BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1539—1545 (1973)

Intramolecular Participation of Sulfide Linkage in the Reactivity of Carbene and Diazoalkanes. I. Alkylcarbenes and Diazoalkanes Bearing Alkylthio, Arylthio, and Allylthio Groups on *α*-Carbon

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(Received October 4, 1972)

α-Alkyl- and α-arylthioalkylcarbenes were thermally or photochemically generated from the corresponding ketones according to a modification of the Bamford-Stevens method. The carbenes thus generated were found to form labile episulfonium ylides, which then rearranged to vinyl sulfides. The episulfonium ylides were trapped with diethyl maleate and dimethyl fumarate. An α-allylthioalkylcarbene was generated by the photolysis of α-allylthioacetophenone tosylhydrazone in the presence of sodium methoxide at −70 °C; this afforded α-allylthiostyrene exclusively. A smooth thio-Claisen rearrangement of the resulting α-allylthiostyrene was also observed. 3-Thiabicyclo[3.1.0]hexane was obtained when α-allylthioacetophenone tosylhydrazone was decomposed thermally at 150 °C, or photochemically at 10 °C in the presence of bases. The mechanisms of these new reactions are also discussed.

The formation of ylides by an intermolecular electrophilic addition of carbenes to the lone pair of hetero atoms is a well-known reaction.[1] This behavior of carbenes led us to postulate that a carbene carbon is transformed into an ylide carbon by the intramolecular participation of the sulfur atom when a sulfide linkage is present in the same molecule. Although an ordinary carbene is electrophilic and can be added to electron-deficient olefins only with great difficulty,[2] the carbene of this type would act as a nucleophilic reagent, similar to the Wanzlick's carbenes[3] and cycloheptatrienylidene.[4] In addition, the above-mentioned intramolecular reaction of carbenes may afford small, hitherto unknown ring ylides, which are difficult to prepare by the usual salt methods.[5] In this respect, we have already reported, in preliminary form, evidence for the intervention of the thietanonium ylide generated from the carbene bearing sulfide linkage on the γ-position.[6,7] We have now investigated the reactions of alkyl carbenes bearing alkylthio, arylthio, and allythio groups on α-carbon. This paper will present a full account of our research into this subject.

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[1] G. Wittig and M. Schlosser, *Tetrahedron*, **18**, 1023 (1962); W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961); W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964); W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); V. Franzen and L. Finketcher, *Ann. Chem.*, **617**, 1(1958); J. Dieckmann, *J. Org. Chem.*, **28**, 2933 (1963); M. Saunders and R. W. Murray, *Tetrahedron*, **6**, 88 (1959); H, Nozaki, R. Noyori, and K. Sisido, *ibid.*, **20**, 1125 (1964).

[2] W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964.

[3] For example, H. W. Wanzlick and E. Schikora, *Angew. Chem.*, **72**, 494 (1960); H. W. Wanzlick and H. J. Kleiner, *Chem. Ber.*, **96**, 3024 (1963).

[4] W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

[5] A. W. Johnson, "Ylid Chemistry," Academic Press (New York), 1966, pp 310—314.

[6] K. Kondo and I. Ojima, *Chem. Commun.*, **1972**, 62.

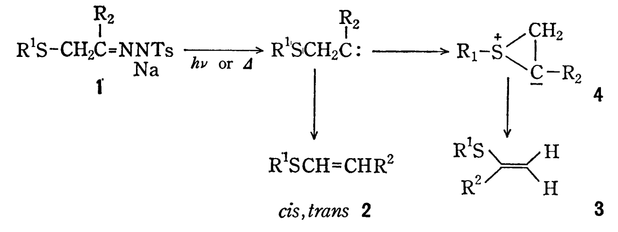
[7] K. Kondo and I. Ojima, *Chem. Lett.*, **1972**, 119.

Results and Discussion

Reactions of α-Alkylthio- and α-Arylthio-alkylcarbenes. In 1967, Kirmse and Buschhoff reported the effects of ether linkage on the β-position,[8] and Robson and Shechter reported those of oxygen, nitrogen, and sulfur on the β-position,[9] in view of the neighboring effects of hetero atoms on carbenes. The effects of hetero atoms on the β-position may be summarized as follows: i) An alkoxy group on the β-position promoted markedly a rearrangement of a methyl on the α-carbon to the carbene carbon. The rate of the rearrangement of the alkoxy group is faster than that of hydrogen in the case of bis(α-alkoxy)alkylcarbene. ii) The rearrangement of an arylthio group on the α-carbon of the carbene is quite effective as compared with those of an alkoxy and alkylamino groups. In the latter communication, they observed an exclusive 1,2-shift of arylthio group to the electron-deficient center and interpreted the reaction as a concerted process through an ylide-like transition state. However, a possibility of the existence of an intermediate ylide still remains. Therefore, the reaction was reinvestigated in detail in the hope of obtaining evidence for the intervention of episulfonium ylide.

Carbenes were generated by the thermal or photochemical decomposition of sodium salts of the tosylhydrazones(**1a**—**d**), in accordance with the Bamford-Stevens method.[10] The results of the thermal decomposition in diglyme at 150 °C and of photolysis using a high-pressure Hg lamp in monoglyme at 10 °C are listed in Table 1, while the supposed reaction paths are described in Scheme 1.

