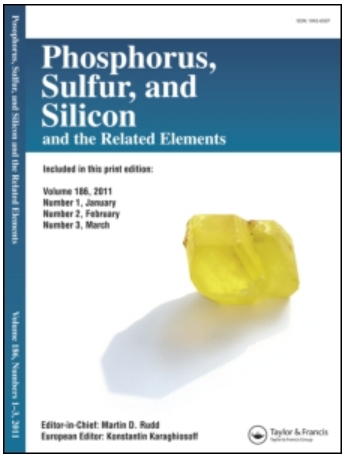

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Thermal and Ionic Cyclizations of Allenic Sulfones and Sulfinates

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THERMAL AND IONIC CYCLIZATIONS OF ALLENIC SULFONES AND SULFINATES

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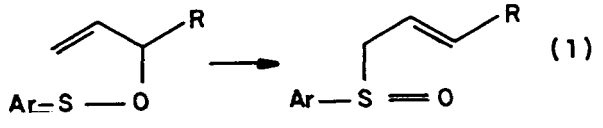
Our interest in the cyclization of allenic sulfones and sulfinates was aroused by previous studies on the [2,3] sigmatropic rearrangement of allylic sulfenates and sulfinates to sulfoxides and sulfones, respectively (eqs. 1,2),



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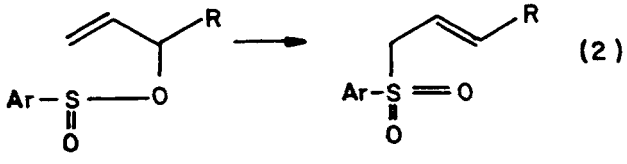

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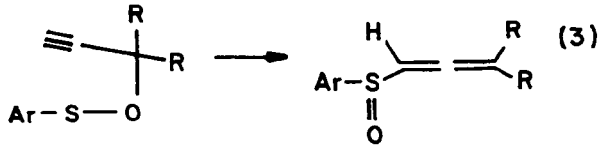

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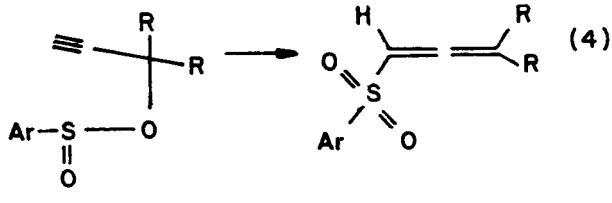
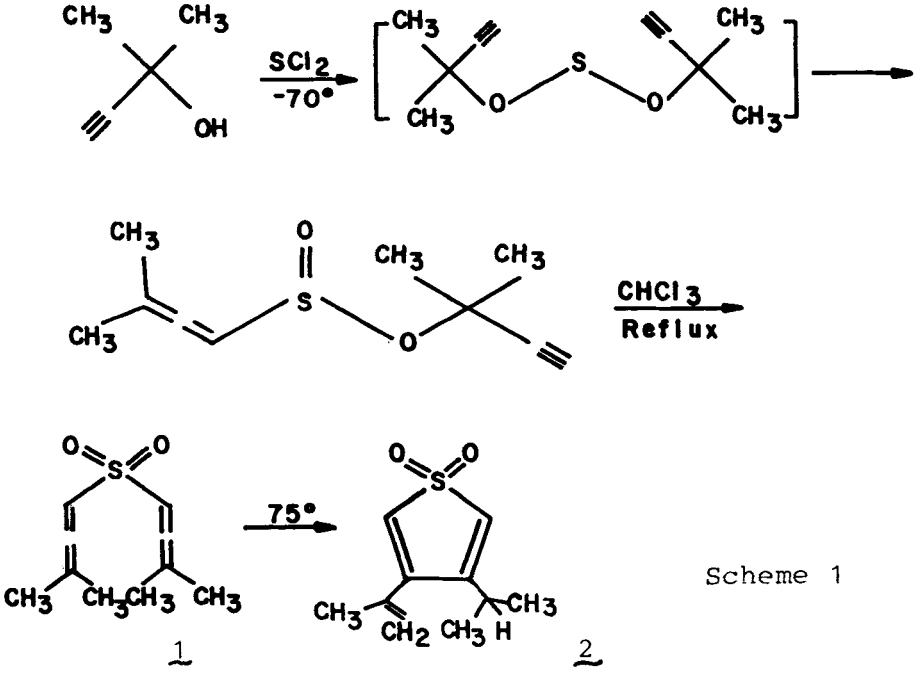


(4)

as well as by the analogous rearrangement of propargylic sulfenates and sulfinates to allenic sulfoxides and sulfones, respectively (eqs. 3,4)[1].

A combination of the last two rearrangements was used to prepare bis-γ,γ-dimethylallenyl sulfone (1)[2]. Reaction of α,α-dimethylpropargyl alcohol with sulfur dichloride gives the corresponding sulfoxylate which on double [2,3] sigmatropic rearrangement is transformed to the desired product (Scheme 1).



Scheme 1

1 2

CYCLIZATION OF DIALLENYL SULFONES

Before I continue, I would like to point out that in contrast to the great amount of work on monoallenes [3], the study of diallenic systems has received relatively little attention in the past. This may be due to the lack of simple and general methods for the synthesis of such compounds. The method I have just described for the preparation of bis-γ,γ-dimethylallenyl sulfone is certainly

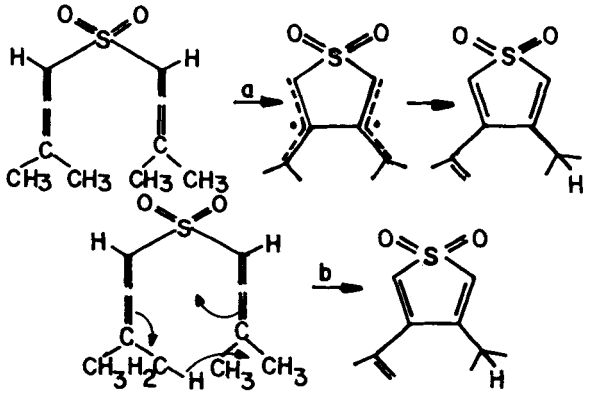
a convenient one, but what is even more important is that this sulfone undergoes a facile cyclization on heating at 75° to the thiophene 1,1-dioxide derivative 2, in quantitative yield (Scheme 1).

TABLE 1: Rate Constants[a] for the Rearrangement of Bis-γ,γ-dimethylallenyl Sulfone[b] to 3-Isopropenyl-4-isopropylthiophene 1,1-Dioxide at 75.0°.

Solvent	$10^5 k$, sec^{-1}	Solvent	$10^5 k$, sec^{-1}
Chloroform	7.48±0.17	Acetonitrile	8.15±0.22
Ethyl acetate	7.97±0.30	Methanol	8.11±0.56
Acetone	6.14±0.33		

[a] Determined by nmr. [b] [Sulfone] = 0.05 M.

