The Intramolecular Participation of Sulfide Linkage on the Reactivity of Carbenes and Diazoalkanes. II. Alkylcarbenes and Diazoalkanes Bearing Arylthio and Allylthio Groups on β-Carbon

Kiyosi Kondo and Iwao Ojima
Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229

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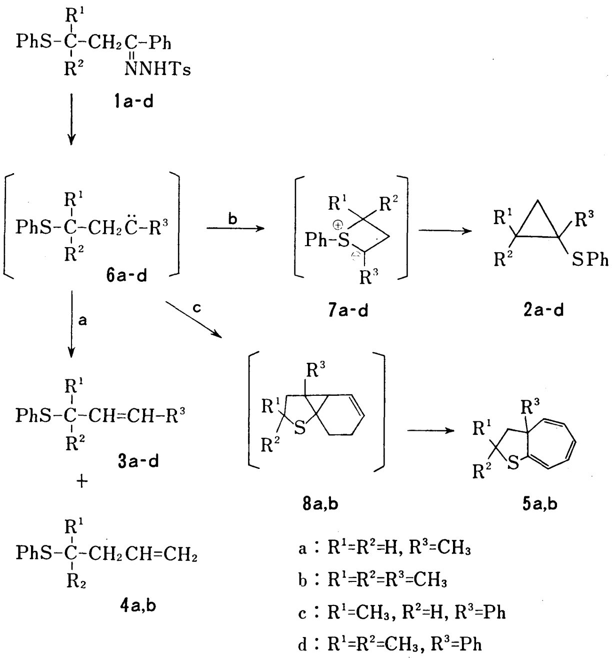
β-Arylthio- and β-allylthioalkylcarbenes were generated from the corresponding ketones by a modification of the Bamford–Stevens method. Chemical evidence for the formation of novel cyclic ylides, *i.e.*, thietanonium ylides, by an intramolecular electrophilic addition of the carbene to the sulfur atom was obtained. The resulting ylides underwent various types of rearrangements to afford cyclopropyl sulfides, thiaazulenes, thietanes, and/or tetrahydrothiophenes. The mechanisms and the relative amounts of the transition energies for these rearrangements are discussed. An intramolecular cycloaddition of β-allyl- and β-crotylthioalkyldiazoalkanes is also described. The final products of the reaction were 3-thiabicyclo[4.1.0]heptanes. A thiabicyclic pyrazoline, which is presumed to be an intermediate of the cycloaddition, could be isolated in the case of the thermal decomposition of 4-allylthio-4-methylpentan-2-one tosylhydrazone.

Many reports on the formation of ylides by the intermolecular electrophilic addition of carbenes to the lone-pair electrons of hetero atoms can be found in the literature.[1] The most representative patterns of these "*intermolecular reactions*" might be summarized as: i) insertion into carbon–hydrogen bonds,[1a] ii) allylic [2,3]sigmatropic rearrangement,[1b] and iii) the formation of stable ylides.[1c] On the contrary, relatively little is known about the *intramolecular* counterpart of this addition, especially in view of the ylide formation.[2,3] When a sulfide linkage is introduced into the same molecule of the carbene, it can be expected that the carbene carbon will be transformed into the ylide carbon by an intramolecular ylide formation.

In the first paper of this series,[4] we reported on the characteristic behavior of the episulfonium ylides produced by the intramolecular addition of α-alkyl and α-arylthioalkylcarbenes. The introduction of the sulfide linkage at the γ-position of the carbene may also cause the cyclization to form four-membered ring ylide. Herein we will describe the behavior of β-aryl-, β-alkyl-, and β-allylthioalkylcarbenes and will present definite evidence for the intramolecular formation of their ylides.[5]

During the course of our study of this subject, we have also found that certain diazoalkanes bearing an allylthio group on β-carbon, a precursor of the carbenes described above, underwent a facile intramolecular cycloaddition to produce bicyclic pyrazolines, which were then transformed into cyclopropanes under the present reaction conditions.[6] As the reaction may open a novel route to thiabicyclic systems, we will also touch briefly on the characteristic behavior of these diazoalkanes.

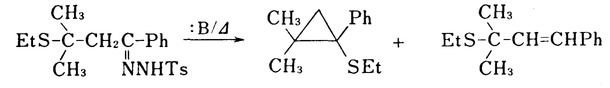
Results



a : R^1=R^2=H, R^3=CH_3
b : R^1=R^2=R^3=CH_3
c : R^1=CH_3, R^2=H, R^3=Ph
d : R^1=R^2=CH_3, R^3=Ph

Scheme 1.

β-Phenylthioalkylcarbenes. The starting materials were prepared by the Michael addition of thiophenol to the appropriate α,β-unsaturated ketones, followed by treatment with *p*-toluenesulfonylhydrazide. The desired carbenes were generated by the thermal decomposition of the sodium salts of the resulting tosylhydrazones (**1a**—**d**) in diglyme at 150—160 °C. The products were separated by column chromatography on silica gel and/or by preparative vpc. The structural assignments were based on the spectra and on the results of elemental analyses. The products caused by intramolecular reactions were olefins (**3** and **4**), cyclopropyl sulfides (**2**), and thiaazulenes (**5**). The patterns for these intramolecular carbene reactions are shown in Scheme 1. The first path, **a**, of these reactions is a usual 1,2-shift of hydrogen, and the second path, **b**, is the intramolecular ylide formation, followed by a novel rearrangement of the phenylthio group. The third path, **c**, is the addition of these carbenes to the benzene nucleus. Thiaazulene might be formed through a valence-bond isomerization of the intermediary-formed norcaradiene, **8**. This is a rare example of the cycloaddition of an alkylcarbene to a benzene nucleus. The finding that no thiaazulenes were obtained in the cases of two carbenes, **6c** and **6d**, must be due to an inherent difference in reactivity between the arylcarbenes and the alkylcarbenes. Accordingly, **3**, **4**, and **5** are supposed to be the products from the carbene process, and **2**, from the ylide process. In order to compare the effect of the phenylthio group with that of the alkylthio group on these two competitive processes, *β*-ethylthio-*β*-methylbutyrophenone tosylhydrazone (**1e**) was decomposed under the same conditions. The product was also found to be a mixture of cyclopropylsulfide (**2e**) and olefins (**3e**) (Scheme 2).

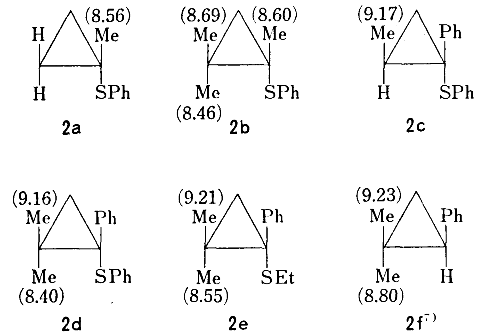


1e 2e 3e

Scheme 2.

Though the photolysis of tosylhydrazone, **1d**, afforded cyclopropyl sulfide, **2d**, in a 37% yield, the olefin, **3d**, was obtained in only 18% yield; the residue was a high-boiling intractable oil. The photolyses of other tosylhydrazones were, therefore, not attempted.

The configuration of the cyclopropyl sulfide, **2c**, was identified as *cis* with respect to the methyl and phenyl groups, based on its NMR spectrum; the methyl of this cyclopropyl sulfide was highly shielded by the *cis* phenyl group and was thus observed at τ 9.17 as a doublet. The discussion of the shielding effect of the *cis* phenyl group in cyclopropane systems advanced by Closs and Moss[7] was also found to be applicable to our systems. In the case of the cyclopropyl sulfide, **2b**, which has no *cis* phenyl group, the methyl absorption was observed at τ 8.69, while the cyclopropyl sulfide, **2d**, displayed an absorption at τ 9.16 which could be assigned to the *cis* methyl, as is shown in Scheme 3.



Scheme 3.

Table 1. Intramolecular reactions of *β*-phenylthio-, and *β*-alkylthioalkylcarbenes in diglyme

Carbene **6**	Total yield(%)[a]	Product ratios (%)[a] **2**	**3**	**4**	**5**
6a	81.2	5.4	77.3[c]	10.6	6.8
6b	90.0	17.4	66.0[d]	7.2	9.4
6c	93.5[b]	31.8	68.2[e]		
6d	94.0	45.5	54.5[d]		
6e	89.5	56.8	43.2[d]		

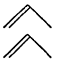
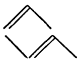
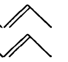
a) Yields were calculated by comparing the vpc peak area of crude products with that of pure samples using a column (1 m) packed with 20% SE-30 or 10% QF-1 on chromosorb W at 140—220 °C. b) There are also obtained 1-methyl-1-phenylthio-2-phenylcyclopropane as an insertion product of the carbene **6c** to a carbon-hydrogen bond. c) *cis*/*trans*=17/83. d) *cis*/*trans*=0/100. e) The olefin **3** (*cis*/*trans*=4/96) contained 1-methyl-3-phenylpropen-1-yl phenyl sulfide (38%), which was proved to be an isomerization product of **3c** by a controlled experiment.[8]

β-Allylthioalkylcarbenes Generated by the Photolyses.