As for the configuration of the olefin **2** produced by the 1,2-hydride shift, it is noteworthy that the ratios of the thermodynamically-unstable *cis*-isomer were predominant in all cases examined: $R^1=R^2=Ph$, *cis*/*trans*=98/2; $R^1=Et$, $R^2=Ph$, *cis*/*trans*=66/34 and $R^1=t\text{-}Bu$, $R^2=Ph$, *cis*/*trans*=69/31. The results can reasonably be explained by considering the conformations of the singlet carbenes. It has generally been accepted that the hydrogen migration occurs in the singlet state.[11] Scheme 2 depicts the Newman projection of the singlet carbene.

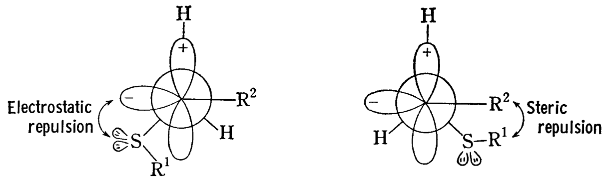


Scheme 1.

Table 1. Products ratios[a] in the decomposition of tosylhydrazones **1a**—**d**

	R^1	R^2	Photolysis **2**	Photolysis **3**	Thermolysis **2**	Thermolysis **3**
a	Ph	Ph	1	99	10	90
b	Et	Ph	30	70	14	86
c	*t*-Bu	Ph	22	78	15	85
d	Ph	Me	0	100	40	60

a) Products ratio was calculated from vpc peak area using a column packed with 20% SE-30 at 150—200 °C.



5a **5b**

Scheme 2.

The *trans*-olefin will be produced from the **5a** conformation and the *cis*-olefin, from **5b**. From the steric point of view, **5a** is expected to be more stable than **5b**. However, from the electronic point of view **5a** is less stable, because of the electrostatic repulsion between the lone pair of the sp^2-hybridized carbene and those of the sulfur atom. The preferential formation of the *cis*-isomers means that the electrostatic repulsion is the dominant factor in determining the conformations of these carbenes. Similar results were observed by Kirmse and Buschhoff in the case of α-alkoxyalkylcarbenes,[8] and by Yamamoto and Moritani in the case of α-carbethoxyalkylcarbenes.[12] As for the olefin, **3**, produced by the rearrangement of the alkylthio or arythio group, the probability of the rearrangement is considerably affected both by the substituent on the carbene carbon and that on the sulfur atom. That is, the ratio of the migration *vs.* the hydride shift seems to be determined by the stability of the hypothetical episulfonium ylide. In general, a phenyl group on ylide carbon delocalizes the negative charge by means of a resonance effect. On the contrary, a methyl group on the same carbon destabilizes the ylide by its inductive effect. In the case of thermolysis, the ratio of the olefin **3** to the olefin **2** was reduced remarkably from 10/90 to 40/60, as the substituent on the ylide carbon was changed from phenyl to methyl; this behavior might reflect the thermal stability of the intermediate episulfonium ylide. In sharp contrast with this, the phenyl substituent on sulfur plays a key role in determining the ratio of the olefin **3** to the olefin **2** when the carbene is produced by photolysis. Though we have no persuasive explanation for the phenomena, the result is probably due to the inherent difference between the two types of carbenes, *i. e.*, thermally- and photochemically-generated carbenes.

All attempts to trap these carbenes by cyclohexene were in vain. Furthermore, no reaction could be observed with such electron-rich olefins as morpholinocyclohexene and dihydropyran. However, these

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[8] W. Kirmse and M. Buschhoff, *Chem. Ber.*, **100**, 1491 (1967).

[9] J. H. Robson and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 7112 (1967).

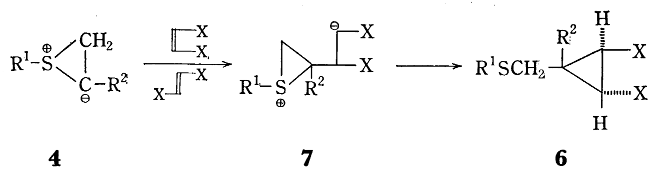
[10] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, **1952**, 4735.

[11] I. Moritani, Y. Yamamoto, and S. Murahashi, *Tetrahedron Lett.*, **1968**, 5755, 5967.

[12] Y. Yamamoto and I. Moritani, *Tetrahedron*, **26**, 1235 (1970).

TABLE 2. REACTIONS OF THE YLIDES **4** WITH ELECTRON-DEFICIENT OLEFINS

6	R^1	R^2	X	Olefin	Yield(%)	NMR (τ) Ring proton	NMR (τ) Methylene
a	Ph	Ph	COOEt	*cis*	72	7.45(1H), 7.10(1H)	6.54(2H, AB)
b	Ph	Me	COOEt	*cis*	67	7.83(2H)	6.82(2H, AB)
c	Ph	Me	COOEt	*trans*	61	7.81(2H)	6.84(2H, AB)

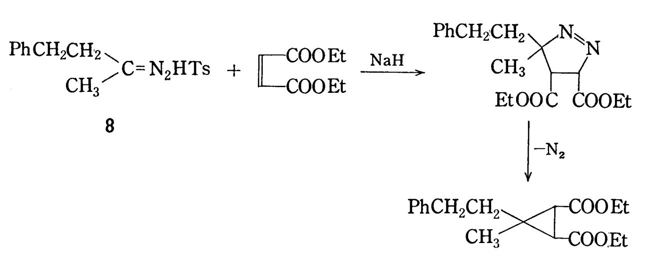


Scheme 3.

carbenes were found to react with electron-deficient olefins, *e. g.*, α, β-unsaturated carboxylic esters, to produce cyclopropanes in good yields.

