied onto a column (540 × 14 mm) of wet-packed (petroleum ether) with activity III Woelm neutral alumina and maintained at *ca.* −15°. The column was eluted first with petroleum ether (400 ml) to yield **8** (25 mg) then with ethyl ether (700 ml) to produce **11** (5.1 g) which was obtained as a colorless crystalline solid (mp 163–164°) on sublimation at 54° (0.01 mm), 5.04 g (85%). An analytical sample of **8** was obtained on recrystallization of the sublimed material from carbon tetrachloride: mp 163.5–164°; ir (KBr) 2870, 1040 (SO), 870, 795, and 710 cm^{-1}; uv (C_6H_{14}) sh 243 nm (ϵ 320); nmr ($CDCl_3$) τ 3.98 (2 H, d, J = 2.0 Hz), 5.8–6.1 (2 H, m), 7.5–8.7 (8 H, m); mass spectrum, parent ion at *m/e* 156, base peak at *m/e* 79.

Anal. Calcd for $C_8H_{12}SO$: C, 61.50; H, 7.74; S, 20.52. Found: C, 61.49; H, 7.78; S, 20.44.

Preparation of 9-Thiabicyclo[4.2.1]nonane (14). To a stirring mixture of sulfide **10** (2.06 g, 0.013 mol) and potassium azodicarboxylate (7.7 g, 0.04 mol) in absolute ethanol (200 ml) was added, at 0° and over a period of 20 min, glacial acetic acid (2.38 g, 0.04 mol) in ethanol (3 ml), and stirring at 0° was continued for 24 hr. More acetic acid (0.79 g, 0.013 mol) in ethanol (1 ml) was then added, and the suspension remained bright yellow after stirring at 0° for 7 days but turned white on subsequent exposure to ambient temperature for 2 days. The precipitate was removed by filtration, the filtrate concentrated to dryness to yield a white solid (2.3 g) which was dissolved in chloroform (20 ml), and the resulting solution washed first with 10% aqueous sodium bicarbonate (10 ml) then with water (2 × 10 ml) and finally dried over calcium sulfate. Concentration at the water aspirator produced a semisolid (1.79 g) which was sublimed to yield **14** (1.36 g, 73%) as a white wax, mp 126.5–128.5°. An analytically pure sample of **14** was obtained by recrystallization from 80:20 methanol–water: mp 129–129.5°; ir (KBr) prominent maxima at 2850, 1440, 942 cm^{-1}; nmr (benzene-d_6) τ 6.3–6.7 (2 H, m), 7.6–9.0 (12 H, m); mass spectrum, parent ion at *m/e* 142, base peak at *m/e* 87.

Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.53. Found: C, 67.79; H, 9.99; S, 22.34.

Preparation of 9-Thiabicyclo[4.2.1]nonane *anti*-9-Oxide (13). To a stirring mixture of sulfoxide **11** (5.04 g, 0.032 mol) and potassium azodicarboxylate (18.9 g, 0.097 mol) in absolute ethanol (200 ml) was added, at 0° and over a period of 2 hr, glacial acetic acid (5.8 g, 0.097 mol) in ethanol (6 ml). After stirring for 7 days at 0–25°, the yellow suspension was filtered and the resulting filtrate concentrated at the water aspirator to produce a yellow semisolid (6 g). This was dissolved in chloroform (30 ml), the resulting solution was washed first with 10% sodium bicarbonate (20 ml) then with water (2 × 10 ml), and the dried ($CaSO_4$) extracts were concentrated at the water aspirator to yield a yellow liquid (5.84 g) consisting of *ca.* 80% **13** by nmr. Preparative vpc (6 ft × 0.25 in., 20% SF-96 on Chromosorb W, 190°) of this mixture afforded **13** as a hydroscopic white wax which was further purified by sublimation at 40° (*ca.* 0.1 mm): mp 182–183.5°; ir (KBr) prominent maxima at 2850, 1450, 1035 (SO) cm^{-1}; nmr (benzene-d_6) τ 6.5–6.9 (2 H, m), 7.2–7.5 (2 H, m), 8.2–9.2 (10 H, m); mass spectrum, parent ion at *m/e* 158, base peak at *m/e* 67.