In order to obtain more definite evidence for the intervention of thietanonium ylide, the thermolysis and photolysis of the tosylhydrazone, **1f**, derived from *β*-allylthioalkylphenylketone were performed. We chose **1f** as the substrate because, once the allyl sulfonium ylide is produced, the ylide may undergo a smooth [2,3]sigmatropic rearrangement.

The photolysis of the sodium salt of *β*-allylthio-*β*-methylbutyrophenone tosylhydrazone (**1f**) in monoglyme at 10 °C afforded three products in a total yield of 68.5%. Each of the components was roughly separated by column chromatography on silica and was finally purified by preparative vpc. The identified products were 2-allyl-2-phenyl-4,4-dimethylthietane (**10a**), 2-vinyl-3-phenyl-5,5-dimethyltetrahydrothiophene (**11a**), and 1-phenyl-3-allylthio-3-methyl-1-butene (**12a**). The formation of thietane **10a** demonstrates that a definite chemical bond is formed between the carbene carbon and the sulfur; that is, there is an intervention of thietanonium ylide, **13a**. The succeeding

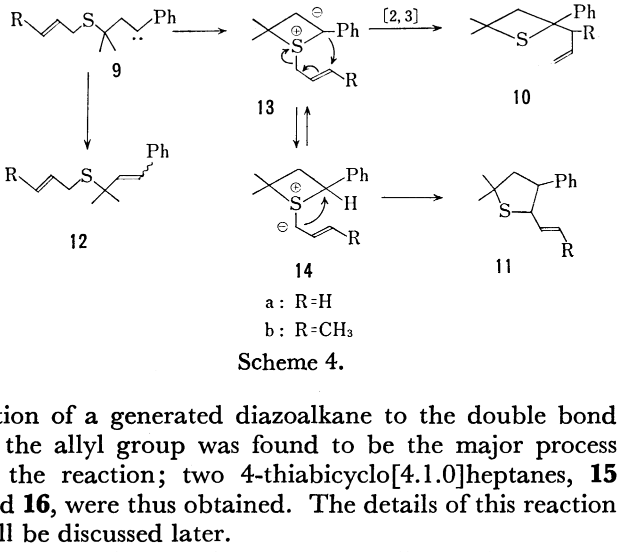
Table 2. Intramolecular reactions of *β*-allylthio- and *β*-benzylthioalkylcarbenes

Carbene **9** R	Method of generation	Total yields[a] (%)	Product ratios[a] **10**	**11**	**12**	**15**
9a 	*hν*	68.5	20.7	32.3[b]	47.0[c]	
9a 	*Δ*	47.7	7.2	—	2.9	89.9
9b 	*hν*	55.8	25.3[d]	33.2[e]	41.5[f]	
9b 	*Δ*	49.8	2.7	3.2	6.2	87.9[g]
9c $PhCH_2$	*hν*	57.2	17.0[h]	33.0[h]	50.0[i]	
9c $PhCH_2$	*Δ*	57.8	20.0	27.3[j]	52.7[k]	

a) See footnote a) in Table 1. b) *cis*/*trans*=58/42. c) *cis*/*trans*=40/60. d) mixture of diastereoisomers in the ratio of 56: 44. e) *cis*/*trans*=58/42. f) *cis*/*trans*=49.5/50.5. g) *exo*/*endo*=74.5/25.5. h) *cis*/*trans*=50/50. i) *cis*/*trans*=0/100. j) *cis*/*trans*=58/42. k) *cis*/*trans*=27/73.

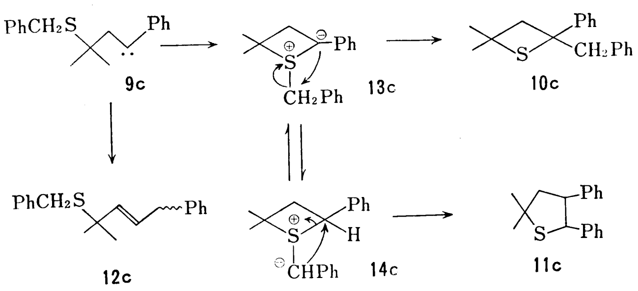
[2,3]sigmatropic rearrangement of the allylsulfonium ylide affords the thietane, **10a**, as the final product. In order to establish the [2,3]sigmatropic rearrangement and to exclude the possibility of a Stevens-type 1,2-shift of the allylic substituent, 3-crotylthio-3-methylbutyrophenone tosylhydrazone (**1g**) was photolyzed under the same conditions. The identified products were 2-(1-methylallyl)-2-phenyl-4,4-dimethylthietane (**10b**), 2-(1-propenyl)-3-phenyl-5,5-dimethyltetrahydrothiophene (**11b**), and 1-phenyl-3-crotylthio-3-methyl-1-butene (**12b**). The thietane, **10b**, was obtained as a mixture of diastereoisomers (56:44); the tetrahydrothiophene, **11b**, was also a mixture of *cis* and *trans* isomers. The facts that no 2-crotyl-2-phenyl-4,4-dimethylthietane was obtained, but **10b** was, clearly indicate the exclusive occurrence of [2,3]sigmatropic rearrangement.

The relatively high yield production of the tetrahydrothiophenes, **11a** and **11b**, deserves to be mentioned. The formation of these five-membered ring products can also be explained by assuming the intervention of the ylide, **13**. Thus, an ylide exchange reaction of **13** to the exocyclic ylide, **14**, followed by a Stevens-type rearrangement, may constitute the ring-enlargement process. The total yield and the products ratio are listed in Table 2. In the thermolyses of the tosylhydrazones, **1f** and **1g**, an intramolecular 1,3-cycloaddition of a generated diazoalkane to the double bond of the allyl group was found to be the major process of the reaction; two 4-thiabicyclo[4.1.0]heptanes, **15** and **16**, were thus obtained. The details of this reaction will be discussed later.



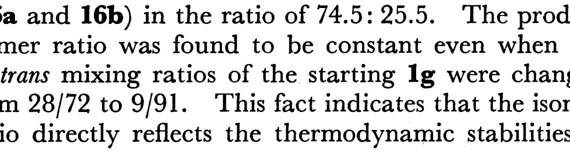
Scheme 4.

β-Benzylthioalkylcarbenes. The ylide-exchange reaction observed in the case of *β*-allylthioalkylcarbene is expected to be characteristic of systems in which the intermediate cyclic ylide has an acidic hydrogen on the exocyclic α-carbon of the sulfonium function. Thus, an intramolecular reaction of the carbene-bearing benzylthio group on *β*-carbon was further investigated. The carbene was generated by the thermolysis or photolysis of the corresponding tosylhydrazone (**1h**). Besides the olefin, **12c**, caused by the carbenic process, two products were isolated from the reaction mixture. One was identified as the tetrahydrothiophene, **11c**, by means of its spectra and by elemental analysis; it is the expected product from the ylide-exchange reaction. The other was proved to be the thietane, **10c**, which must be formed through a Stevens-type rearrangement of the intermediate ylide, **13c**.



Scheme 5.

β-Allylthioalkyl Diazoalkanes Generated by the Thermolyses. *β*-Allylthio-*β*-methylbutyrophenone tosylhydrazone (**1f**) was thermally decomposed in diglyme in the presence of sodium methoxide at 150 °C. When the reaction mixture was chromatographed on silica, 4,4-dimethyl-6-phenyl-3-thiabicyclo[4.1.0]heptane (**15**) was obtained as the predominant product (Scheme 6). The analysis of the reaction mixture revealed that small amounts of thietane, **10a**, and the **12a** olefin were also present in the product (Table 2). Similarly, the thermolysis of *β*-crotylthio-*β*-methylbutyrophenone tosylhydrazone (**1g**) afforded 6-phenyl-4,4,7-trimethyl-3-thiabicyclo[4.1.0]heptane (**16**) in a 44% yield, accompanied by small amounts of thietane, **10b**, tetrahydrothiophene, **11b**, and the **12b** olefin. The photolyses of these *β*-allylthio compounds at 10 °C underwent a completely different process, *i.e.*, a carbenic process, as has been described in the previous section. Thus, the formation of the two 3-thiabicyclo[4.1.0]heptanes, **15** and **16**, may mean that an intramolecular cycloaddition of the diazoalkane moiety to the double bond of the allylthio group and a subsequent elimination of the molecular nitrogen really do occur under the thermolysis conditions.

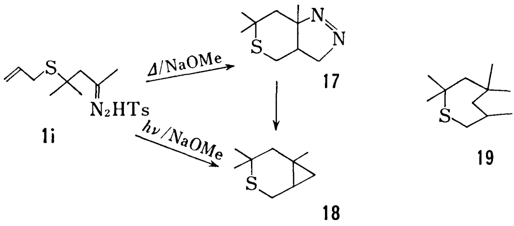


Scheme 6.

The NMR spectrum and vpc analysis of the product indicated that **16** is a mixture of *exo*- and *endo*-isomers (**16a** and **16b**) in the ratio of 74.5:25.5. The product isomer ratio was found to be constant even when the *cis-trans* mixing ratios of the starting **1g** were changed from 28/72 to 9/91. This fact indicates that the isomer ratio directly reflects the thermodynamic stabilities of the products.