The configuration of the obtained cyclopropanes was found to be *trans* about the substituent, **X**, irrespective of the configurations of the starting olefins. The configuration was determined on the basis of its NMR spectrum, in which the methylene protons adjacent to the sulfur atom displayed an AB quartet caused by asymmetric vicinal carbon. The results are summarized in Table 2. Consequently, as is shown in Scheme 3, the reaction should proceed in a two-step mechanism *via* betain, **7**. It might be said that the expected transformation of carbene to ylide was successfully realized by its nucleophilic addition to electron-deficient olefins. However, much as in the case of cycloheptatrienylidene[4] the possibility of the formation of cyclopropane *via* pyrazoline can not be rigorously excluded, because the diazoalkane is knwon to be the precursor of the carbene in the decomposition of tosylhydrazones by the Bamford-Stevens procedure.[10,13,23] To clarify this possibility, the tosylhydrazone **8** which has a structure quite analogous with **1d** except for the absence of sulfide linkage in the same molecule, was reacted under the same conditions in the presence of diethyl maleate.

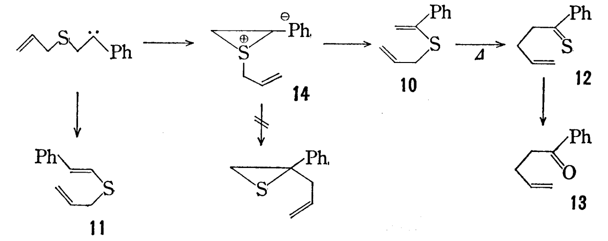
The cyclopropane **9**, which is considered to be formed through the 1,3-cycloaddition of the diazoalkane to the olefin, was obtained in only a 15% yield. This result indicates that a part of the cyclopropane **6** might be produced by the 1,3-cycloaddition route. However, the major path should be the ylide process. These results suggest that the reaction might become a useful synthetic device for the formation of cyclopropanes which can not be obtained by the usual carbene process.



Scheme 4.

Intramolecular Reactions of α-Allylthioalkylcarbene. The reaction of the α-allylthioalkylcarbene obtained from the sodium salt of α-allylthioacetophenone tosylhydrazone (**1e**) was investigated. In sharp contrast with that observed at 10 °C (*vide infra*), the photochemically-produced carbene showed a characteristic behavior.

At least three types of reactions leading to the final products are possible for this carbene, as is shown in Scheme 5: The 1,2-hydride shift to the olefin **11**, the 1,2-migration of the allylthio group through the intermediate ylide, **14**, and the [2,3]sigmatropic rearrangement[6] of the ylide **14**. A careful examination of the photolysate by NMR indicated that the carbene was transformed into a mixture of allyl 1-phenylvinyl sulfide, **10** (89%), and allyl 2-phenylvinyl sulfide, **11** (11%), in an almost quantitative yield. The ratio of *cis*-**11** to *trans*-**11** was found to be 79 : 21, which is again in good agreement with the results observed in the cases of alkylthio- and arylthio-alkylcarbenes. The allyl vinyl sulfide, **10**, obtained was thermally unstable. Thus, the structure was determined by measuring the NMR spectrum of the photolysate at −23 °C. The spectrum clearly demonstrated that the predominant component in the photolysate was the olefin **10**. In this case, the episulfonium ylide, **14**, can also be assumed to be an intermediate in the reaction.



Scheme 5.

When the photolysate was kept in the dark at room temperature for a few hours, an intensive violet color spread over the solution and its NMR spectrum became completely different from that of **10**. This compound was stable under a nitrogen atmosphere, and its electronic spectrum displayed an absorption maximum at 560 nm which was almost the same as that of thioaceto-

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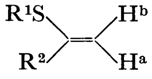
[13] D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

[14] J. Fabian, H. Viola, and R. Mayer, *Tetrahedron*, **23**, 4323 (1967).

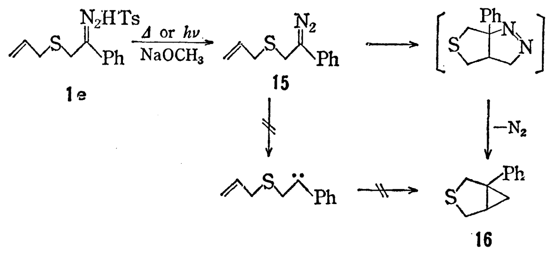
[23] J. W. Powell and M. C. Whiting, *ibid.*, **7**, 305 (1959).