Anal. Calcd for $C_8H_{14}SO$: C, 60.72; H, 8.92; S, 20.26; O, 10.11. Found: C, 60.60; H, 8.68; S, 20.15; O, 10.17.

Preparation of 9-Thiabicyclo[4.2.1]nonane *syn*-9-Oxide (12). To a stirring mixture of sulfoxide **5** (1.0 g, 0.065 mol) and potassium azodicarboxylate (7.55 g, 0.039 mol) in absolute ethanol (70 ml) was added, at 0° and over a period of 1 hr, glacial acetic acid (2.34 g, 0.039 mol) in ethanol (2 ml); stirring at 0° was continued for an additional 75 hr, more acetic acid (1.2 g) was added, and the mix-

ture was first allowed to warm to ambient temperature then filtered free of solid. Concentration of the yellow filtrate at the water aspirator and *ca.* 45° afforded a pale yellow semisolid residue (*ca.* 1 g) which was dissolved in chloroform (20 ml), and the resulting solution was washed first with 10% sodium bicarbonate (10 ml) then with water (2 × 10 ml) and finally dried over calcium sulfate. Concentration at the water aspirator afforded a light yellow semisolid (0.91 g). This was dissolved in the minimum amount of diethyl ether and the resulting solution applied on a column (300 × 14 mm) wet-packed (petroleum ether) with silica gel and maintained at *ca.* −15°. Elution was carried out first with 2:3 (v/v) ethyl ether–petroleum ether (300 ml) to yield a mixture (300 mg), then with 1:1 (v/v) of the same solvent mixture (800 ml) to afford sulfoxide **12** (570 mg). This was further purified by sublimation at *ca.* 30° (0.01 mm) to produce an analytically pure sample (525 mg, 55%) as white crystals: mp 192.5–194°; ir (KBr) prominent maxima at 2830, 1440, and 1050 (SO) cm^{-1}; nmr (CCl_4) τ 6.3–6.7 (2 H, m), 7.5–8.6 (12 H, m); mass spectrum, parent ion at *m/e* 158, base peak at *m/e* 41.

Anal. Calcd for $C_8H_{14}SO$: C, 60.72; H, 8.92; O, 10.11. Found: C, 60.49; H, 8.94; O, 10.40.

Oxidation of 6 with *m*-Chloroperbenzoic Acid. To a stirring solution of sulfide **6** (157 mg, 1.14 mmol) in methylene chloride (15 ml) was added, under nitrogen at *ca.* −35° and over a period of 20 min, a solution of *m*-chloroperbenzoic acid (85% pure, 298 mg, 1.67 mmol) in methylene chloride (15 ml). After the addition was completed, the mixture was first allowed to warm to *ca.* −25°, then saturated with a stream of ammonia, and the resulting precipitate removed by filtration. Concentration of the filtrate at the water aspirator produced a yellow oil (131 mg, 75%) shown by nmr ($CDCl_3$) to consist of *ca.* 92% **7** and 8% **5**.

Oxidation of 14 with *m*-Chloroperbenzoic Acid. A procedure analogous to that described for the oxidation of **6** was employed. Sulfide **14** (142 mg, 1.00 mmol) thus afforded a colorless solid mixture (145 mg, 92%) consisting (nmr; $CDCl_3$) of *ca.* 95% **13** and 5% **12**.