Conclusive evidence for the intramolecular thermal cycloaddition of these diazoalkanes was obtained when 4-allylthio-4-methyl-2-pentanone tosylhydrazone (**1i**) was used as a substrate. That is, the thermal decomposition of **1i** in the presence of sodium methoxide at 150 °C afforded the bicyclic pyrazoline, **17**, in a 33% yield. On the other hand, the photolysis of the sodium salts of **1i** at 10 °C for two hours yielded 4,4,6-trimethyl-3-thiabicyclo[4.1.0]heptane (**18**) in a 48% yield. Furthermore, the irradiation of the bicyclic pyrazoline,

17, under the same conditions produced the same product, **18**, in a good yield.



Scheme 7.

Two orientations are possible in considering the intramolecular cycloaddition. The one possible product is **17**, and the other is **19**. The structure of the obtained product was deduced to be **17** on the basis of its NMR spectrum: the chemical shift of the C-3 methylene of the pyrazoline ring was observed at 4.31 ppm (2H) from TMS. This value is in accordance with that reported for vicinal methylenes of the azo function in a usual pyrazoline system.[9] On the other hand, the C-9 methylene of the diazabicyclononene, **19**, is expected to absorb in a much higher field.[9]

The photochemical *in-situ* generation of carbenes from tosylhydrazones has been reported to proceed through diazo precursors.[10] Therefore, it can be concluded that the intramolecular thermal cycloaddition of the diazo compound derived from **1i** is a facile process, even at 10 °C, and that the succeeding elimination of nitrogen is an effective process under photolytic conditions.

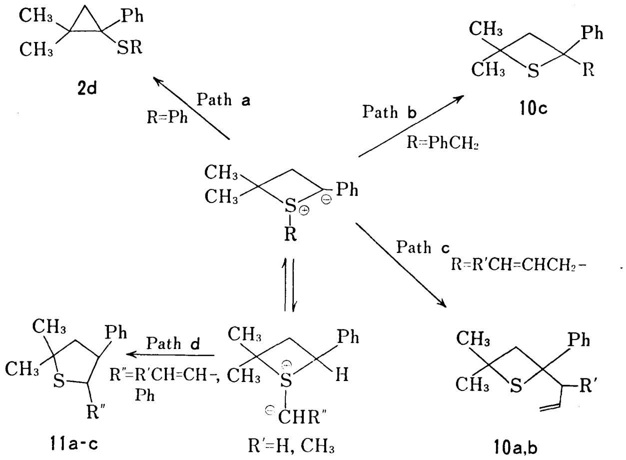
Discussion

In all the cases examined, the carbene with sulfide functions on β-carbon underwent two types of reaction: i) a normal carbene reaction, and ii) an intramolecular formation of the cyclic ylide. The relative dominance of these two processes, however, seems to be markedly affected by the nature of the substituents. The relative ratios of these two processes, along with the variation in the substituents, are summarized in Table 3.

The data on the reaction of the carbenes, **6a**—**6d**, clearly indicate that the ylide process is dramatically favored when the substituent on the carbene carbon is changed from methyl to phenyl and when the number of substituents on the β-carbon is increased. These phenomena can be explained as follows. The phenyl on the ylide carbon may stabilize the ylide by its inductive effect, and the methyl(s) on the β-carbon may favor the formation of the four-membered ring by their steric repulsion. From the steric and electronic points of view, it seems plausible that an alkylthio group on the β-carbon of the carbene would favor the intramolecular formation of the ylide, as compared with the phenylthio group. However, the data on the reactivities of the **6d** and **6e** carbenes tell us that there is no significant difference between these two groups. The results indicate that the basicity of the sulfur atom, as well as the steric bulk of the substituent on the sulfur, may not be at all important in determining the ratio of these two processes. On the other hand, a comparison of the data on the reactivities of the **6e** carbene with those on **9a**—**9c** suggests that the efficiency of the product-forming steps, *i.e.*, the rearrangement of the intermediate ylide, seems to have influence on the relative dominance of these two processes. That is, the results indicate that the ylide process gains an advantage over the carbene process when the thietanonium ylide thus formed can undergo a rearrangement with a lower transition energy (*vide infra*).

Table 3. The percentage ratios of the carbene process *vs.* ylide process

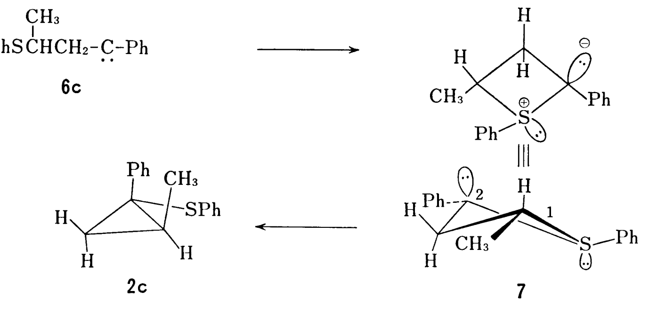
	$R^1S\text{-}\overset{R^2}{\underset{R^3}{C}}\text{-}CH_2\text{-}\underset{\cdot\cdot}{C}\text{-}R^4$				Carbene (%)	Ylide (%)
No.	R¹	R²	R³	R⁴		
6a	Ph	H	H	Me	94.6	5.4
6b	Ph	Me	Me	Me	82.6	17.4
6c	Ph	Me	H	Ph	68.2	31.8
6d	Ph	Me	Me	Ph	54.5	45.5
6e	Et	Me	Me	Ph	56.8	43.2
9a	C_3H_5	Me	Me	Ph	47.0	53.0
9b	C_4H_7	Me	Me	Ph	41.5	58.5
9c	$PhCH_2$	Me	Me	Ph	50.0	50.0



Scheme 8.

On the basis of the results collected in Tables 1 and 2, a discussion of the relative heights of the transition energies in the rearrangements of the thietanonium ylides can now be undertaken. Four different pathways of the rearrangements observed are summarized in Scheme 8. Path **a** is the rearrangement process which affords cyclopropyl sulfides. Path **b** is the Stevens-type rearrangement of the benzyl group on sulfur to give the thietane. Path **c** is the [2,3]sigmatropic rearrangement observed in the β-allylthio system, and Path **d** is the ring-enlargement process *via* the ylide-exchange reaction. In the β-allylthio and β-crotylthio systems, all four pathways are, in principle, possible. However, only two products through Paths **c** and **d** could be observed in the reaction mixture. Accordingly, the thietane formation by [2,3]sigmatropic rearrangement and tetrahydrothiophene formation by ylide-exchange reaction may have lower transition energies than those of Paths **a** and **b**. Furthermore, the product ratios listed in Table 2 reveal that Path **d** predominates over Path **c**. In the β-benzylthio system, only Paths **b** and **d** were observed, though Path **a** was also a possible candidate for this system. Thus, it can be said that Path **a** has the highest transition energy. In conclusion, the order of the transition energies in these four processes may be as follows: Path **a**>Path **b**>Path **c**>Path **d**.

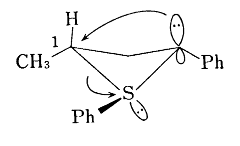
The next discussion will concern the stereospecificity of the reaction which affords the only isomer of the cyclopropyl sulfide (**2c**). An inspection of the Dreiding model indicated that the most stable conformation of the ylide might be the one that minimizes the steric repulsion between substituents and the electronic repulsion between lone pairs; this conformation has two phenyl groups and a methyl group in *pseudo-equatorial* positions, and two lone paris in *pseudo-axial* positions, as is shown in Scheme 9. Therefore, in order to accommodate the observed stereospecificity, an inversion of the configuration at C^1 or C^2 must occur during the ring contraction.



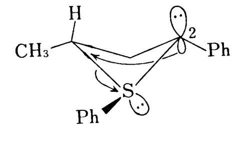
Scheme 9.

Three mechanisms (Scheme 10) can be considered for this stereospecific reaction. The first one is a concerted mechanism with an inversion of the configuration at C^1; the ylide lone pair attacks from the back side of the cleaving carbon–sulfur bond (Mechanism 1.).

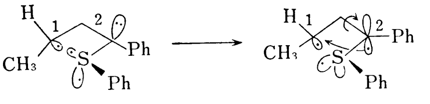
Mechanism 1. Concerted process (inversion at C^1)



Mechanism 2. Concerted process (inversion at C^2)

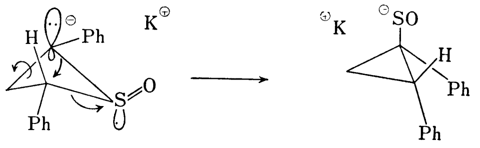


Mechanism 3. Radical pair process (inversion at C^2)



Scheme 10.

The second one is also a concerted mechanism, but with an inversion at C^2; a partially developed back lobe of the carbanion attacks C^1 from the front side, with a retention of the configuration at C^1. This mechanism has some similarity to the so-called "*double inversion mechanism*" proposed by Bordwell *et al.* in the case of the 1,3-elimination of α-halosulfones.[11] The third one is a radical-pair mechanism. This mechanism has been confirmed for the Stevens rearrangements of certain ylides[12] and is known to proceed with a retention of the configuration at the migrating carbon, C^1.[13] This means that the inversion must occur at C^2. As far as we know, however, there has never been observed such a stereospecificity at the migrating terminus in a Stevens rearrangement. On the other hand, a stereospecific rearrangement of 2,4-diphenylthietane-1-oxide to the anion of cyclopropylsulfenic acid in the presence of a base has recently been reported by Dodson *et al.*[14] They proposed that the stereospecific reaction proceeded through the most stable conformation of the anion produced and that, therefore, an inversion of the configuration should occur at the carbanion carbon.