Table 3. NMR Spectral data for the olefinic protons of **2**, **3**, **10** and **11** (τ, CCl_4)

R^1	R^2		$R^1S-CH^a=CH^b-R^2$ *cis*	 *trans*
Ph	Ph	4.82, s, (H^b) 4.48, s, (H^a)	3.61, ABq $J_{ab}=$ 11Hz	3.33, ABq $J_{ab}=$ 17Hz
Et	Ph	4.93, s, (H^b) 4.67, s, (H^a)	3.84, ABq $J_{ab}=$ 11Hz	3.57, ABq $J_{ab}=$ 17Hz
t-Bu	Ph	4.40, d, (H^b) 4.33, d, (H^a) $J_{ab}=$ 1Hz	3.71, ABq $J_{ab}=$ 12Hz	3.36, ABq $J_{ab}=$ 16Hz
Ph	Me	5.23, s, (H^b) 5.00, s, (H^a)	4.40—3.80, m	
Allyl	Ph	4.80, s, (H^b) 4.53, s, (H^a)	3.69, ABq $J_{ab}=$ 11Hz	3.41, ABp $J_{ab}=$ 16Hz

phenone and which could be assigned to the n–π^* transition of the thio-carbonyl function. On the basis of these spectra, this compound was assigned to thioketone, **12**. Chemical evidence for the thioketone, **12**, was also obtained; the violet color of the thioketone, **12**, gradually disappeared under atmospheric conditions. The products were separated and purified by column chromatography on silica, and the ketone, **13**, and sulfide, **11**, were finally isolated. The structure of the ketone, **13**, was determined by studying its NMR, IR, and mass spectra. Although the thio-Claisen rearrangements were observed in many systems,[15] that of a simple allyl vinyl sulfide system has not yet been reported. A recent report by Corey and Shulman[16] described how their attempted thermal thio-Claisen rearrangement of $R_2C=CHSCH_2CH=CH_2$ at 160—180 °C was unsuccessful, and how mercuric oxide was found to be an effective catalyst to promote the rearrangement and produce aldehyde directly. In our system, however, the thio-Claisen rearrangement occurs quite smoothly at room temperature without the aid of any catalyst. The substituent on the vinyl group seems to have a decisive effect on the ease of this rearrangement. That is, though two allyl vinyl sulfides were obtained in our system, only one, *i. e.*, the sulfide **10**, underwent thio-Claisen rearrangement, while the other, *i. e.*, the sulfide **11**, was recovered unchanged. The ease must be due partly to the stability of the product.

Intramolecular 1,3-Cycloaddition of α-Allylthioalkyldiazoalkane. α-Allylthioacetophenone tosylhydrazone (**1e**) was thermally decomposed in diglyme in the presence of sodium methoxide at 150 °C. The distillation of the reaction mixture under reduced pressure or the purification of the product by column chromatography afforded 1-phenyl-3-thiabicyclo[3.1.0]hexane (**16**) as the sole isolable product in a 68.5% yield; no olefins caused by the carbenic process could be detected in the product. The photodecomposition of the sodium salts of tosylhydrazone, **1e**, in monoglyme at 10 °C also afforded 3-thiabicyclo[3.1.0]hexane **16** in an 87.5% yield. The carbenic process of this α-allylthio system was observed only when the photolysis was carried out at −70 °C. Thus, the cycloaddition must involve a thermal process at some stage of the consecutive reactions. The formation of 3-thiabicyclo[3.1.0]hexane, **16**, can be explained by assuming an intramolecular cycloaddition of the diazoalkane to the double bond of the allylthio group to afford the bicyclic pyrazoline and the subsequent elimination of a molecular nitrogen, as is shown in Scheme 6.



Scheme 6.

A similar behavior was also observed when a β-allylthioalkyldiazoalkane was generated by the thermal decomposition of the corresponding tosylhydrazone. In the latter case, we could actually isolate the bicyclic pyrazoline.[17] The first step of the thermolysis is known to be the formation of the diazo compounds.[23] As far as we know, there has been no report on the formation of the diazo compounds from the corresponding sodium salts of tosylhydrazones under photolytic conditions. We could, however, actually observe a characteristic red color of the compounds during the initial stage of the photolyses of **1a**~**1e**. Thus, the intramolecular 1,3-cycloaddition of the transient diazo function to the allyl moiety seems to be a quite effective process, even at 10 °C. The reason for the ease of this cycloaddition might be its intramolecular nature. The high performance of the reaction may open a novel synthetic route to thiabicyclic systems.

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 samples as neat liquid, KBr disks, or Nujol mulls. The nuclear magnetic resonance spectra were obtained by the use of a Varian HA-100 or Hitachi R20-B spectrometer, using TMS as the internal standard. The mass spectra were measured with the use of 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 detecter using a 1 m×3 mm column packed with 20% SE-30 or 10% QF-1 on chromosorb W. Photolyses were carried out with the use of a 450-W high-pressure mercury lamp (Ushio Electric Inc.).

Materials. *α-Phenylthioacetophenone Tosylhydrazone (**1a**):* Benzenethiol (13.8 g, 0.125 mol) was added to a solution of

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15) For example, D. J. W. Schuijl, and L. Brandsma, *Rec. Trav. Chim. Pays-Bas*, **87**, 957 (1968); H. Kwart and T. J. George, *Chem. Common.*, **1970**, 433.

16) E. J. Corey and J. I. Schulman, *J. Amer. Chem. Soc.*, **92**, 5522 (1970).

17) K. Kondo and I. Ojima, *Chem. Commun.*, **1972**, 63.