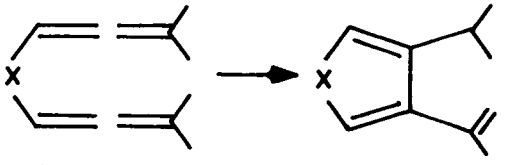
A kinetic study of this cyclization in various solvents indicated that the rate of rearrangement was practically insensitive to the change in ionizing power of the solvent (Table 1). This result rules out the operation of an ionic mechanism but is consistent with two alternative mechanisms shown in Scheme 2[2].



Scheme 2

The first possible mechanism (a) is a two-step process involving intramolecular formation of a 2,2'-bis-allyl-type diradical intermediate in the first, rate determining stage followed by a fast intramolecular hydrogen abstraction and formation of the new double bond. The second possible mechanism (b) is based on the assumption that the reaction is essentially an intramolecular and concerted ene reaction[4]. In order to distinguish between these two mechanisms we have examined the kinetic isotope effect, and found that bis-hexadeuterio-γ,γ-dimethyl-allenyl sulfone undergoes cyclization at practically the same rate as the undeuterated compound[6]. Obviously, this result excludes the concerted ene mechanism. Additional support for the diradical mechanism can be obtained from examination of the substituent effect which shows that substitution by an ethyl group at the α and α' positions enhances the rate of cyclization by a factor of 4 relative to the diallenyl sulfone 1[6].

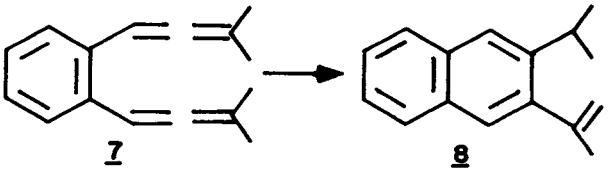
CYCLOAROMATIZATION OF BRIDGED DIALLENES



(5)

1' X=S
3 X=O
5 X=Se

2' X=S
4 X=O
6 X=Se

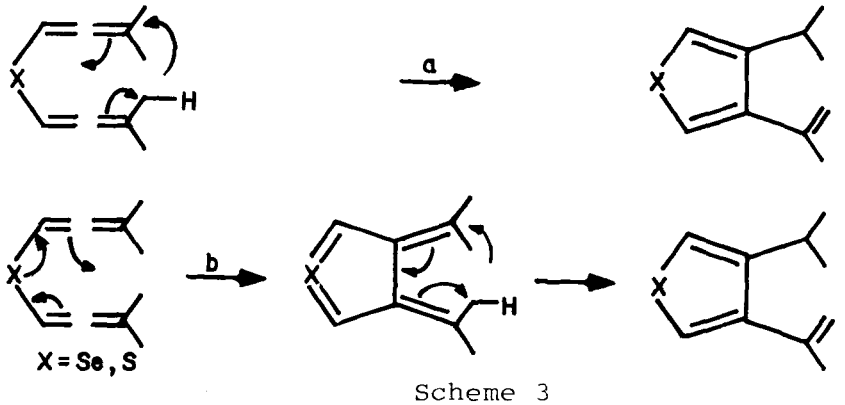


(6)

7 8

As a natural extension of this work we next decided to investigate the cyclization of some other bridged diallenes, whose cyclization would be accompanied by simultaneous aromatization, and consequently gain an extra driving

force for the reaction. The systems selected include the bis-γ,γ-dimethylallenyl sulfide (1'), ether (3), selenide (5) and o-benzene (7). On attempted synthesis of these compounds we found it impossible to isolate or even detect the first two bridged diallenes because of spontaneous cyclization to the corresponding thiophene (2') and furan (4) derivatives (eq.5)[7]. On the other hand the bis-γ,γ-dimethylallenyl selenide (5) and o-benzene (7) were relatively stable; could be isolated and identified Furthermore, the transformation of selenide 5 to the selenophene 6, as well as the transformation of 7 to the naphthalene derivative 8, proceeded at a measurable rate at room temperature and in quantitative yield.



Scheme 3

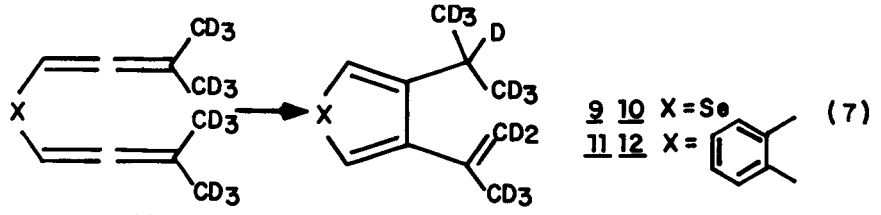
Once again, there are three possible mechanisms which can be related to the cycloaromatization of diallenes 1', 5: an ionic mechanism, an intramolecular ene reaction (mechanism a) or a two-step process involving an electrocyclic six-electron reaction in the first step followed by 1,5 hydrogen shift (mechanism b, Scheme 3).
A kinetic study of the cyclization of the diallenyl selenide 5 in various solvents indicated that the rate of the rearrangement was practically insensitive to the change in ionizing power of the solvent (Table 2). These

TABLE 2: Rate Constants[a] for the Rearrangement of Selenide 5 to Selenophene 6 (k_H), and Selenide 9 to Selenophene 10 (k_D)

Solvent	Temp. °C	$10^5 k_H$, sec^{-1} [b]	$10^5 k_D$, sec^{-1} [b]	k_H/k_D
Carbon Tetrachloride	30	1.229 ± 0.090	1.134 ± 0.013	1.08
Chloroform-d_1	30	1.446 ± 0.009	1.410 ± 0.026	1.02
Acetone-d_6	30	1.359 ± 0.030		

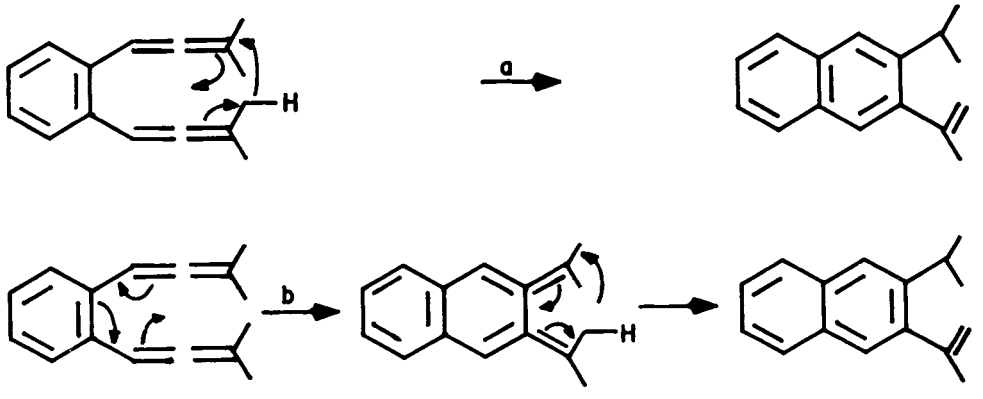
[a] Determined by nmr. [b] [diallene] = 0.45 - 0.9 M.

results eliminate the possibility of an ionic mechanism. To distinguish between the two other alternatives the bis-hexadeuterio-γ,γ-dimethylallenyl selenide 9 was prepared and its rate of cyclization to 10 (eq. 7) under the same conditions was measured. The observed values of k_H/k_D of 1.08 in carbon tetrachloride and 1.02 in chloroform (Table 2) clearly indicate that the mechanism is a two-step process involving formation of the quinodimethane type intermediate in the first, rate determining step, followed by a fast hydrogen transfer in the second step (mechanism b, Scheme 3).