Thermal Interconversion of Sulfoxides 2 and 4. The thermal interconversion between **2** and **4** was monitored by nmr. On heating vacuum-sealed samples of **4** (*ca.* 50 mg) and diphenyl ether (1–2 drops) in benzene-d_6 (*ca.* 0.4 ml) at 110.7, 121.0, and 141.3°, there resulted, in each case, a clean, time-invariant, two-component mixture of 90% **2** and 10% **4** (nmr). In each case, kinetic measurements were made by monitoring the loss of **4** against the internal standard (diphenyl ether) and the information processed, in conjunction with the known final composition of the mixture, to calculate the rate of approach to equilibrium from either direction. Rate constants and activation parameters are given in Table I.

Positive identification of the components present at equilibrium was made as follows. The three mixtures were combined, and the resulting solution was eluted with tetrahydrofuran–ethyl ether (2:3 v/v) through a column packed with activity III Woelm neutral alumina (*ca.* 60 g) to yield diphenyl ether (32 mg) in the first fraction (100 ml), **2** (128 mg) in the second fraction (200 ml), and **4** (19 mg) in the final cut (300 ml).

It was established that **2** also produces a 90:10 equilibrium mixture of **2** and **4** (nmr) when heated in benzene-d_6 at 138° *in vacuo*.

Thermal Interconversion of Sulfoxides 5 and 7. The thermal interconversion of **5** and **7** was monitored by nmr. Upon heating separate vacuum-sealed tubes containing **5** (*ca.* 50 mg), diphenyl ether (1–2 drops) in benzene-d_6 (*ca.* 0.4 ml) and **7** (*ca.* 50 mg), diphenyl ether (1–2 drops) in benzene-d_6 (*ca.* 0.4 ml), at 141.4°, there resulted in each case a clean, time-invariant, two-component mixture consisting of 80% **7** and 20% **5** (nmr). In both cases, kinetic measurement was made by monitoring (nmr) the formation of product against the internal standard (diphenyl ether) and the information processed, in conjunction with the known final composition of the mixture, to calculate the rate of approach to equilibrium from either direction. Rate constants and activation parameters are given in Table I.

Positive identification of the components present at equilibrium was made as follows. The two mixtures were combined, the solvent was evaporated, the resulting residue was dissolved in the minimum amount of dichloromethane, and the solution was applied onto a column (300 × 14 mm) wet-packed (ethyl ether) with activity III Woelm neutral alumina and maintained at *ca.* −15°. The column was eluted, first with ethyl ether (180 ml) to yield diphenyl ether (20 mg), then with tetrahydrofuran–ethyl ether (1:9 v/v; 300 ml) to afford **5** (15 mg), and finally with tetrahydrofuran–ethyl ether (3:7 v/v; 200 ml) to supply **7** (56 mg).

Attempted Thermal Interconversion of Sulfoxides 8 and 11. A vacuum-sealed sampled sulfoxide **8** (*ca.* 50 mg) underwent rapid first-order thermolysis (see Table I) on heating in benzene-d_6 (*ca.* 0.4 ml), containing diphenyl ether (1–2 drops), for 4 hr at 179°. Elution of the resulting thermolysate through a column (760 × 13 mm) wet-packed (petroleum ether) with activity III Woelm neutral alumina, employing ethyl ether–petroleum ether (1:4 v/v; 50 ml) afforded a yellow solid (40 mg). This was first sublimed at 110° (0.1 mm) then recrystallized from methanol to yield a white solid (31 mg), mp 91.5–93.5°.

Similar thermal treatment of **11** at 194° for 10 hr produced no detectable change.

LIS Nmr Studies on Sulfoxides 2, 4, 8, and 11. To each of four nmr tubes containing **2, 4, 8,** and **11** (*ca.* 33 mg each) in $CDCl_3$ (0.3 ml) were gradually added known portions of the "shift" reagent $Eu(fod)_3$-d_{27} yielding *linearly correlatable* downfield shifts. Compounds **2** and **4** thus yield the plots depicted in Figures 2 and 3. Sulfoxide **8** experienced the following downfield shifts at the maximum employed molar ratio (0.473) of "shift" reagent to substrate: H_1 (2 H), 2.35 ppm; exo H (4 H), 3.58 ppm; endo H (4 H), 1.40 ppm; H_7 (2 H), 0.66 ppm. Sulfoxide **11** displayed the following downfield shifts at the maximum employed molar ratio (0.380) of "shift" reagent to substrate: H_1 (2 H), 2.58 ppm; endo H + exo H (8 H), 0.52 ppm; H_7 (2 H), 1.17 ppm.