200 ml of absolute ethanol and 2.88 g of sodium (0.125 g-atom). To this solution, 25 g of α-bromoacetophenone (0.125 mol) in 100 ml of ethanol was added slowly, and then the mixture was gradually heated to reflux for 2 hr. After the reaction mixture had been cooled to room temperature, the precipitated sodium bromide was filtered off and the filtrate was concentrated. The residue was dissolved in chloroform, washed with water, and dried over anhydrous magnesium sulfate. After the solvent had been removed, the oily product was cooled with dry ice to afford yellow crystals. The product was recrystallized from ethanol; 15.7 g (55%) of pure α-phenylthioacetophenone were thus obtained. Mp 52 °C (lit,[18] 53—54 °C).

A mixture of 12 g (0.65 mol) of tosylhydrazide and 11.4 g (0.05 mol) of α-phenylthioacetophenone in 100 ml of ethanol was heated for half an hour under reflux. Then, the solution was cooled with dry ice; white needles of the tosylhydrazone, **1a**, were thus precipitated (16.8 g, 85%). Mp 105—106 °C. Found: C, 63.72; H, 4.93; N, 6.98; S, 16.13%. Calcd for $C_{21}H_{20}N_2O_2S_2$: C, 63.51; H, 5.08; N, 7.06; S, 16.17%.

In a similar manner, α-ethylthioacetophenone tosylhydrazone (**1b**) and α-*t*-butylthioacetophenone tosylhydrazone (**1c**) were prepared. α-Ethylthioacetophenone: bp 120 °C/1.5 mmHg (lit,[19], 106 °C/0.3 mmHg). Tosylhydrazone **1b**: Colorless needles, mp 126—127 °C. Found: C, 58.43; H, 5.69; N, 8.05; S, 18.41%. Calcd for $C_{17}H_{20}N_2O_2S_2$: C, 58.59; H, 5.78; N, 8.04; S, 18.40%. α-*t*-Butylthioacetophenone: bp 124 °C/2.5 mmHg. Tosylhydrazone **1c**: Colorless needles, mp 175—176 °C. Found: C, 60.44; H, 6.27; N, 7.27; S, 17.10%. Calcd for $C_{19}H_{24}N_2O_2S_2$: C, 60.61; H, 6.42; N, 7.44; S, 17.03%.

*α-Phenylthioacetone Tosylhydrazone (**1d**)*: α-Phenylthioacetone was prepared from 20 g (0.182 mol) of benzenethiol, 4.2 g (0.182 g-atom) of sodium, and 25 g (0.183 mol) of bromoacetone in 150 ml of absolute ethanol in a manner similar to that used in the case of α-phenylthioacetophenone; 17.5 g (57%) of the ketone were thus obtained. Bp 100—102 °C/1.0 mmHg (lit,[20] 160—165 °C/22 mmHg). The tosylhydrazone of α-phenylthioacetone was prepared from 16.7 g (0.1 mol) of the ketone and 20 g (0.107 mol) of tosylhydrazide in the presence of a few drops of concentrated sulfuric acid in 150 ml of ethanol at room temperature (29.1 g, 87%). mp 148—149 °C. Found: C, 57.36; H, 5.15; N, 8.29; S, 19.17%. Calcd for $C_{16}H_{18}N_2O_2S_2$: C, 57.46; H, 5.42; N, 8.38; S, 19.17%.

*Thermal Decomposition of the Tosylhydrazones, **1a-d***: A typical procedure will be described for the thermal decomposition of α-phenylthioacetophenone tosylhydrazone (**1a**).

The tosylhydrazone **1a** (396 mg, 1.0 mmol) was dissolved in 50 ml of diglyme, and then a 60-mg portion (*ca.* 1.2 mmol) of sodium hydride (50% suspension in mineral oil) was stirred in. After the evolution of hydrogen had ceased, the reaction flask was immersed into an oil bath which was maintained at 180 °C. The reaction mixture was heated under reflux for a few minutes; during this time the evolution of nitrogen was observed. After the precipitated sodium *p*-toluenesulfinate had been filtered off, the reaction mixture was concentrated under reduced pressure, dissolved in chloroform, washed with water, and then dried over anhydrous magnesium sulfate. The products were determined by studying the NMR spectrum, which was measured after the crude products had been distilled under reduced pressure. The yields and products ratios were calculated by comparing the vpc peak area of the crude products with that of pure samples, which had been prepared from benzenethiol and phenylacetylene,[21] and by analysing the integration of the NMR spectrum of the crude products. The total yield (**2a**+**3a**) was 44.5%.

In a similar manner, other tosylhydrazones (**1b**—**d**) were decomposed; olefins (**2** and **3**) were thus obtained in similar yields and were detected by means of the vpc and/or NMR spectra. Authentic samples were prepared from ethanethiol and phenylacetylene,[21] 2-methyl-2-propanethiol and phenylacetylene, and benzenethiol and allen.[22] The NMR spectral data for the olefinic protons of these vinyl sulfides are listed in Table 3.

*Photolyses of the Tosylhydrazones, **1a—d***: A typical procedure will be described for the photolysis of α-phenylthioacetophenone tosylhydrazone (**1a**).