(7)

Very similar results were obtained for the kinetic study of the cycloaromatization of the diallenylbenzene 7 to the naphthalene derivative 8 (Table 3) and therefore an identical mechanistic interpretation is suggested with mechanism b preferred to mechanism a (Scheme 4).



Scheme 4

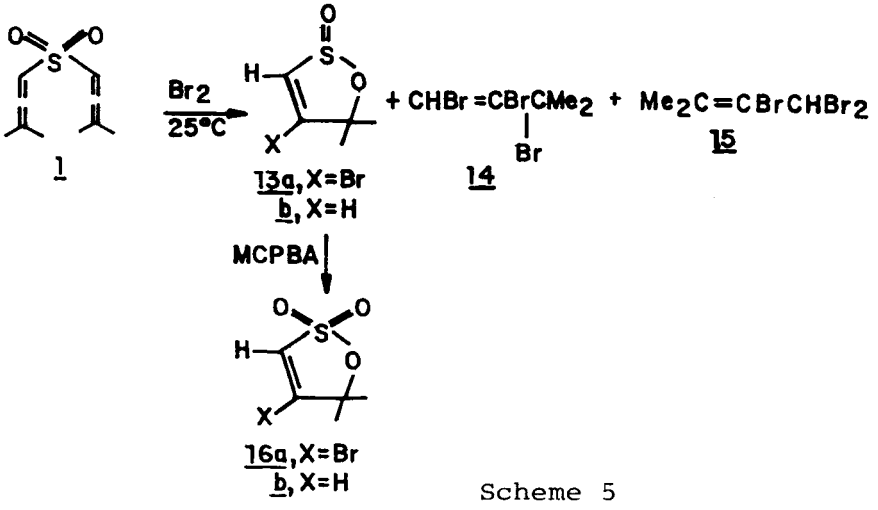
TABLE 3: Rate Constants[a] for the Rearrangement of Diallenylbenzene 7 to Naphthalene 8 (k_H), and Diallenylbenzene 11 to Naphthalene 12 (k_D)

Solvent	Temp. ^0C	$10^5 k_H$, sec^{-1} [b]	$10^5 k_D$, sec^{-1} [b]	k_H/k_D
Carbon Tetrachloride	30	7.625 ± 0.188	7.753 ± 0.289	0.98
Chloroform-d_1	30	9.430 ± 0.244	9.386 ± 0.179	1.00
Acetone-d_6	30	8.707 ± 0.205		

[a] Determined by nmr [b] [diallene] = 0.45 - 0.8 M

ELECTROPHILIC FRAGMENTATION-CYCLIZATION OF ALLENIC SULFONES AND SULFINATES.

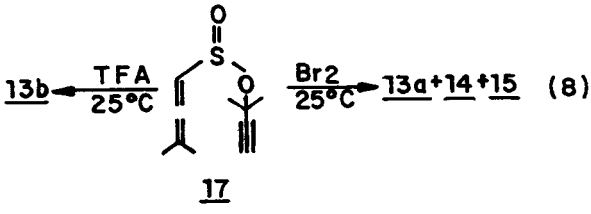
Surprisingly, we have found that addition of a carbon tetrachloride solution of bromine to sulfone 1 at room temperature resulted in spontaneous and quantitative fragmentation of the sulfone, with formation of the cyclic α,β-unsaturated sulfinate (γ-sultine) 13a (X=Br) and the tribromoproducts 14 and 15 (Scheme 5)[8]. Analogously, we have found that treatment of sulfone 1 with trifluoroacetic acid at room temperature gives rise to γ-sultine 13b (X=H). Besides the standard spectral evidence, the structures of the sultines 13a and 13b have also been confirmed by their ^{13}C NMR spectra[8] as well as by oxidation to the corresponding sultones 16a and 16b.



Scheme 5

While the rearrangement of acyclic sulfinates to sulfones is fairly common [1a,b,2] and is thermodynamically a favored process, several reports on the rearrangement of cyclic sulfones to sultines have also been published in the past [9]. The first rearrangements of this type were reported to occur under electron impact of various benzo- and

dibenzothiophene dioxides [9a-c]. More recently, the rearrangement of thiete 1,1-dioxide to 5H-1,2-oxathiole 2-oxide, the parent substance of 13, on heating at high temperatures in solution or in the vapor phase, was reported [9e]. The results have been rationalized in terms of a mechanism involving vinyl sulfene as a reactive intermediate, which is formed and reacts in a concerted manner. Apparently, the release of ring strain present in the starting material provides considerable driving force. However, we are not aware of any literature reports on the conversion of sulfone to sulfinate under electrophilic conditions such as those employed by us.



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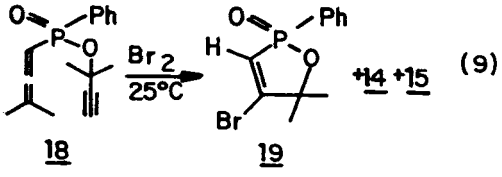
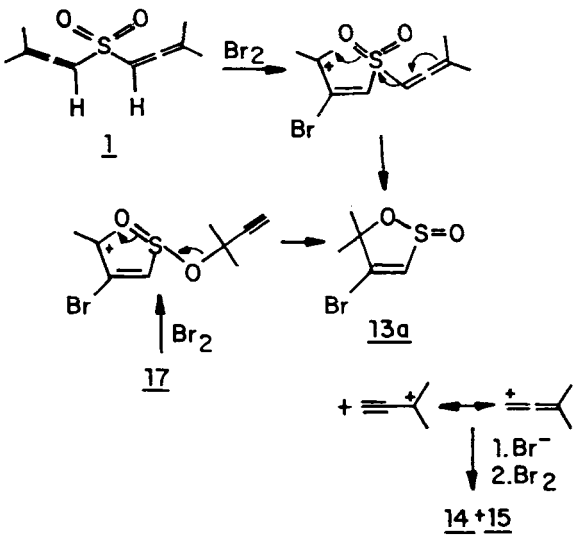


18 19

It is interesting to note that from a synthetic point of view it is not even necessary to prepare the diallenyl sulfone 1, since one can use its sulfinate precursor 17 to obtain exactly the same results, under the same conditions (eq. 8). Furthermore, the generality of this process is demonstrated by the spontaneous fragmentation-cyclization of the phosphinate 18 to the 1,2-oxaphosphol-3-ene 2-oxide derivative 19, under similar conditions to those employed with sulfone 1.