Their observation corresponds well to the results obtained in our system and supports the concerted Mechanism 2 for the rearrangement of the thietanonium ylide, **7**.

In connection with the mechanism of the formation of the 3-thiabicyclo[4.1.0]heptanes, **15** and **16**, it is worth-while to discuss the stereochemistry of the reaction. The cycloaddition of a diazoalkane to carbon–carbon double bonds is assumed to be a stereospecific concerted process.[15] Therefore, the formation of *exo*-methylpyrazoline (A) from the tosylhydrazone bearing *trans*-crotyl group is an allowed process, while the formation of the corresponding *endo*-isomer from the same precursor is strongly forbidden.

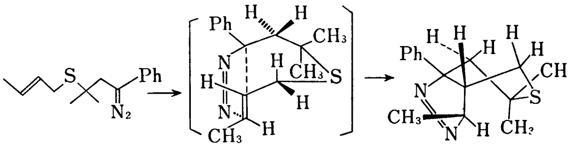
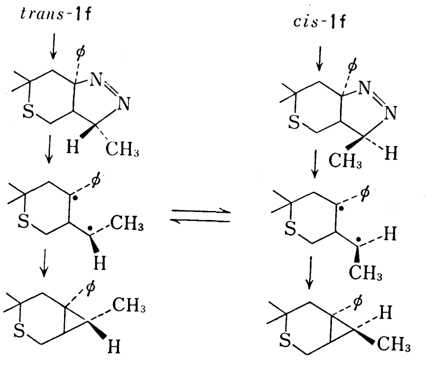


Fig. 2.

The final product, **16**, which is produced by the nitrogen elimination of the intermediary-formed pyrazoline, dose not retain the stereochemical integrity of the starting materials. Thus, the stereochemical crossover should occur at the stage of radical recombination, as is shown in the following scheme.

The high efficiency of the *intramolecular* cycloaddition observed in the β-allylthio system is probably due chiefly to the intramolecular nature of the reaction. Another factor, however, must be considered in order to explain the results, because the addition of a diazoalkane to nonconjugated olefins is usually a very slow and difficult process.[15,16] One possible interpretation is that some kind of activating effect of the allylic sulfur atom on the double bond is operating in these systems.[17]



16a 16b

Scheme 11.

Experimental

Measurements. The melting points and boiling points were uncorrected. The infrared spectra were recorded on a Hitachi-Perkin-Elmer Model 337 Infracord or a Hitachi EPI-G3 spectrophotometer, using as samples neat liquids, KBr disks, or Nujol mulls. The nuclear magnetic resonance spectra were obtained by the use of a Varian HA-100 or a Hitachi R20-B spectrometer, using TMS as the internal standard. The mass spectra were measured using a Hitachi RMU-6E spectrometer at 70 eV. Analytical gas chromatography (vpc) was carried out on a Hitachi K-53 equipped with a flame-ionization detector. The total yield and product ratios were determined by the vpc using a column packed with 20% SE-30 or 10% QF-1 on Chromosorb W. Preparative gas chromatography was performed with an Aerograph A-700 instrument or a Hitachi KGL-2B instrument using a 4 mm×1 m column packed with 3% SE-30 or 20% XF-1150 on Chromosorb W. The photolyses were carried out with the use of a 450-W high-pressure mercury lamp (Ushio Electric, Inc.).

Preparation of Tosylhydrazones. The Bamford-Stevens method[18,19] was employed for the *in-situ* generation of carbenes and diazoalkanes. Thus, the required tosylhydrazones were prepared by the condensation of the corresponding ketones with *p*-toluenesulfonylhydrazide.

*4-Phenylthio-2-butanone Tosylhydrazone (**1a**).* 4-Phenylthio-2-butanone was prepared by the addition of thiophenol to methyl vinyl ketone.[20] 4-Phenylthio-2-butanone (5 g, 0.0278 mol) and *p*-toluenesulfonylhydrazide (6 g, 0.0322 mol) were dissolved in 100 ml of ethanol, after which the solution was heated to reflux for an hour. The reaction mixture was cooled with dry ice and gradually warmed to room temperature. The precipitated colorless needles of the corresponding tosylhydrazone (**1a**) were collected by filtration. Yield: 8.24 g; 85%; mp 100—101 °C. Found: C, 58.38; H, 5.84; N, 8.15; S, 18.53%. Calcd for $C_{17}H_{21}N_2O_2S_2$: C, 58.59; H, 5.78; N, 8.04; S, 18.40%.

*4-Phenylthio-4-methyl-2-pentanone Tosylhydrazone (**1b**).* To a mixture of mesityl oxide (25 g, 0.255 mol) and thiophenol (28 g, 0.255 mol), we added a few drops of piperidine. After an initial exothermic reaction had subsided, the reaction mixture was further stirred with a magnetic stirrer overnight at room temperature. 4-Phenylthio-4-methyl-2-pentanone[21] was obtained by the distillation of the reaction mixture under reduced pressure. Yield: 42.5 g; 80%; bp 109 °C/0.35 mmHg. NMR (CCl_4): τ 8.65 (s, 6H), 7.97 (s, 3H), 7.44 (s, 2H), and 2.90—2.40 (m, 5H). The corresponding tosylhydrazone (**1b**) was prepared by a method similar to that described above. Mp 109—110 °C (colorless needles). Found: C, 60.38; H, 6.59; N, 7.37; S, 16.88%. Calcd for $C_{19}H_{25}N_2O_2S_2$: C, 60.61; H, 6.42; N, 7.44; S, 17.03%.

*3-Phenylthiobutyrophenone Tosylhydrazone (**1c**).* Phenyl propenyl ketone was prepared from crotonyl chloride and benzene employing the Friedel-Crafts method.[22] The base-catalyzed addition of thiophenol to the ketone, as has been described in the previous section, produced 3-phenylthiobutyrophenone; 86%; bp 167 °C/0.25 mmHg. Tosylhydrazone **1c**: mp 128—129 °C (colorless needles). Found: C, 64.65; H, 5.95; N, 6.43; S, 15.09%. Calcd for $C_{23}H_{25}N_2O_2S_2$: C, 64.86; H, 5.70; N, 6.60; S, 15.10%.

*3-Phenylthio-3-methylbutyrophenone Tosylhydrazone (**1d**).* Isopropylideneacetophenone was prepared from 3-methylcrotonyl chloride and benzene by the method of Smith and Engelhardt,[23] with some modifications. 3-Phenylthio-3-methylbutyrophenone was synthesized by the base-catalyzed addition of thiophenol to the ketone; 88%; bp 178—181 °C/1.0 mmHg, NMR (CCl_4): τ 8.57 (s, 6H), 6.90 (s, 2H) and 2.95—2.20 (m, 10H). Tosylhydrazone **1d**: mp 110—111 °C (colorless needles). Found: C, 65.74; H, 5.97; N, 6.45; S, 14.51%. Calcd for $C_{24}H_{26}N_2O_2S_2$: C, 65.72; H, 5.97; N, 6.39; S, 14.62%.

*3-Ethylthio-3-methylbutyrophenone Tosylhydrazone (**1e**).* The base-catalyzed addition of ethanethiol to isopropylideneacetophenone afforded 3-ethylthio-3-methylbutyrophenone: bp 127 °C/0.4 mmHg. NMR (CCl_4): τ 8.80 (t, J=7 Hz, 3H), 8.52 (s, 6H), 7.43 (quartet, J=7 Hz, 2H), 6.81 (s, 2H,) and 2.80—1.90 (m, 5H). Tosylhydrazone **1e**: mp 160—161 °C (colorless needles). Found: C, 61.55; H, 6.65; N, 7.45; S, 16.42%. Calcd for $C_{20}H_{26}O_2S_2N_2$: C, 61.51; H, 6.71; N, 7.17; S, 16.65%.

*3-Allylthio-3-methylbutyrophenone Tosylhydrazone (**1f**).* 3-Allylthio-3-methylbutyrophenone was prepared by the addition reaction of 2-propenethiol to isopropylideneacetophenone: bp 122 °C/0.3 mmHg. NMR (CCl_4): τ 8.52 (s, 6H), 6.80 (s, 2H), 6.78 (d, J=7 Hz, 2H), 5.10—4.65 (m, 2H), 4.50—3.90 (m, 1H) and 2.70—2.00 (m, 5H). The ketone was converted to the corresponding tosylhydrazone by treatment with an equimolar amount of tosylhydrazide in the presence of a catalytic amount of sulfuric acid. The use of an excess of tosylhydrazide should be avoided, as it was found that the existing allylic double bond was partially hydrogenated under such circumstances. Tosylhydrazone **1e**: mp 135—136 °C (colorless prisms). Found: C, 62.60; H, 6.26; N, 7.13; S, 15.66%. Calcd for $C_{21}H_{26}N_2O_2S_2$: C, 62.65; H, 6.51; N, 6.96; S, 15.93%.

*3-Crotylthio-3-methylbutyrophenone Tosylhydrazone (**1g**).* 2-Butenethiol was prepared from crotyl alcohol according to the standard procedure.[24] The *cis/trans* isomer ratio of crotyl alcohol was determined on the basis of the NMR spectrum, employing $Eu(DPM)_3$ as a shift reagent, and by vpc analysis, using a column packed with 20% XF-1150. According to the spectrum, a commercial-grade crotyl alcohol has a *trans/cis* ratio of 72/28. An alcohol with a *trans/cis* ratio of 91/9 was obtained by fractional distillation through a spinning-band column.