The tosylhydrazone, **1a** (396 mg, 1.0 mmol), was dissolved in 20 ml of monoglyme, and then 60 mg (*ca.* 0.12 mmol) of sodium hydride in mineral oil was added to a pyrex cell. After the initial evolution of hydrogen had ceased, the reaction mixture was bubbled with dry nitrogen gas and then irradiated externally with a 450-W high-pressure Hg lamp for several hours. After the irradiation, the reaction mixture was concentrated, dissolved in chloroform, washed with water, and dried over anhydrous magnesium sulfate. The products were detected by NMR and vpc, as has been described above. The total yield (**2a**+**3a**) was 82%.

Similarly, other tosylhydrazones were photolysed; olefins (**2** and **3**) were thus obtained in similar yields.

*Thermal Decompositions of the Tosylhydrazones (**1a**, **1d**, and **8**) in the Presence of Electron-deficient Olefins.* A typical procedure will be described for the thermolysis of α-phenylthioacetone tosylhydrazone (**1d**) in the presence of diethyl maleate.

α-Phenylthioacetone tosylhydrazone (**1d**) (1.00 g, 3.0 mmol) was dissolved in 50 ml of diglyme, and then a 180-mg portion (ca. 3.6 mmol) of sodium hydride in mineral oil was added. After the evolution of hydrogen had been completed, a 2.6-g portion (15.1 mmol) of diethyl maleate was added. Then, the reaction flask was immersed into an oil bath, the temperature of which was maintained at 180°C with stirring. After the evolution of nitrogen had ceased, the reaction mixture was refluxed for an hour. The sodium *p*-toluenesulfinate thus precipitated was filtered off using a glass filter, and the filtrate was distilled to remove the solvent and unreacted diethyl maleate. The residue was dissolved in chloroform, washed with water, and dried over anhydrous magnesium sulfate. The solution was concentrated and chromatographed on silica (WAKO C-200). The cyclopropane **6b** (664 mg, 67%) was eluted by benzene.

In a similar manner, the cyclopropanes **6a**, **6c**, and **9** were obtained in 72, 61, and 15% yields, respectively. The yields of the cyclopropanes, as calculated from the vpc peak areas, were about ten percent higher than those obtained from chromatographic separations. 1-Phenyl-1-phenylthiomethyl-2,3-dicarboethoxycyclopropane (**6a**): NMR (CCl_4, TMS): τ 9.05 (H^a: t, J_{ae}=7Hz, 3H), 8.70 (H^b: t, J_{bd}= 7 Hz, 3H), 7.32 (H^f, H^g; AB$_q$, J_{fg}=6 Hz, 2H), 6.54 (H^e:

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18) W. J. Kenny, J. A. Walsh, and D. A. Davenport, *J. Amer. Chem. Soc.*, **83**, 4019 (1961).

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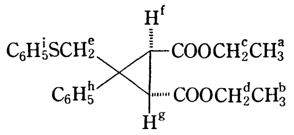
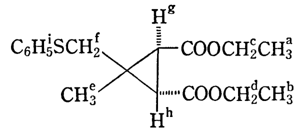
AB_q, $J_{ee}=12$ Hz, 2H), 6.23 (H^c: quartet, $J_{ac}=7$ Hz, 2H), 5.88 (H^a: quartet, $J_{bd}=7$ Hz, 2H), 2.98 (H^h: broad s, 5H) and 2.82 (H^i: broad s, 5H).



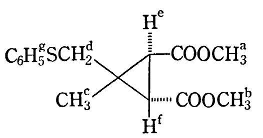
IR (neat): 1730 ($\nu_{C=O}$) and 1180 cm^{-1} (ν_{C-O}) Mass: 384 M$^+$. Found: C, 68.31; H, 6.28; S, 8.44%. Calcd for $C_{22}H_{24}O_4S$: C, 68.72; H, 6.29; S, 8.34%.

1-Methyl-1-phenylthiomethyl-2,3-dicarboethoxycyclopropane (**6b**): NMR (CCl_4, TMS): τ 8.74 (H^a, H^b: t, $J_{ac}=J_{bd}=7$ Hz, 6H), 7.83 (H^g, H^h: s, 2H), 6.82 (H^f; AB_q, $J_{ff}=13$ Hz, 2H), 5.95 (H^c, H^d: quartet, $J_{ac}=J_{bd}=7$ Hz, 4H) and 2.5—3.0 (H^i; m, 5H).



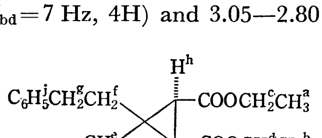
IR (neat): 1720 ($\nu_{C=O}$), and 1160 cm^{-1} (ν_{C-O}). Mass: 322 M$^+$. Found: C, 63.01; H, 6.75; S, 10.15%. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88; S, 9.94%.

1-Methyl-1-phenylthiomethyl-2,3-dimethoxycyclopropane (**6c**): NMR (CCl_4, TMS): τ 8.62 (H^c: s, 3H), 7.81 (H^e, H^f: s, 2H), 6.84 (H^d: AB_q, $J_{dd}=12$ Hz, 2H), 6.42 (H^a: s, 3H), 6.39 (H^b: s, 3H), and 2.5—3.0 (H^g: m, 5H).



IR (neat): 1730 ($\nu_{C=O}$) and 1165 cm^{-1} (ν_{C-O}). Mass: 294 M$^+$. Found: C, 61.28; H, 5.88; S, 10.78%. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16; S, 10.89%.