Scheme 6

We tentatively suggested[8] that both the fragmentation-cyclization of sulfone 1 as well as that of sulfinate 17 take place by essentially the same mechanism as depicted in Scheme 6, for the reactions with bromine. This mechanism is supported by several observations. First, treatment of either α,α-dimethylpropargyl or γ,γ-dimethylallenyl bromide with bromine gives the same mixture of 14 and 15, as obtained in the reaction of 1. Second, reactions of the unsubstituted diallenyl sulfone did not result in the fragmentation-cyclization described above for sulfone 1 under the same conditions. Similarly, no γ-sultine was obtained on treatment of γ,γ-dimethylallenyl p-tolyl or methyl sulfone with bromine, while γ,γ-dimethylallenyl t-butyl sulfone gave compound 13a and t-butyl bromide. These results indicate that in the absence of a departing stable carbocation such as α,α-dimethylpropargyl or t-butyl, no fragmentation and subse-

quent cyclization are possible under the mild conditions employed. However, further work has shown that this prerequisite is only required in the case of allenic sulfones and not of allenic sulfinates [10]. For example, the reaction of methyl γ,γ-dimethylallenesulfinate with bromine affords γ-sultine 13a and methyl bromide under normal conditions. We therefore suggested that the fragmentation-cyclization mechanism in the case of allenic sulfinates involves an alternative S_N2 attack of bromide ion on the O-alkyl group of the reaction intermediate formed by attack of the substrate on bromine, and affording directly the reaction products [10]. The absence of an S_N2 type mechanism in the case of methyl γ,γ-dimethylallenyl sulfone may be due to the strong retarding effect exerted by the sulfonyl group on S_N2 displacement at the α-carbon atom, as a result of steric and field effects [11].

STEREOCHEMISTRY OF THE ELECTROPHILIC FRAGMENTATION-CYCLIZATION OF ALLENIC SULFONES AND SULFINATES

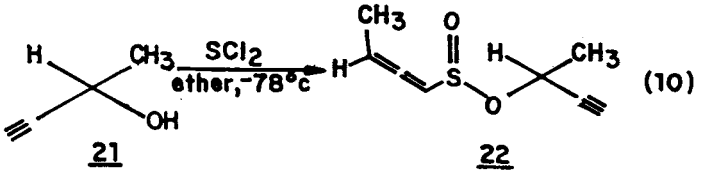
The electrophilic cyclization of a variety of functionalized allenes to heterocyclic systems [12-15] has received considerable attention due to its synthetic utility and remarkable stereoselectivity [12a,f,13,14,15a]. In a continuation of our previous study on the electrophilic fragmentation-cyclization of allenic sulfones and sulfinates to α,β-unsaturated γ-sultines, we have investigated the stereochemistry of this reaction.

TABLE 4: Cyclization of Chiral Allenic Sulfones and Sulfinates to Chiral γ-Sultines

Substrate	$[\alpha]_D^{25}$, deg	X^+	γ-sultine	$[\alpha]_D^{25}$, deg	yield %
(-)-22[a]	-97.6	Br^+	(-)-29	-73.7 (c 2.7)	87
(+)-22[a]	+41.7	Br^+	(+)-29	+14.6 (c 1)	85
(+)-22[b]	+32.0	MeS^+	(+)-31	+20.5(c 2.2)	35
(-)-27[c]	-47.5	Br^+	(+)-29	+16.9(c 1.2)	87
(-)-28[d]	-58.5	Br^+	(+)-30	+15.6(c 3.6)[f]	55
(-)-27[b]	-47.5	MeS^+	(+)-31	+23.7(c 6.2)	80
(-)-28[b]	-63.5	MeS^+	(+)-32	+15.9(c 6.1)	73

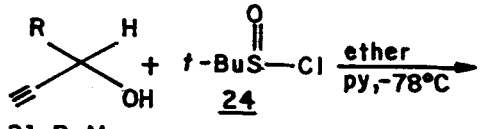
[a] In CCl_4 at 25°C. [b] In CH_2Cl_2 at -20°C. [c] In CCl_4 at -10°C.
[d] In CCl_4 at -20°C. [e] In acetone. [f] Contains some 8% of sulfone.

Treatment of (R)-(+)-1-butyn-3-ol ((+)-21[16], $[\alpha]^{25}D$ + 17.7° (c 1.o, dioxane)) and of (S)-(-)-21[16], $[\alpha]^{25}D$-49.4° (c 3.2, dioxane) with sulfur dichloride, as previously described [2], afforded sulfinates (+)-22 ($[\alpha]^{25}D$ + 41.7° (c 1.o, acetone, yield 8o%)) and (-)-22 ($[\alpha]^{25}D$ - 97.6° (c 1.7, acetone, yield 8o%)), respectively (eq. 1o).

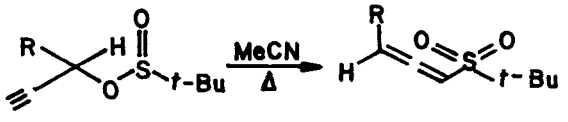


(10)

Racemic γ-methyl- and γ-tert-butylallenyl tert-butyl sulfones (27, 28) were prepared by a previously reported method [1b] (eq. 11).



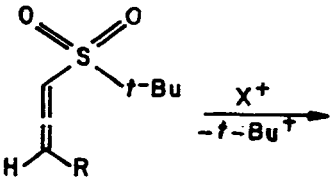
21, R=Me
23, R=t-Bu



(11)

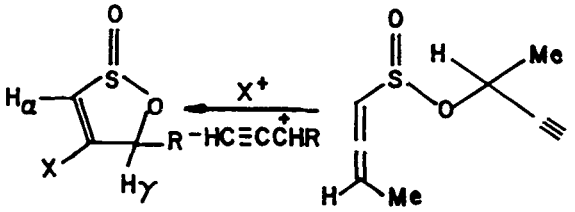
25, R = Me (64%) 27, R = Me (95%)
26, R = t-Bu (67%) 28, R = t-Bu (100%)

Optically active sulfones (-)-27 ($[\alpha]^{25}D$-47.5° (c 1.4, acetone, yield 7o%)) and (-)-28 ($[\alpha]^{25}D$-58.5° (c 2.8, acetone, yield 66% , mp 87-88° C) were obtained by the elegant method of kinetic resolution [17]. Treatment of optically active sulfinate 22 and sulfones 27 and 28 with bromine and methanesulfenyl chloride gave optically active γ-sultines 29-32 (eq. 12) as summarized in Table 4.