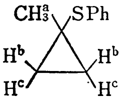
3-Crotylthio-3-methylbutyrophenone was synthesized from the 2-butanethiol and isopropylideneacetophenone in a manner similar to that described before: bp 142 °C/0.2 mmHg. NMR (CCl_4): τ 8.54 (s, 6H), 8.32 (d, J=4 Hz, 3H), 6.84 (d, J= 7 Hz, 2H), 6.82 (s, 2H), 4.64—4.20 (m, 2H), and 2.70—2.00 (m, 5H).

The condensation of the ketone with tosylhydrazide afforded the corresponding tosylhydrazone (**1g**): mp 97—98 °C (colorless prisms). Found: C, 63.88; H, 6.67; N, 6.55; S, 15.77%. Calcd for $C_{22}H_{28}N_2O_2S_2$: C, 63.63; H, 6.77; N, 6.72; S, 15.39%.

*3-Benzylthio-3-methylbutyrophenone Tosylhydrazone (**1h**).* The desired tosylhydrazone was prepared from tosylhydrazide and 3-benzylthio-3-methylbutyrophenone. The latter was obtained by the addition of phenylmethanethiol to isopropylideneacetophenone in a manner similar to that described previously. 3-Benzylthio-3-methylbutyrophenone: NMR (CCl_4): τ 8.52 (s, 6H), 6.90 (s, 2H), 6.27 (s, 2H) and 2.90—2.10 (m, 10H). Tosylhydrazone **1h**: mp 93—94 °C (colorless prisms). Found: C, 65.88; H, 6.27; N, 6.24; S, 14.14%. Calcd for $C_{25}H_{28}N_2O_2S_2$: C, 66.04; H, 6.24; N, 6.19; S, 14.17%.

*4-Allylthio-4-methyl-2-pentanone Tosylhydrazone (**1i**).* The base-catalyzed addition of 2-propenethiol to mesityl oxide produced 4-allylthio-4-methyl-2-pentanone, which was then further converted to the corresponding tosylhydrazone (**1i**). 4-Allylthio-4-methyl-2-pentanone: bp 67 °C/1.0 mmHg. NMR (CCl_4): τ 8.60 (s, 6H), 7.80 (s, 3H), 7.37 (s, 2H), 6.82 (d, J=7 Hz, 2H), 5.10—4.65 (m, 2H) and 4.50—3.80 (m, 1H). Tosylhydrazone **1i**: mp 75—76 °C (colorless prisms). Found: C, 56.41; H, 6.99; N, 8.36; S, 18.84%. Calcd for $C_{16}H_{24}N_2O_2S_2$: C, 56.44; H, 7.10; N, 8.23; S, 18.83%.

*Thermal Decomposition of **1a**.* In a flask equipped with a reflux condenser a 1.04 g portion (3.0 mmol) of the **1a** tosylhydrazone was dissolved in 40 ml of diglyme, and then a 180 mg portion (*ca.* 0.35 mmol) of sodium hydride (50% suspension in mineral oil) was stirred in. After the gas evolution had ceased, the reaction flask was immersed in an oil bath heated at 180 °C. Thermolysis was monitored by nitrogen evolution, which was completed in the temperature range of 130—150 °C. The reaction mixture was heated to reflux for 15 minutes and was then left to cool at room temperature. The sodium *p*-toluenesulfinate thus precipitated was filtered off, and the filtrate was distilled under reduced pressure to remove the solvent. The residue was then submitted to column chromatography on silica (WAKO C-200), using *n*-hexane as the eluent. 1-Methylcyclopropyl phenyl sulfide (**2a**), 3a-methyl-1,2,3,3a-tetrahydro-1-thiaazulene (**5a**), and a mixture of 2-butenyl phenyl sulfide (**3a**) and 3-butenyl phenyl sulfide (**4a**) were eluted, in this order. Although the **3a** and **4a** olefins could not be completely separated by either column chromatography on silica or gas chromatography, the NMR spectrum of the mixture supported the structures. The ratio of these olefins could be calculated from the spectrum. When sodium methoxide was used as the base, cyclopropyl sulfide, **2a**, could not be detected in the product; furthermore, the total yield of the isolable product decreased. **2a**: NMR (CCl_4): τ 9.14 (H^b and H^c: ABq, J=7 Hz, 4H), 8.56 (H^a: s, 3H) and 3.00—2.70 (Ph: m, 5H).



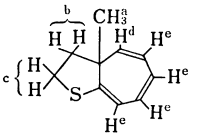
3a: NMR (CCl_4): *cis* and *trans* τ 8.43 (*cis*-H^a: d, Jad=7 Hz) and 8.35 (*trans*-H^a: d, Jad=7 Hz) (3H), 6.65—6.45 (H^b: m, 2H), 4.62—4.44 (H^c and H^d: m, 2H), and 3.00—2.65 (Ph: m, 5H). IR (neat): 958 cm⁻¹ ($\delta_{HC=CH}$). Mass: 164 (M^+), 149 (M^+-CH_3), 110 ($PhSH^+$), 109 (PhS^+), 77 (Ph^+), and 55 (M^+-PhS).

$$\mathrm{PhS\overset{b}{C}H_2\overset{c}{C}H{=}\overset{d}{C}H{-}\overset{a}{C}H_3}$$

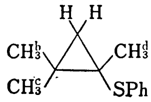
4a: NMR (CCl_4): τ 7.66 (H^b: q, Jab=Jbc=7 Hz, 2H), 7.10 (H^a: t, Jab=7 Hz), 5.10—4.65 (H^c and H^d: m, 3H), and 3.00—2.65 (Ph: m, 5H).

$$\mathrm{PhS\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H{=}\overset{d}{C}H_2}$$

5a: NMR (CCl_4): τ 9.15 (H^a: s, 3H), 7.65 (H^b: octet, 2H), 7.20 (H^c: octet, 2H), 5.01 (H^d: d, Jde=10 Hz, 1H), and 4.20—3.80 (H^e: m, 4H). Found: (a mixture of products, **2a**—**5a**): C, 73.00; H, 7.15; S, 19.25%. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36; S, 19.52%.



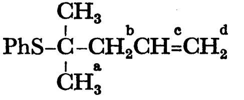
*Thermal Decomposition of **1b**.* The sodium salt of **1b** was prepared and decomposed in diglyme under the conditions described above. The crude products were chromatographed on silica, and 1,3,3-trimethylcyclopropyl phenyl sulfide (**2b**), 2,2,3a-trimethyl-1,2,3,3a-tetrahydro-1-thiaazulene (**5b**), 4-phenylthio-4-methyl-2-pentene (**3b**), and 4-phenylthio-4-methyl-1-pentene (**4b**) were eluted by *n*-hexane. The pure **3b** olefin was obtained by column chromatography, but the **4b** olefin could not be separated from the **3b** olefin. The pure sample of the **4b** olefin was, however, obtained from the reaction performed in a protic solvent. Although cyclopropyl sulfide, **2b**, and thiaazulene, **5b**, were obtained as a mixture by column chromatography on silica, further purification by preparative vpc afforded pure samples. In this case, the use of sodium methoxide as a base resulted in similar products. **2b**: NMR (CCl_4): τ 9.29 (H^a: ABq, J=5.0 Hz, 2H), 8.69 (H^b: s, 3H), 8.60 (H^d: s, 3H), 8.46 (H^c: s, 3H), and 3.20—2.80 (Ph: m, 5H). Mass: 192 (M^+, base peak), 177 (M^+-CH_3). 110 ($PhSH^+$), 109 (PhS^+), 83 (M^+-PhS), and 77 (Ph^+). Found: C, 74.78; H, 8.16; S, 16.89%. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39; S, 16.67%.



3b: NMR (CCl_4): *trans* τ 8.70 (H^a: s, 6H), 8.39 (H^b: d, Jbd=6 Hz, 3H), 5.00 (H^d: octet, Jcd=16 Hz, 1H), 4.52 (H^c: d, Jcd=16 Hz, 1H), and 2.95—2.50 (Ph: m, 5H). IR (neat): 963 cm⁻¹ ($\delta_{HC=CH}$).

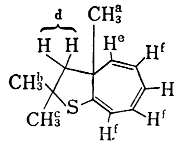
$$\mathrm{PhS{-}\underset{\overset{|}{\overset{a}{C}H_3}}{\overset{\overset{a}{C}H_3}{\underset{|}{C}}}{-}\overset{c}{C}H{=}\overset{d}{C}H{-}\overset{b}{C}H_3}$$

4b: NMR (CCl_4): τ 8.82 (H^a: s, 6H), 7.83 (H^b: d, Jbc=6 Hz, 2H), 4.40—3.75 (H^c and H^d: m, 3H), and 2.95—2.50 (Ph: m, 5H). Found (a mixture of **3b** and **4b**): C, 74.82; H, 8.35; S, 16.66%. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39; S, 16.67%.



$$\mathrm{PhS{-}\underset{\overset{|}{\overset{a}{C}H_3}}{\overset{\overset{a}{C}H_3}{\underset{|}{C}}}{-}\overset{b}{C}H_2\overset{c}{C}H{=}\overset{d}{C}H_2}$$

5b: NMR (CCl_4): τ 9.07 (H^a: s, 3H), 8.53 (H^b: s, 3H), 8.40 (H^c: s, 3H), 7.70 (H^d: s, 2H), 4.94 (H^e: d, Jef=10 Hz, 1H), and 4.20—3.70 (H^f: m, 4H). Found: C, 74.68; H, 8.40; S, 16.94%. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39; S, 16.69%.