1-Methyl-1-(2-phenylethyl)-2,3-dicarboethoxycyclopropane (**9**): NMR (CCl_4, TMS): τ 8.72 (H^a, H^b: t, $J_{ac}=J_{bd}=7$ Hz, 6H), 8.65 (H^e: s, 3H), 8.3—8.0 (H^f: m, 2H), 7.88 (H^h, H^i: s, 2H), 7.70—7.25 (H^g: m, 2H), 5.93 (H^c, H^d: quartet, $J_{ac}=J_{bd}=7$ Hz, 4H) and 3.05—2.80 (H^j: m, 5H).

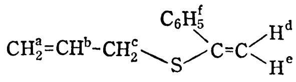


IR (neat): 1730 ($\nu_{C=O}$) and 1170 cm^{-1} (ν_{C-O}) Mass: 304 M$^+$. Found: C, 71.05; H, 8.10%. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95%.

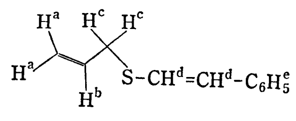
*α-Allylthioacetophenone Tosylhydrazone (**1e**).* To 150 ml of absolute ethanol, a 1.55-g portion (0.068 g-atom) of sodium was added. After the evolution of hydrogen had ceased, a 5.0-g portion (0.068 mol) of allylmercaptan was added to the solution, and the mixture was stirred for an hour. Into the solution we then stirred a solution of 13.5 g (0.068 mol) of bromoacetophenone in 100 ml of absolute ethanol; then, the reaction mixture was gradually heated to reflux over a 1-hr period. The sodium bromide thus precipitated was filtered off, and the filtrate was concentrated. The residue was dissolved in chloroform, washed with water, dried over anhydrous magnesium sulfate, and distilled. Yield, 61%. $PhCOCH_2SCH_2CH_2{=}CH_2$: bp 102—104 °C/0.2 mmHg, IR (neat): 1690 ($\nu_{C=O}$) 985 and 920 cm^{-1} $\left(\delta\ {}^{H}_{H}\!\!>\!C{=}C\!<_{H}\right)$.

The tosylhydrazone, **1e**, was prepared from 3.78 g (0.0207 mol) of α-allylthioacetophenone and 3.66 g (0.0207 mol) of tosylhydrazide in 95% ethanol in the presence of a drop of concentrated sulfuric acid. Tosylhydrazone **1e**: Colorless prisms, mp 106—107 °C, Found: C, 59.55; H, 5.79; N, 7.67; S, 17.84%. Calcd for $C_{18}H_{20}N_2O_2S_2$: C, 59.97; H, 5.59; N, 7.77; S, 17.79%.

*Photolysis of α-Allylthioacetophenone Tosylhydrazone (**1e**) in the Presence of Sodium Methoxide at Low Temperatures.* The tosylhydrazone **1e** (360 mg, 1.0 mmol) was dissolved in 30 ml of monoglyme in the photolysis vessel, and a 60-mg portion (1.1 mmol) of sodium methoxide was added. The solution was bubbled with nitrogen, and then stirred with a magnetic stirrer for an hour and irradiated. The temperature of the dry ice-ethanol solution was kept constant at −70 °C during the irradiation. The solution was irradiated for about 2.5 hr until the pink-color of the diazo compound had disappeared; then, the precipitated sodium *p*-toluenesulfinate was filtered off rapidly. The cool filtrate was concentrated under a vacuum; the residue was dissolved in cold ether and was washed with ice water as quickly as possible and the organic layer was dried over anhydrous magnesium sulfate in a dry ice box. The solution was then again concentrated by the use of a vacuum pump; the residue was dissolved in deuterochloroform including tetramethylsilane and poured into a NMR sample tube under a stream of nitrogen, after which the tube was closed. The NMR sample was stored in a dry ice–ethanol solution, and the NMR spectrum was measured at −23 °C. The predominant product was found to be 1-phenylvinyl allyl sulfide (**10**). **10**: NMR ($CDCl_3$, TMS, −23°C): τ 6.71 (H^c: d, $J_{bc}=7$ Hz, 2H), 5.10—4.85 (H^a: m, 2H), 4.80 (H^e: s, 1H), 4.54 (H^d; s, 1H), 4.40—3.90 (H^b: m, 1H), and 2.80—2.30 (H^f: m, 5H).



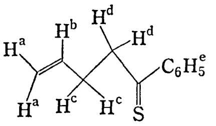
The structures of the minor products, *cis*- and *trans*-2-phenylvinyl allyl sulfides, were determined by studying their nmr and mass spectra. The pure sample was obtained by chromatography on silica, employing *n*-hexane as the eluent. **11**: NMR (CCl_4, TMS, *cis*, *trans* mixture): τ 6.69 (H^c: d, $J=7$ Hz, 2H), 5.00—4.70 (H^a: ,m 2H), 4.40—3.90 (H^b: m, 1H),



$$\left.\begin{array}{l} 3.80\ (\textit{cis}\text{-}H^d;\ AB_q,\ J=11\ \text{Hz} \\ 3.51\ (\textit{trans}\text{-}H_d:\ AB_q,\ J=15\ \text{Hz}) \end{array}\right\}\ (2H)$$