27, 28

(12)



22

29, X=Br; R=Me
30, X=Br; R=t-Bu
31, X=MeS; R=Me
32, X=MeS; R=t-Bu

All the γ-sultines were obtained as diastereomeric mixtures (ca. 1:1, by NMR). While each one of γ-sultines (+)-30 and (+)-32 (R=t-Bu) was separated into two diastereomers A and B by means of column chromatography (silica, CH_2Cl_2), the structural assignment of the two diastereomers of (+)-29 and (+)-31 could only be obtained by double irradiation ^1H NMR. Irradiation of each one of the H_γ quartets showed a change to a singlet of the related methyl doublet. The results are summarized in Table 5.

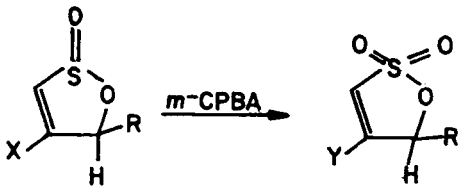
The oxidation of γ-sultines (+)-29, obtained from both (+)-22 and (-)-27, as well as of (-)-30A, (+)-30B, and (+)-31 to the optically active sultones 33-35, which lack a chiral sulfur (eq. 13), may be taken as proof that the observed optical activity in the sultines is also due to the γ-carbon.

Table 5. ^{1}H NMR Data[a] amd Optical Rotations[b] of γ-Sultine Diastereomers

γ-sultine	diastereo-isomer	H_α	H_γ	CH_3	t-Bu	CH_3S	$[\alpha]^{25}_D$, deg
29	A	6.85 (d, J=2)	5.65 (q, J=8)[c]	1.60 (d, J=8)			
	B	6.85 (d, J=2)	5.25 (q, J=8)[c]	1.75 (d, J=8)			
30	A	6.88 (d, J=2)	5.35 (d, J=2)		1.12 (s)		-17.90
	B	6.80 (d, J=2)	4.90 (d, J=2)		1.20 (s)		+75.76
31	A	6.15 (d, J=1)	5.75 (q, J=6)[c]	1.52 (d, J=2)		2.50 (s)	
	B	6.15 (d, J=1)	5.28 (q, J=6)[c]	1.72 (d, J=2)		2.50 (s)	
32	A	6.15 (d, J=2)	5.38 (d, J=2)		1.09 (s)	2.49 (s)	+32.16
	B	6.05 (d, J=2)	4.85 (d, J=2)		1.18 (s)	2.46 (s)	+66.07

[a] 60-MHz spectra in $CDCl_3$ with internal Me_4Si; J values given in hertz. [b] In acetone.

[c] Each signal shows allylic coupling, J = 2 Hz.

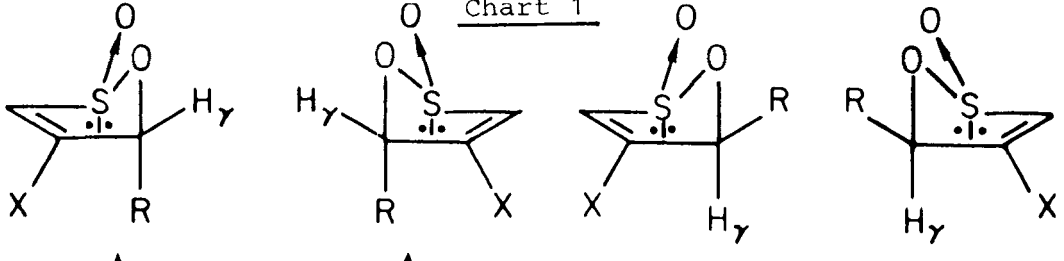


(13)

	$[\alpha]^{25}_D$, deg		$[\alpha]^{25}_D$, deg
29	+14.6	33, R=Me; Y=Br	+3.8
29	+16.9	33	+2.7
30A	-17.0	34, R=t-Bu; Y=Br	+9.8
30B	+75.8	34	+12.6
31	+23.7	35, R=Me; Y=$MeSO_2$	-3.7

The two chiral centers present in γ-sultines 29-32 give rise to four diastereomers for each sultine. These can be divided into structural types A and B, as shown in Chart 1.

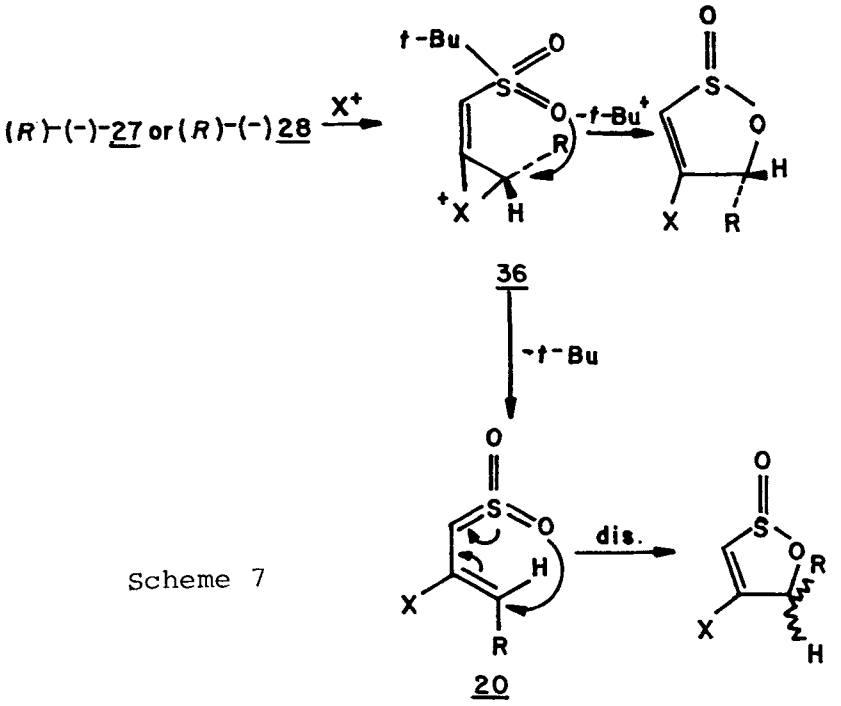
Chart 1



A $(R)^C$-$(S)^S$ A $(S)^C$-$(R)^S$ B $(S)^C$-$(S)^S$ B $(R)^C$-$(R)^S$

Since it is well-known that a γ-proton cis to the S→O bond in closely related γ-sultines is deshielded with respect to the same proton cis to a sulfur nonbonding electron pair [18], one may conclude from the analysis of the NMR data shown in Table 5 that diastereomers 29A-32A have type-A structure and diastereomers 29B-32B are all of type-B structure (Chart 1).