Preparation of 1,6-Dideuterio-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide[27] (17). To a stirring solution of sulfone **16** (336 mg, 2.0 mmol) in *dry* tetrahydrofuran maintained at −78° and under nitrogen was added, *via* syringe and over a period of 4 min, a 2.25 *M* solution of *n*-butyllithium in hexane (2.0 ml), and the resulting dark-purple to maroon colored mixture was stirred at −78° for 1.5 hr. Acetic acid-*O*-*d* (1 ml) was then added in one operation, and the resulting yellow solution was first allowed to warm gradually (*ca.* 1 hr) to ambient temperature and then concentrated at the water aspirator. The resulting yellow semisolid (0.96 g) was then dissolved in dichloromethane (30 ml), washed, first with 10% aqueous sodium bicarbonate (20 ml) then water (3 × 20 ml), and finally dried over calcium sulfate. Concentration of the resulting yellow solution at the water aspirator afforded a yellow solid (230 mg) which was recrystallized from dichloromethane–ethyl ether (*ca.* 2:1) to yield a pure sample of **17** (211 mg, 62%) as white crystals, mp 190° dec.

Preparation of 1,6-Dideuterio-9-thiabicyclo[4.2.1]nona-2,4,7-triene *anti*-9-Oxide (18). To a stirring solution of **17** (340 mg, 2.0 mmol) in dichloromethane (20 ml), maintained under nitrogen and at ambient temperature, was added *via* syringe and over a period of 1 min, a 0.66 *M* solution of diisobutylaluminum hydride (10 ml, 6.6 mmol), and the resulting solution was maintained at the reflux temperature for 24 hr. Water (*ca.* 1 ml) was then carefully added, the ensuing gel washed with chloroform (30 ml), and the filtrate dried over calcium sulfate. Concentration at the water aspirator afforded a malodorous light yellow solid (180 mg) shown by nmr ($CDCl_3$) to consist chiefly of sulfoxide **18** (*ca.* 92%) and 1,6-dideuterio-9-thiabicyclo[4.2.1]nona-2,4,7-triene (*ca.* 8%). The mixture was then dissolved in the minimum amount of chloroform and the resulting solution applied on a column (540 × 14 mm) wet-packed (ethyl ether) with activity III Woelm neutral alumina and maintained at *ca.* −15°. Elution was carried out first with ethyl ether (200 ml) to yield a mixture of sulfone **17** and 1,6-dideuterio-9-thiabicyclo[4.2.1]nona-2,4,7-triene (67 mg) and then with tetrahydrofuran (500 ml) to afford pure sulfoxide **18** (110 mg, 36%) in the form of white crystals: mp 90–91°; ir (KBr) prominent maxima at 1030 (SO), 846, 740, and 690 cm^{-1}; nmr ($CDCl_3$) τ 4.10 (4 H, s), 4.23 (2 H, s); mass spectrum, parent ion at *m/e* 154, base peak at *m/e* 106.