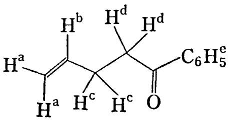
and 2.90—2.50 (H^e: m, 5H) mass: *m/e*=176 M$^+$, 135 M$^+$−41, base peak, 91 $C_7H_7^+$, and 77 Ph$^+$. When the sample which had been subjected to the NMR measurement was left at room temperature for half an hour, a violet color spread over the solution. The NMR spectrum was again measured at room temperature. The spectrum showed the disappearance of the olefin **10** and the production of new species which showed a benzoyl-type spectrum. The electronic spectrum of the sample showed an absorption maximum at 560 nm in the visible region; such an absorption maximum is characteristic of thiophenones. On the basis of these spectra, the new species which was produced thermally was assigned to buten-3-yl phenyl thioketone (**12**). When the sample was left under atmospheric conditions at room temperature overnight, the violet color completely faded. The precipitated, white solid, which was probably sulfur, was filtered off, and the filtrate was chromatographed on silica. Buten-3-yl phenyl ketone (**13**) was eluted with benzene. The NMR spectrum of the ketone, **13**, closely resembled that of the thioketone, **10.**

10: NMR ($CDCl_3$, TMS): τ 7.44 (H^c: quartet, J=7 Hz, 2H), 6.70—6.50 (H^d: m, 2H), 5.20—4.70 (H^a: m, 2H), 4.35—3.85 (H^b: m, 1H), 2.85—2.35 and 2.10—1.90 (H^e: m, 5H).



Although the absorption assigned to $CH_2{}^d$ was considered to be a triplet, it appeared as a multiplet. Therefore, a decoupling technique was employed to ascertain the assignments of $CH_2{}^c$ and $CH_2{}^d$. No unusual coupling could, however, be observed. That is, the absorption peak assigned to $CH_2{}^c$ appeared as a doublet (J=6 Hz) when $CH_2{}^d$ was irradiated, and the peak assigned to $CH_2{}^d$ appeared as a singlet when $CH_2{}^c$ was irradiated. Consequently, it is unclear why the peak assigned to $CH_2{}^d$ did not appear as a triplet.

13: NMR (CCl_4, TMS): τ 7.58 (H_c: quartet, J=7 Hz, 2H), 7.04 (H^d: t, J=7 Hz, 2H), 5.20—4.85 (H^a: m, 2H), 4.40—3.90 (H^b: m, 1H), and 2.90—2,50, 2.20—2.00 (H^e: m, 5H).



IR (neat): 1680 ($\nu_{C=O}$), 1635 (ν_{C-O}) and 970, 910 cm^{-1} $\left(\delta\ {}_{\mathrm{H}}\rangle\!=\!\langle{}^{\mathrm{H}}_{\mathrm{H}}\right)$.

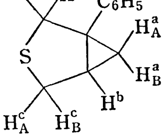
Mass: 160 M$^+$, 105 PhCO$^+$, base peak, and 77 Ph$^+$.

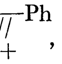
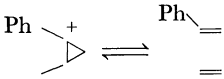
*The Thermal Decomposition and Photolysis of α-Allylthioacetophenone Tosylhydrazone (**1e**).* The tosylhydrazone, **1e** (360 mg, 1.0 mmol), and 60 mg (1.1 mmol) of sodium methoxide were dissolved in 40 ml of monoglyme in the photolysis vessel and stirred. The solution was bubbled with a dry nitrogen stream, and the vessel was closed. Photolysis was carried out using a 450-W high-pressure Hg lamp for 3 hr, after which the vessel was cooled by a water stream during irradiation. The sodium *p*-toluenesulfinate thus precipitated was filtered off, and the residue was concentrated and chromatographed on silica. 1-Phenyl-3-thiabicyclo[3.1.0]hexane (**16**) (87.5%) was eluted, with benzene as the sole product.

The thermal decomposition of the tosylhydrazone **1e** was carried out in a manner similar to that used in the case of the decomposition of the **1a-d** tosylhydrazones, though sodium methoxide was used instead of sodium hydride. The vacuum distillation of the reaction mixture afforded 3-thiabicyclo[3.1.0]hexane(**16**) in a 68.5% yield.

The yields were calculated by comparing the vpc peak area of the crude product with that of pure samples.

16: NMR (CCl_4, TMS): τ 9.17 ($H_A{}^a$: quartet, J_{ab}=8 Hz, 1 H), 8.49 ($H_B{}^a$: t, J_{ab}=4 Hz, J_{aa}=1 H, 6 Hz), 8.23 (H^b: quintet, J_{ab}=8 Hz, 4 Hz, J_{bc}=4 Hz, 0 Hz, 1H), 7.14 ($H_A{}^c$: d, J_{cc}=11 Hz, J_{bc}=0 Hz, 1H), 6.90 (H^d: AB_q, J_{dd}=11 Hz, 2H), 6.79 ($H_B{}^c$: quartet, J_{bc}=4 Hz, J_{cc}=11 Hz, 1H), and 3.00—2.70 (H : m, 5H).



Mass: 176 M$^+$ base peak, 143 M$^+$–SH, 135 M$^+$−41 , 128 M$^+$−48, , 91 C_7H_7, and 77 Ph$^+$. Found: C, 74.98; H, 6.74; S, 18.23%. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86; S, 18.19%.