We suggest that the absolute configuration of (+)-22, derived from (R)-(+)-21, is (R)-(+)-α-methylpropargyl (R)-γ-methylallene-(R,S)-sulfinate, since we assume that both electron pairs on sulfur in the sulfoxylate



Scheme 7

intermediate (R,R)-[HC≡CCH-$(CH_3)O]_2S$ should be equally reactive and since the [2,3] sigmatropic rearrangement is known to occur with nearly complete transfer of chirality [14b,19]. The absolute configuration of both sulfones (-)-27 and (-)-28 was assigned as R by the use of the Lowe-Brewster rules [20] and the substituent polarizability order RSO_2 > H and alkyl > H. Further support for the assignment of the R configuration to the allenyl group in both sulfinate (+)-22 and sulfone (-)-27 comes from their cyclizations with bromine and MeSCl, which give the same γ-sultines, (+)-29 and (+)-31, respectively (Table 4).

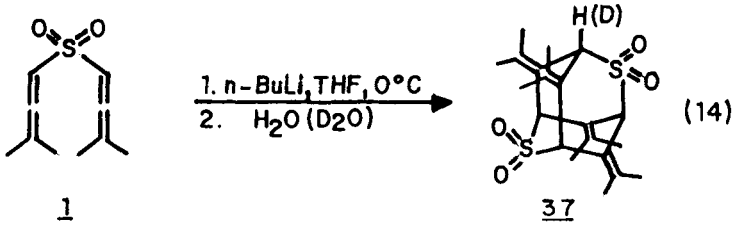
The intermediacy of vinylsulfene 20 [21] in the reaction mechanism (Scheme 7) appears to be excluded, since its disrotatory closure would lead to racemic γ-carbon in the product. On the other hand, the spatial arrangement of the γ-carbon in the bridged onium ion 36 will be pre-

served also during the nucleophilic attack by sulfonyl oxygen [12a,f] and as a result this carbon will retain its optical activity in the γ-sultine, as actually observed.

The identity in sign and similarity in optical rotations of sultones (+)-34, obtained from (-)-30A and (+)-30B (eq. 13) indicate that the absolute configuration of the γ-carbon in both sultones as well as both sultines is the same. In conclusion, we suggest that γ-sultines 29A-32A and 29B-32B (Chart 1, Table 5) may be assigned the $(R)^{C}$-$(S)^{S}$ and $(R)^{C}$-$(R)^{S}$ absolute configurations, respectively.

CARBANIONIC CYCLODIMERIZATION OF ALLENYL SULFONES

In continuation, we have also studied the behaviour of the diallenyl sulfone 1 under basic conditions [22]. Unexpectedly, we have found that treatment of a solution of 1 in tetrahydrofuran or ether with n-butyllithium at 0° results in a novel and fast dimerization-cyclization of the diallenyl sulfone to give the 2,6-dithiaadamantane derivative 37 (eq. 14).



1 37 (14)

Although the spectral evidence was in accord with the assigned structure of 37 unequivocal structure proof was obtained by X-ray crystallographic analysis (Figure 1).

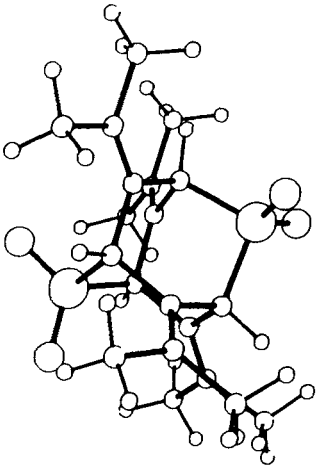
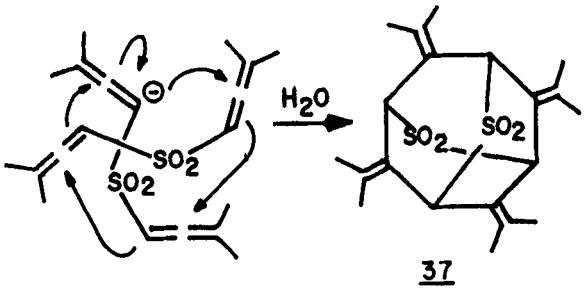
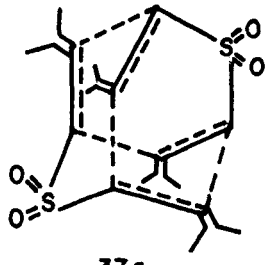


Figure 1: An OPTEP Drawing of the molecular Structure of 37.

The conversion of 1 to 37 represents a facile synthesis of a dithiaadamantane system. Furthermore, and to the best of our knowledge, it appears to be the first reported example of a base-catalyzed cyclodimerization of an allenic derivative. The cyclodimerization of 1 was explained by a novel mechanism (Scheme 8) in which an allenic α-sulfonyl carbanion initiates a series of four consecutive inter-intramolecular Michael additions, with final return of the negative charge to its original carbon. This process, named by us "carbanion walk" is further illustrated by a dashed line in 37a, with no claim for concertedness [22].