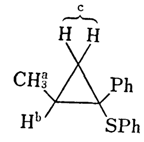


Thermal Decomposition of **1c**. The **1c** tosylhydrazone (1.49 g, 4.0 mmol) was decomposed in the presence of 220 mg of sodium methoxide in diglyme under the conditions described above. The crude products were submitted to column chromatography on silica, and 3-methyl-1-phenylcyclopropyl phenyl sulfide (**2c**), 3-phenyl-1-methylcyclopropyl phenyl sulfide (**20**), and 1-phenyl-3-phenylthio-1-butene, **3c**, (*cis* and *trans*) were eluted by *n*-hexane. Although cyclopropyl sulfide, **20**, could not be separated from cyclopropyl sulfide, **2c**, by the column chromatography, purification by preparative vpc gave a pure sample. Both *cis* and *trans* **3c** olefins were successfully isolated by column chromatography.

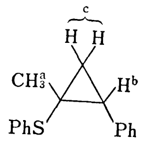
When sodium hydride was used as a base instead of sodium methoxide, 1-phenyl-3-phenylthio-2-butene (*cis*/*trans*=50/50) (**3c′**) was obtained, together with the **3c** olefin in the ratio of 38/62. Pure samples of *cis* and *trans* isomers of the **3c′** olefin were obtained by column chromatography on silica.

In a control experiment, the **3c** olefin (100 mg) was treated with 20 mg of sodium hydride in 50 ml of diglyme under reflux for 15 min.[8] The reaction mixture was concentrated under reduced pressure, dissolved in chloroform, washed with water, dried over anhydrous magnesium sulfate, and then concentrated again. A study of the NMR spectrum of the reaction mixture revealed the formation of a mixture of the **3c** and **3c′** olefins in the ratio of 60/40.

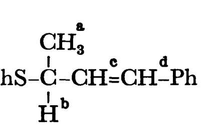
2c: NMR (CCl_4): τ 9.17 (H^a: d, *J*ab=6 Hz, 3H), 9.00—8.20 (H^b and H^c: m, 3H), and 3.10—2.75 (Ph: m, 10H). Mass: 240 (M^+). 225 (M^+-CH_3), 163 (M^+-Ph), 131 (M^+-PhS, base peak), 110 ($PhSH^+$), 109 (PhS^+), and 77 (Ph^+). Found: C, 79.72; H, 6.49; S, 13.60%. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71; S, 13.34%.



20: NMR (CCl_4): τ 9.10—8.10 (H^b and H^c: m, 3H), 8.57 (H^a: s, 3H), and 3.10—2.70 (Ph: m, 10H). Mass: 240 (M^+-CH_3), 131 (M^+-PhS, base peak), 109 (PhS^+), 91 ($C_7H_7^+$), and 77 (Ph^+). Found: S, 13.44%. Calcd: S, 13.34%.

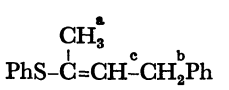


3c: NMR (CCl_4): *trans* τ 8.55 (H^a: d, *J*ab=7 Hz, 3H), 6.40—6.10 (H^b: m, 1H), 4.05—3.95 (H^c and H^d: m, 2H), and 3.00—2.60 (Ph: m, 10H). IR (neat): 960 cm^{-1} ($\delta_{HC=CH}$). Mass: 240 (M^+), 131 (M^+-PhS, base peak), 110 ($PhSH^+$), 109 (PhS^+), 91 ($C_7H_7^+$), and 77 (Ph^+). NMR (CCl_4): *cis* τ 8.62 (H^a: d, *J*ab=7 Hz, 3H), 5.82 (H^b: octet, *J*bc=11 Hz, *J*ab=7 Hz, 1H), 4.56 (H^c: t, *J*bc=11 Hz, 1H), 3.71 (H^d: d, *J*cd=11 Hz, 1H), and 3.10—2.70 (Ph: m, 10H). Found: C, 79.75; H, 6.75; S, 13.46%. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71; S, 13.34%.



$$PhS\text{-}\overset{CH_3^{a}}{\underset{H^b}{C}}\text{-}\overset{c}{CH}{=}\overset{d}{CH}\text{-}Ph$$

3c′: NMR (CCl_4): *trans* τ 8.07 (H^a: s, 3H), 6.61 (H^b: d, *J*bc=8 Hz, 2H), 4.12 (H^c: t, *J*bc=8 Hz, 1H), and 3.10—2.70 (Ph: m, 10H). *cis* τ 8.11 (H^a: s, 3H), 6.40 (H^b: d, *J*bc=8 Hz, 2H), 4.17 (H^c: t, *J*bc=8 Hz, 1H), and 3.10—2.70 (Ph: m, 10H). Mass: 240 (M^+), 225 (M^+-CH_3), 131 (M^+-PhS, base peak), 110 ($PhSH^+$), 109 (PhS^+), 105 ($PhCH_2CH_2^+$), 91 ($PhCH_2^+$), and 77 (Ph^+).

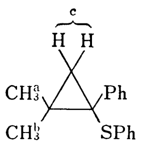


$$PhS\text{-}\overset{CH_3^{a}}{C}{=}\overset{c}{CH}\text{-}\overset{b}{CH_2}Ph$$

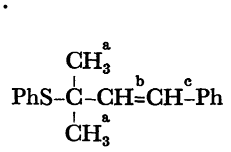
Thermolysis and Photolysis of **1d**. The sodium salt of **1d** was prepared and themally decomposed in diglyme under the conditions described above. When the crude products were chromatographed on silica, 3,3-dimethyl-1-phenylcyclopropyl phenyl sulfide (**2d**) and 3-methyl-3-phenylthio-1-phenyl-1-butene (**3d**) were obtained. The same products were obtained in similar yields when sodium methoxide was used as the base.

The photolysis of the sodium salt of **1d** (219 mg, 0.5 mmol) was carried out in 50 ml of monoglyme, using a Pyrex cell cooled with water and employing a 450 W high-pressure Hg lamp. The same treatment of the crude products described above afforded cyclopropyl sulfide, **2d** (37%), and the **3d** olefin (18%). It seems that the **3d** olefin was polymerized or decomposed under the photolytic conditions.

2d: NMR (CCl_4): τ 9.16 (H^a: s, 3H), 8.80 (H^c: ABq, *J*=5 Hz, 2H), 8.40 (H^b: s, 3H), and 3.10—2.85 (Ph: m, 10H). Mass: 254 (M^+, base peak), 239 (M^+-CH_3), 177 (M^+-Ph), 145 (M^+-PhS), 110 ($PhSH^+$), 109 (PhS^+), and 77 (Ph^+). Found: C, 80.50; H, 7.18; S, 12.64%. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.18; S, 12.64%.



3d: NMR (CCl_4): *trans* τ 8.56 (H^a: s, 6H), 4.00 (H^b and H^c: ABq, *J*=16 Hz, 2H), and 3.10—2.60 (Ph: m, 10H). IR (neat): 958 cm^{-1} ($\delta_{HC=CH}$). Mass: 254 (M^+), 145 (M^+-PhS), 110 ($PhSH^+$), 109 (PhS^+), 91 ($C_7H_7^+$), and 77 (Ph^+). Found: C, 80.00; H, 7.22; S, 12.36%. Calcd. for $C_{17}H_{18}S$: C, 80.26; H, 7.14; S, 12.60%.

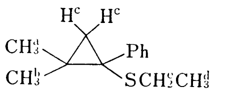


$$PhS\text{-}\overset{CH_3^{a}}{\underset{CH_3^{a}}{C}}\text{-}\overset{b}{CH}{=}\overset{c}{CH}\text{-}Ph$$

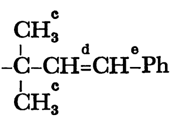
Thermal Decomposition of **1e**. The sodium salt of the **1e** tosylhydrazone was prepared from 1.56 g (4.0 mmol) of the tosylhydrazone and 240 mg of sodium hydride in mineral oil (50%), and was decomposed in diglyme under the conditions described above. When the crude products were chromatographed on silica gel, 3,3-dimethyl-1-phenylcyclopropyl ethyl sulfide (**2e**) and 3-ethylthio-3-methyl-1-phenyl-1-butene (**3e**) were obtained.

2e: NMR (CCl_4): τ 9.21 (H^a: s, 3H), 8.96 (H^c: ABq, *J*=5 Hz, 2H), 8.92 (H^d: t, *J*=7 Hz, 3H), 8.55 (H^b: s, 3H), 7.72 (H^e:

quartet, $J=7$ Hz, 2H), and 2.88 (Ph: 2, 5H), Found: C, 75.52; H, 8.88; S, 15.49%. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.54%.