Thermal Rearrangement of 1,6-Dideuterio-9-thiabicyclo-[4.2.1]nona-2,4,7-triene *anti*-9-Oxide (18). The thermal rearrangement of **18** was monitored by nmr. Upon heating two separate vacuum sealed samples of **18** (*ca.* 50 mg) in benzene-d_6 (*ca.* 0.4 ml) containing diphenyl ether (1–2 drops) at 111.0 and 140.5°, there was obtained a time-invariant mixture of **2**-d_2 and **4**-d_2 which was processed kinetically to yield the information collected in Table I. The contents of the two nmr tubes were then combined and concentrated at the water aspirator. The resulting residue was then

dissolved in the minimum amount of chloroform and the solution applied on a column (300 × 14 mm) wet-packed (diethyl ether) with activity III Woelm neutral alumina and maintained at *ca.* −15°. The column was eluted, first with diethyl ether (150 ml) to yield diphenyl ether (9 mg), then with tetrahydrofuran–ethyl ether (1:4 v/v; 1 l.) to afford **2**-d_2 (81 mg) in the form of white crystals: mp 120–121°; nmr (60 MHz; $CDCl_3$) τ 3.3–3.5 (m, $H_3 + H_4$), 3.9–4.3 (m, $H_2 + H_5$), and 5.6–5.9 (m, $H_1 + H_6$) in an area ratio of 1.00:1.05:1.05:0.99; *m/e* 154 (P^+; 48%). Further elution with the same solvent pair yielded trace amounts of a mixture of **2**-d_2 and **4**-d_2.

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References and Notes

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(17) Only unreacted **4** and its perhydro analog **13** could be detected (nmr) on 19-fold increase of the contact time between **4** and hydrogen gas at 60 psi in the presence of Rh/C.
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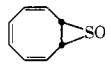
(29) The question, of course, arises here as to whether the observed interconversion between **2** and **4** might materialize through the fleeting intermediacy of a [6.1.0] skeleton, i.e., the bicyclic thiirane oxide shown in i. At first glance, this possibility emerges all the more appealing insofar as all attempts to synthesize i by low-temperature (−30 to 0°) oxidation of the corresponding episulfide with either periodate or MCPBA resulted in the exclusive isolation of the [4.2.1] counterpart **2**. Nonetheless, examination of the stereoelectronic factors controlling the generation of i reveals that adoption by this substance of the same migratory mode in its reversion to the [4.2.1] relative can only result in the regeneration of **4**. In other words, when restricted to the same migratory mode the interconversion between [6.1.0] and [4.2.1] sulfoxide cannot account for the **4** → **2** process. It may easily be shown, for instance, that a reversible shift can only interconvert **4** with *endo*-i by a $(1,3)_{ss}$ process and with *exo*-i by a $(1,5)_{ss}$ motion. By contrast, activation of a $(1,7)_{ss}$ circumambulatory shift in i may be readily seen to interconvert the endo and exo forms and hence also **2** and **4** by the reverse process.



i

ii

Experiments with specifically tagged ii, now in progress within our laboratories, would hopefully provide a means of distinguishing between this combination process and the simple $(1,3)_{ss}$ shift of Scheme IVb for the interconversion between **2** and **4**.
(30) The structural identity of the thermal product(s) of syn sulfoxide **8** is not known at this stage. Nonetheless, the greater thermal lability of the syn isomer **8** compared with the anti counterpart **11** suggests that the thermal product(s) results from abstraction of a butane hydrogen by the closely located syn SO group. Indeed, upon monitoring the process by nmr, one detects a sharp singlet whose chemical shift varies with concentration, and which might be indicative of the initial generation of an S–OH function.
(31) All melting points and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 137B spectrophotometer, nmr spectra were determined either on a Varian A-60 or a Bruker HX-60E spectrometer, ultraviolet spectra were recorded either on a Perkin-Elmer 202 or Cary 18 spectrophotometer, and mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-6E single-focusing spectrometer. Gas chromatographic analyses were performed on a Varian Aerograph A90-P3, and microanalyses were carried out by Galbraith Laboratories, Knoxville, Tenn. All solvents were acid free "ACS Reagent Grade" and were used without further purification. "Dry" tetrahydrofuran and ethyl ether were freshly distilled from lithium aluminum hydride.
(32) Prepared as described by J. Thiele, *Justus Liebigs Ann. Chem.*, **271**, 127 (1892).