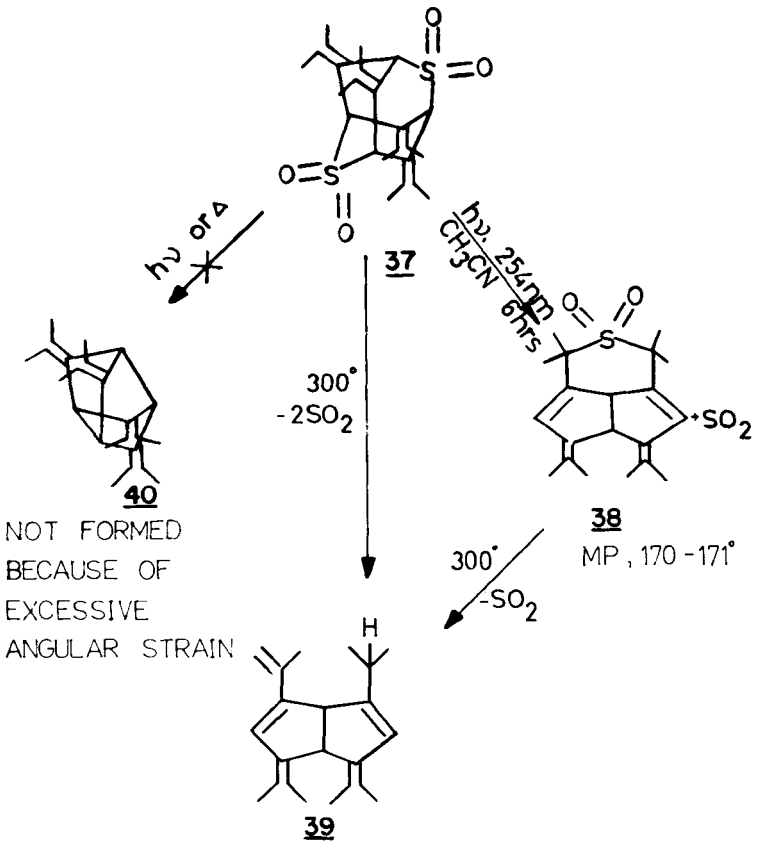
37



37a

Scheme 8

Surprisingly, we have also found that compound 37 shows a strong ultraviolet absorption at γ_{max} = 236 nm with $\varepsilon \sim 29000$ in acetonitrile although none of its π systems are conjugated [23]. In view of this observation, as well as the considerable recent interest in the pyrolysis of cyclic sulfones as a synthetic method for the preparation of cyclic and polycyclic hydrocarbons [24], we have investigated the thermal and photochemical elimination of sulfur dioxide from disulfone 37 (Scheme 9) [25]. Direct irradiation of dithiaadamantane 37 in acetonitrile at 254 nm results in the extrusion of only one molecule of sulfur dioxide, together with a double allylic rearrangement of the second sulfonyl group, and formation of the tricyclic sulfone 38. Unequivocal proof for the assignment of structure 38 was obtained by X-ray crystallographic analysis (Figure 2).



Scheme 9

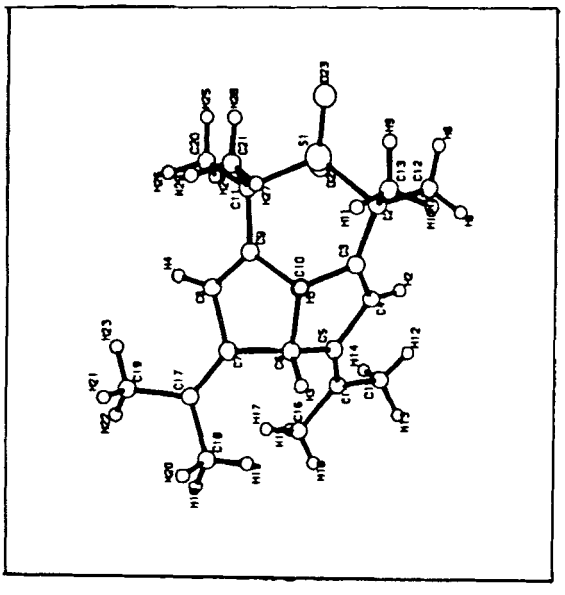
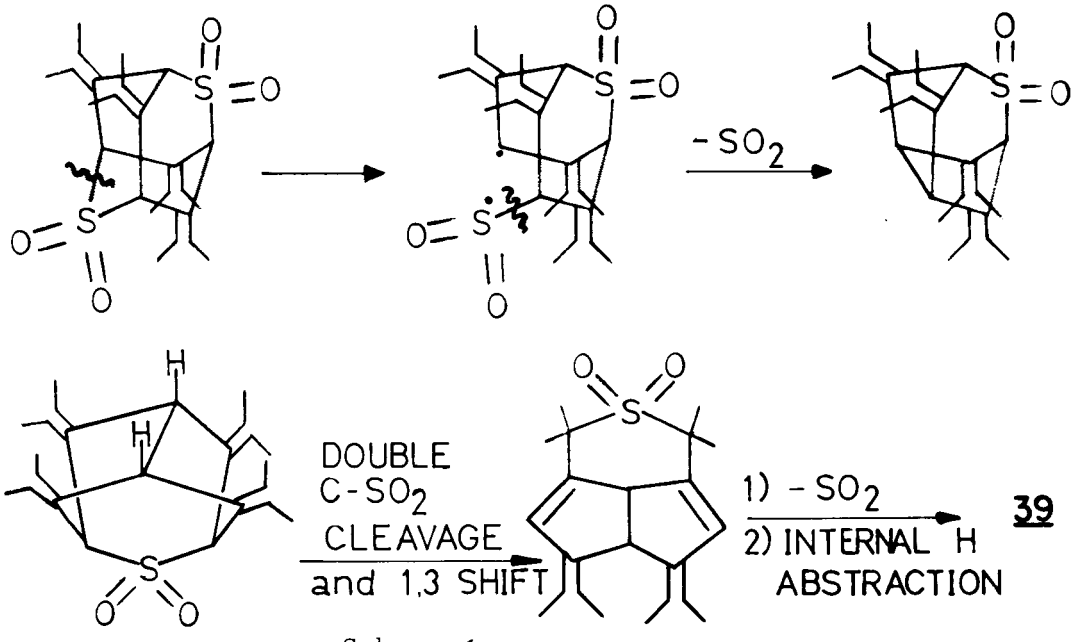


Figure 2: An ORTEP Drawing of the Molecular Structure of 38.

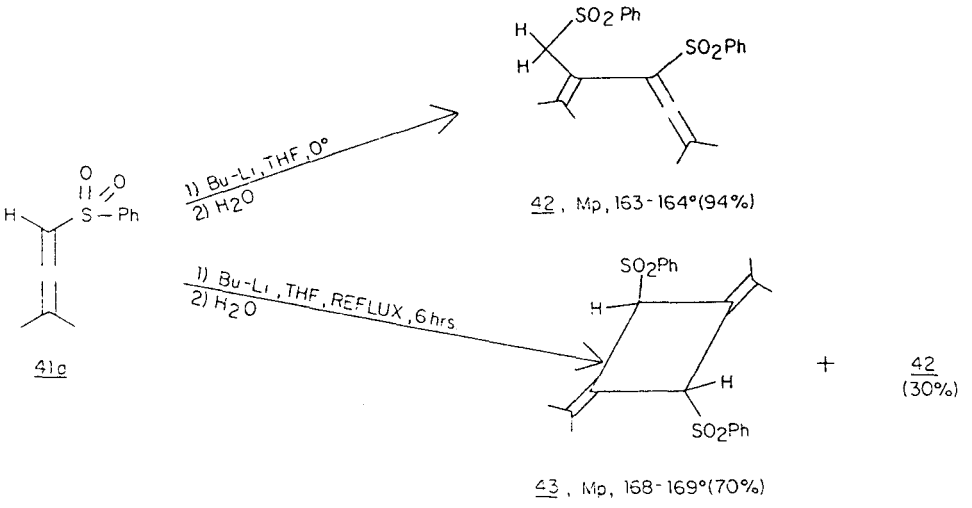
In contrast to the photochemical results, pyrolysis of compound 37 at ca. 300° results in extrusion of both SO_2 groups and formation of the bicyclic hydrocarbon 39, with essentially the same rearranged carbon skeleton as in product 38 (Scheme 9).