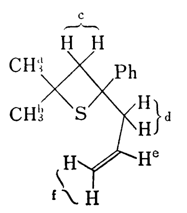
3e: NMR (CCl_4): *trans* τ 8.83 (H^a: t, $J=7$ Hz, 3H), 8.56 (H^c: s, 6H), 7.60 (H^b: quartet, $J=7$ Hz, 2H), 3.76 (H^d, H^e: s, 2H) and 3.00—2.40 (Ph: m, 5H). IR (neat): 960 cm^{-1} ($\delta_{HC=CH}$). Found: C, 75.60; H, 8.86; S, 15.52%. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.54%.



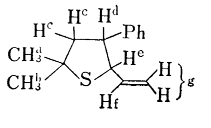
$$\overset{a}{CH_3}\overset{b}{CH_2}S-\underset{\underset{CH_3^{c}}{|}}{\overset{\overset{CH_3^{c}}{|}}{C}}-\overset{d}{CH}=\overset{e}{CH}-Ph$$

Photolysis of 1f. The **1f** tosylhydrazone (1.07 g, 4.0 mmol) and sodium methoxide (280 mg) were dissolved in 80 ml of monoglyme in a Pyrex photolysis vessel. After a stream of nitrogen had been bubbled into the photolysis vessel, the mixture was irradiated with a 450 W high-pressure Hg lamp for 4 hr under stirring and cooling by water. The sodium *p*-toluenesulfinate thus precipitated was filtered off. The filtrate was concentrated under reduced pressure, dissolved in chloroform, washed with water, and dried over anhydrous magnesium sulfate. The crude products were submitted to column chromatography on silica, using *n*-hexane as the eluent. 2-Allyl-4,4-dimethyl-1-phenylthietane (**10a**), 3-allylthio-3-methyl-1-phenyl-1-butene (**12a**) (*cis* and *trans*), and 2-vinyl-5,5-dimethyl-3-phenyltetrahydrothiophene (**11a**) were eluted in this order. Although the diastereoisomers of tetrahydrothiophene (**11a**) could not be separated from each other, purification by preparative vpc (20% SE-30 at 180 °C) afforded each component in the pure form. The use of sodium hydride as a base resulted in the hydrogenation of the allylic double bond.

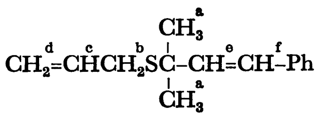
10a: NMR (CCl_4): τ 8.62 (H^a: s, 3H), 8.44 (H^b: s, 3H), 7.30 (H^d: d, $J=7$ Hz, 2H), 7.06 (H^c: ABq, $J=12$ Hz, 2H), 5.40—5.00 (H^f: m, 2H), 4.80—4.20 (H^e: m, 1H), and 3.00—2.65 (Ph: m, 5H).



11a: NMR (CCl_4): *cis* (as for phenyl and vinyl) τ 8.53 (H^a: s, 3H), 8.50 (H^b: s, 3H), 7.87 (H^c: octet, Jcc=16 Hz, Jcd=2 Hz, 6 Hz, 2H), 6.80 (H^d: octet, 1H), 6.01 (H^e: q, Jde=10 Hz, Jef=8 Hz, 1H), 5.30—5.00 (H^g: m, 2H), 4.55—4.15 (H^f: m, 1H), and 2.90—2.65 (Ph: m, 5H). *trans* τ 8.51 (H^a: s, 3H), 8.44 (H^b: s, 3H), 7.88 (H^c: octet, Jcc=12 Hz, Jcd=4 Hz, 12 Hz, 2H), 6.05 (H^e: d, Jef=7 Hz, Jde=0, 1H), 6.05 (H^d: octet, 1H), 5.30—4.95 (H^g: m, 2H), 4.75—4.20 (H^f: m, 1H), and 2.95—2.65 (Ph: m, 5H).



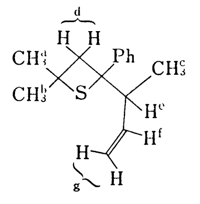
12a: *cis*: NMR (CCl_4): τ 8.76 (H^a: s, 6H), 6.85 (H^b: d, Jbc=7 Hz, 2H), 5.10—4.75 (H^d: m, 2H), 4.50—4.05 (H^c: m, 1H), 4.40 (H^e: d, Jef=12 Hz, 1H), 3.54 (H^f: d, Jef=12 Hz, 1H), and 2.90—2.70 (Ph: m, 5H). IR (neat): 1640 ($\nu_{C=C}$), 980, 910 ($\delta_{HC=CH_2}$), and 780 cm^{-1} ($\delta_{HC=CH}$). *trans* NMR (CCl_4): τ 8.56 (H^a: s, 6H), 7.01 (H^b: d, Jbc=7 Hz, 2H), 5.20—4.80 (H^d: m, 2H), 4.50—4.05 (H^c: m, 1H), 3.83 (H^e, H^f: m, 2H), and 2.90—2.60 (Ph: m, 5H). IR (neat): 1640 ($\nu_{C=C}$), 978, 910 ($\delta_{HC=CH_2}$), and 960 cm^{-1} ($\delta_{HC=CH}$) Found (a mixture of **10a, 11a**, and **12a**): C, 76.99; H, 8.10; S, 14.43%. Calcd for $C_{14}H_{18}S$: C, 77.01; H, 8.31; S, 14.68%.



$$\overset{d}{CH_2}=\overset{c}{CH}\overset{b}{CH_2}S\underset{\underset{CH_3^{a}}{|}}{\overset{\overset{CH_3^{a}}{|}}{C}}-\overset{e}{CH}=\overset{f}{CH}-Ph$$

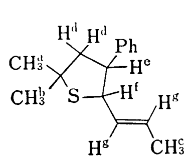
Photolysis of 1g. The **1g** tosylhydrazone was photolyzed in a manner similar to that described above, and the crude products were chromatographed on silica. 4,4-Dimethyl-2-(1-methylallyl)-2-phenylthietane (**10b**), 5,5-dimethyl-3-phenyl-2-(1-propenyl)tetrahydrothiophene (**11b**), and 3-crotylthio-3-methyl-1-phenylbutene (**12b**) (*cis* and *trans*) were eluted by *n*-hexane, in this order.

10b: NMR (CCl_4): diastereoisomer-(A) τ 9.34 (H^c: d, Jce=7 Hz, 3H), 8.72 (H^a: s, 3H), 8.57 (H^b: s, 3H), 7.44 (H^e: quintet, 1H), 7.04 (H^d: ABq, $J=12$ Hz, 2H), 5.20—4.90 (H^g: m, 2H), 4.40—4.00 (H^f: m, 1H), and 3.00—2.60 (Ph: m, 5H).

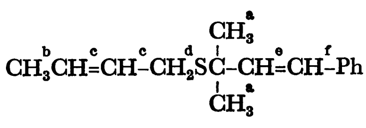


diastereoisomer-(B) τ 9.21 (H^c: d, Jce=7 Hz, 3H), 8.70 (H^a: s, 3H), 8.49 (H^b: s, 3H), 7.25—6.90 (H^e: m, 1H), 7.03 (H^d: ABq, $J=12$ Hz, 2H), 5.25—4.60 (H^f and H^g: m, 3H), and 3.00—2.70 (Ph: m, 5H).

11b: NMR (CCl_4): τ 8.60—8.30 (H^a, H^b, and H^c: m, 9H), 8.15—7.50 (H^d: m, 2H), 7.05—6.50 (H^e: m, 1H), 6.50—5.85 (H^f: m, 1H), 5.10—4.40 (H^g: m, 2H), and 3.00—2.60 (Ph: m, 5H).



12b: NMR (CCl_4): *cis* τ 8.76 (H^a: s, 6H), 8.35 (H^b: d, Jbc=5 Hz, 3H), 6.91 (H^d: d, Jcd=6 Hz, 2H), 4.70—4.40 (H^c: m, 2H), 4.40 (H^e: d, Jef=12 Hz, 1H), 3.54 (H^f: d, Jef=12 Hz, 1H), 2.95—2.70 (Ph: m, 5H). IR (neat): 955 (δ *trans* –CH=CH–), 775 cm^{-1} (*cis* –CH=CH–). NMR (CCl_4): *trans* τ 8.58 (H^a: s, 6H), 8.40 (H^b: d, Jbc=5 Hz, 3H), 7.07 (H^d: d, Jcd=6 Hz, 2H), 4.80—4.50 (H^c: m, 2H), 3.84 (H^e and H^f: s, 2H), 2.90—2.60 (Ph: m, 5H). IR (neat): 970 (δ *trans* –CH=CH–), 955 cm^{-1} (δ *trans* –CH=CH–).

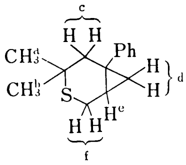


$$\overset{b}{CH_3}\overset{c}{CH}=\overset{c}{CH}-\overset{d}{CH_2}S\underset{\underset{CH_3^{a}}{|}}{\overset{\overset{CH_3^{a}}{|}}{C}}-\overset{e}{CH}=\overset{f}{CH}-Ph$$

Found (a mixture of **10b**, **11b**, and **12b**): C, 77.85; H, 9.03; S, 13.88%. Calcd for $C_{15}H_{20}S$: C, 77.53; H, 8.67; S, 13.80%.