The question whether the first SO_2 extrusion, which is common to both processes, is preceded or followed by the skeletal rearrangement has not been answered as yet. Nevertheless, a tentative mechanism based on the second possibility is presented in Scheme 10.



Scheme 10

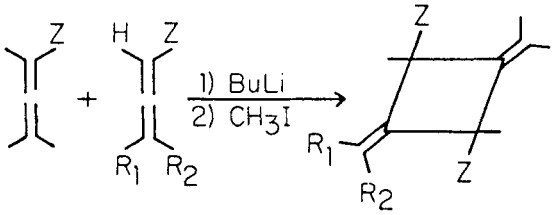
The thermal cyclodimerization of allenes to 1,2-dimethylenecyclobutanes has been of long standing interest because of its mechanistic aspects and its synthetic utility [3]. Prompted by our results on the cyclodimerization of diallenyl sulfones by the "carbanion walk" mechanism described above, we decided to investigate the possibility of cyclodimerization of monoallenyl sulfones to 1,3-dimethylenecyclobutanes by the same mechanism [26].



Scheme 11

Treatment of γ,γ-dimethylallenyl phenyl sulfone 41a with n-BuLi in THF at 0° resulted in dimerization to vinylallene 42. However, if the same reaction is run at reflux temperature instead, the expected cyclodimer 43 is obtained, together with the open isomer 42, thus indicating a temperature dependent equilibrium between the two. Obviously, formation of a 1,3-dimethylenecyclobutane requires a higher activation energy than formation of the 2,6-dithiaadamantane skeleton. Subsequently, however, it was found that it is possible to obtain derivatives of 1,3-dimethylenecyclobutane exclusively, even at room temperature or below, if the reaction is performed in the following modified manner (Scheme 12) [26].

For example, reaction of γ,γ-dimethylallenyl phenyl sulfone (41a, R_1=R_2=Me) with n-BuLi in a 1:1 ratio at -78°C gave the corresponding allenyl anion which, on addition of one mole of α,γ,γ-trimethylallenyl phenyl sulfone (44) at the same temperature, followed by trapping with



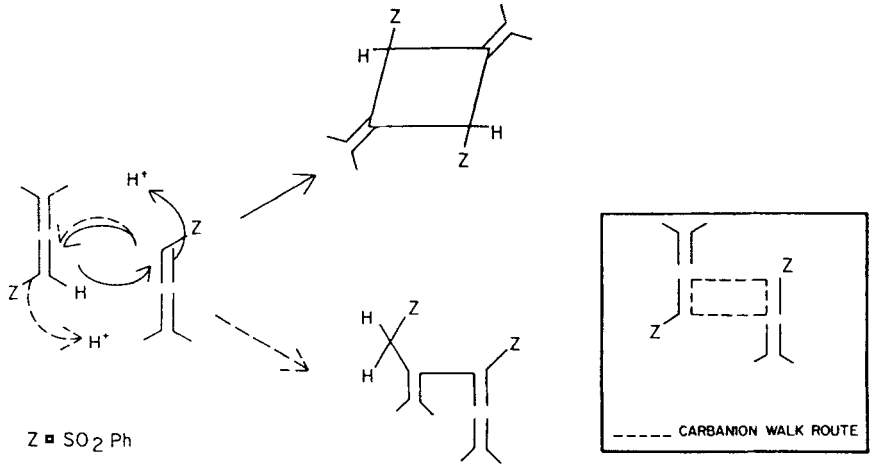
44 41a-c 45-47

	R_1	R_2
45	CH_3	CH_3
46	CH_3	CH_2CH_3
47	CH_3	Ph

Z = SO_2Ph

Scheme 12

iodomethane gave the 1,3-dimethylenecyclobutane derivative 45, as the only product. This result may be explained in terms of the general mechanism suggested for the formation of both vinylallenes and 1,3-dimethylenecyclobutanes (Scheme 13).



Scheme 13

Apparently, the ease of cyclization to compound 43 or compound 45 is controlled by the relative stability of the "allylic" carbanion in the corresponding vinylallene precursor. The exact stereochemistry of compound 45 is shown in Figure 3.

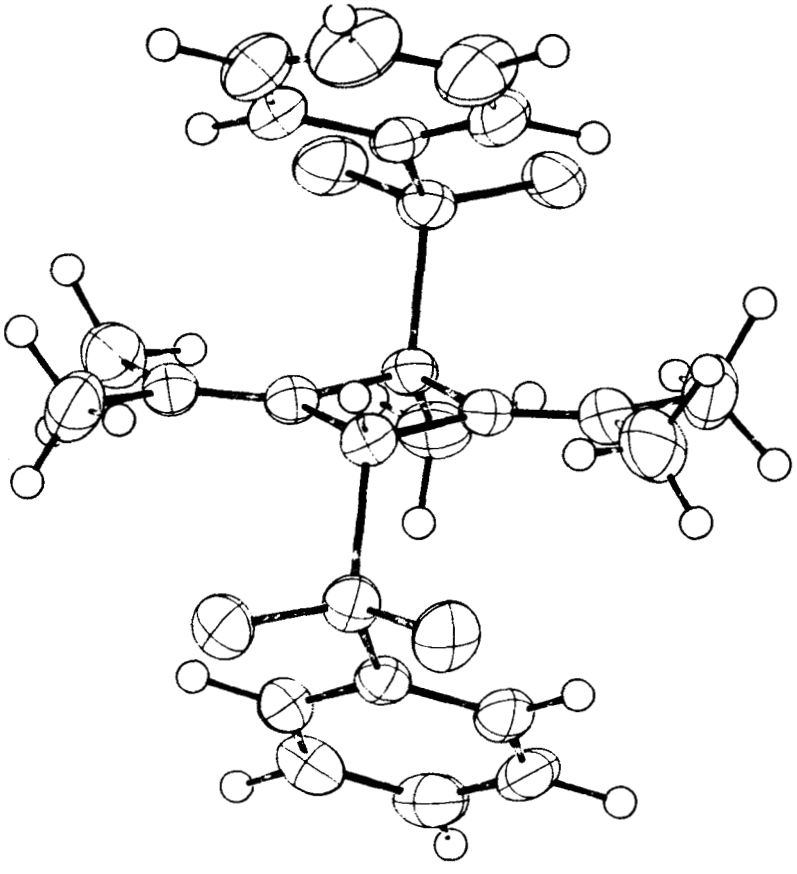


Figure 3: An ORTEP Drawing of the Molecular Structure of 45.

Besides its mechanistic significance both reactions (Scheme 11) are of considerable synthetic utility, especially after reductive desulfurization.
For example, vinylallenes have been of particular interest recently due to their facile [1,5] sigmatropic rearrangement to conjugated trienes [27], while the synthesis of 1,3-dimethylenecyclobutanes nicely complements the thermal cyclodimerization of allenes [3a].

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