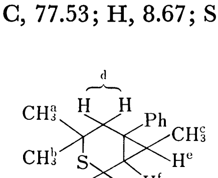
Thermal Decomposition of ***1f***. The **1f** tosylhydrazone (804 mg, 2.0 mmol) was dissolved in 50 ml of diglyme, and then we added 130 mg of sodium methoxide. Thermolysis was performed in accordance with the procedure described previously. The products were purified by column chromatography on silica. 6-Phenyl-4,4-dimethyl-3-thiabicyclo[4.1.0]heptane (**15**) was obtained from the eluate of *n*-hexane. Yield, 196 mg (45%). The analytical vpc (20% SE-30, 200 °C) of the crude products, however, showed the formation of small amounts of thietane, **10a**, and the **12a** olefin, as is shown in Table 2.

15: NMR (CCl_4): τ 9.20—8.40 (H^d and H^e: m, 3H), 8.84 (H^a: s, 3H), 8.62 (H^b: s, 3H), 8.01 (H^c: s, 2H), 7.01 (H^f: octet, *J*ef=2 Hz, 4 Hz, 2H), and 3.10—2.80 (Ph: m, 5H). Found: C, 77.14; H, 8.20; S, 14.40%. Calcd for $C_{14}H_{18}S$: C, 77.01; H, 8.31; S, 14.68%.



Thermal Decomposition of ***1g***. The **1g** tosylhydrazone was decomposed at 150 °C in the presence of a slight excess of sodium methoxide, as has been described previously. Two products were observed in the analytical vpc (20% SE-30, 220 °C) of the crude product. Separation by column chromatography on silica afforded 1-phenyl-4,4-dimethyl-7-(*exo*)-methyl-3-thiabicyclo[4.1.0]heptane (**16a**) and its *endo* isomer (**16b**) in the pure form. Their structures were assigned based on the NMR spectra; the absorption peak of the methyl in the *exo*-isomer appeared at τ 9.29, while that of the *endo*-isomer was at τ 8.68.

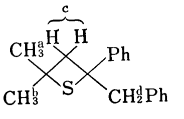
16: NMR (CCl_4): *exo* τ 9.29 (H^c: d, *J*ce=5.5 Hz, 3H), 9.00—8.60 (H^e and H^f: m, 2H), 8.89 (H^a: s, 3H), 8.78 (H^b: s, 3H), 8.03 (H^d: s, 2H), 6.98 (H^g: octet, *J*gg=14 Hz, *J*fg=1.5 Hz, 4 Hz, 2H), and 3.00—2.70 (Ph: m, 5H). *endo* τ 8.95—8.40 (H^e and H^f: m, 2H), 8.81 (H^a: s, 3H), 8.73 (H^b: s, 3H), 8.68 (H^c: d, *J*ce=6 Hz, 3H), 8.09 (H^d: ABq, *J*=14 Hz, 2H), 7.06 (H^g: octet, *J*gg=13 Hz, *J*fg=2 Hz, 4 Hz, 2H), and 3.10—2.70 (Ph: m, 5H). Found: C, 77.39; H, 8.87; S, 13.90%. Calcd for $C_{15}H_{20}S$: C, 77.53; H, 8.67; S, 13.80%.



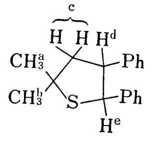
Thermolysis and Photolysis of ***1h***. The **1h** tosylhydrazone (904 mg, 2.0 mmol) was thermally decomposed in the presence of 130 mg of sodium methoxide in diglyme under the conditions described previously. The crude products were then chromatographed on silica, and 2-benzyl-2-phenyl-4,4-dimethylthietane (**10c**), 2,3-diphenyl-5,5-dimethyltetrahydrothiophene (**11c**), and 3-benzylthio-3-methyl-1-phenylbut-1-ene (**12c**, *trans*) were eluted by *n*-hexane. The tetrahydrothiophene, **11c**, was a mixture of diastereoisomers, and each component was sufficiently separated by column chromatography on silica. The isomer ratio was determined to be 50:50, based on the NMR spectrum.

The photolysis of the **1h** tosylhydrazone was performed in a manner similar to that described previously. Thietane, **10c**, tetrahydrothiophene, **11c**, and the **12c** olefin were also obtained, but the **12c** olefin was a mixture of *cis* and *trans* isomers (*cis*/*trans*=27/73).

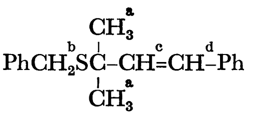
10c: NMR (CCl_4): τ 8.69 (H^a: s, 3H), 8.50 (H^b: s, 3H), 6.96 (H^c: ABq, *J*=12 Hz, 2H), 6.79 (H^d: ABq, *J*=13 Hz, 2H), and 3.40—2.80 (Ph: m, 10H). Found: C, 80.58; H, 7.26; S, 11.79%. Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51; S, 11.95%.



11c: NMR (CCl_4) *cis* τ 8.45 (H^a: s, 3H), 8.34 (H^b: s, 3H), 7.95—7.65 (H^c: m, 2H), 6.20—5.80 (H^d: m, 1H), 5.48 (H^e: d, *J*de=10 Hz, 1H), and 3.40—2.75 (Ph: m, 10H). *trans* τ 8.40 (H^a: s, 3H), 8.29 (H^b: s, 3H), 7.80—7.40 (H^c: m, 2H), 6.30—5.80 (H^d: m, 1H), 5.42 (H^e: d, *J*de=7.5 Hz, 1H), and 3.40—2.75 (Ph: m, 10H). Found: C, 80.31; H, 7.24; S, 11.93%. Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51; S, 11.95%.



12c: NMR (CCl_4): *trans* τ 8.58 (H^a: s, 6H), 6.46 (H^b: s, 2H), 3.80 (H^c and H^d: s, 2H), and 3.00—2.65 (Ph: m, 10H). *cis* τ 8.49 (H^a: s, 6H), 6.34 (H^b: s, 2H), 3.96 (H^c and H^d: ABq, *J*cd=12 Hz, 2H), and 3.10—2.65 (Ph: m, 10H). Found: C, 80.26; H, 7.25; S, 12.21%. Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51; S, 11.95%.



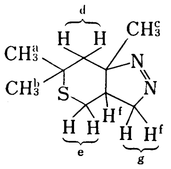
$$\mathrm{Ph\overset{b}{CH_2}S\underset{\underset{a}{CH_3}}{\overset{\overset{a}{CH_3}}{C}}-\overset{c}{CH}=\overset{d}{CH}-Ph}$$

Thermolysis and Photolysis of ***1i***. The **1i** tosylhydrazone (1.70 g, 5.0 mmol) was thermally decomposed in the presence of 300 mg of sodium methoxide in diglyme. The subsequent purification of the crude products by column chromatography on silica gave 4,4,6-trimethyl-3,7,8-thiadiazabicyclo[4.3.0]-nonene (**17**), 303 mg (33%). The Δ^1-pyrazoline, **17**, is thermally stable, but sensitive to light.

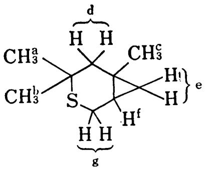
The photolysis of the **1i** tosylhydrazone was performed in monoglyme in a manner similar to that described previously. The identifiable product obtained by column chromatography (silica/*n*-hexane) was found to be 4,4,6-trimethyl-3-thiabicyclo[4.1.0]heptane (**18**) (48%).

The Δ^1-pyrazoline (**17**) was irradiated in monoglyme with a 450 W high-pressure Hg lamp at room temperature, using a Pyrex filter. The solvent was evacuated off, and the residue was dissolved in carbon tetrachloride. The NMR spectrum of the reaction mixture showed the formation of 3-thiabicyclo[4.1.0]heptane **18**. The analytical vpc (20% SE-30, 140 °C) also supported the formation of the isomeric mixture of **18**.

17: NMR (CCl_4): τ 8.92 (H^a: s, 3H,) 8.85 (H^b: s, 3H), 8.67 (H^c: s, 3H), 7.88 (H^d: ABq, *J*=14 Hz, 2H), 7.69 (H^e: octet, *J*ee=14 Hz, *J*ef=5.5 Hz, 8 Hz, 2H), 8.35—7.80 (H^f: m, 1H), and 5.69 (H^g: octet, *J*gg=17 Hz, *J*fg=4 Hz, 6 Hz, 2H). Mass: 184 (M^+), 156 (M^+-N_2), 141 ($156-CH_3$), 123, 115, 107 (base peak). Found: C, 58.65; H, 8.90; S, 17.69%. Calcd for $C_{19}H_{16}N_2S$: C, 58.65; H, 8.75; S, 17.40%.



18: NMR (CCl_4) τ 9.75—9.10 (H^e and H^f: m, 3H), 8.95 (H^c: s, 3H), 8.87 (H^a: s, 3H), 8.72 (H^b: s, 3H), 8.35 (H^d: ABq, J=14 Hz, 2H), and 7.11 (H^g: octet, Jgg=14 Hz, Jfg=1 Hz, 2H). Found: C, 68.89; H, 10.21; S, 20.81%. Calcd for $C_9H_{16}S$: C, 69.17; H, 10.32; S, 20.52%.



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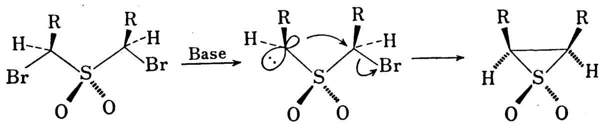

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