Reactions of Unsaturated Sulfides with Carbenes. 22. Reactivities of Sulfur and Double Bond, and Formation of Unsaturated Sulfonium Ylides[1,2]

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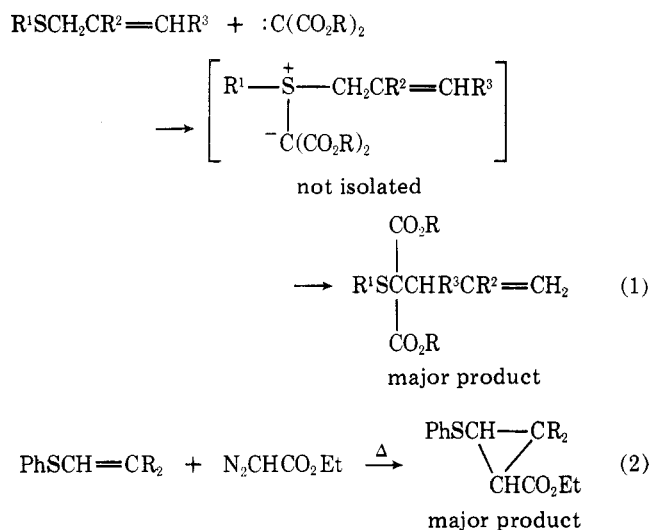
Hirofumi Higuchi and Toshihiko Migita

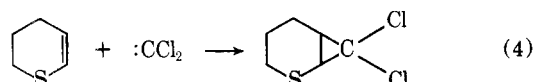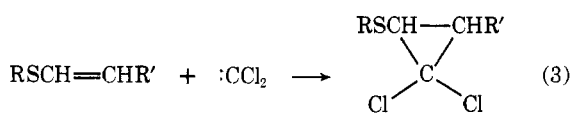*Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan*

The reaction of vinyl sulfides with carbomethoxycarbene leads to the formation of methyl vinylthioacetate as major product and some cyclopropane adduct as minor product. The reaction of vinyl sulfides with biscarbomethoxycarbene leads to the corresponding stable sulfonium ylide which decomposed thermally to vinylthiomalonate. The NMR spectra of vinyl sulfides and vinyl sulfonium biscarbomethoxymethylide are discussed. Although the reactions of vinyl sulfide with dichlorocarbene lead to the formation of cyclopropane derivatives, the reaction of allyl vinyl sulfide inhibits the formation of cyclopropane adduct from the double bond of the vinyl sulfide part. The course of these reactions is also discussed.

In previous studies, we observed that the reaction of allylic sulfides with carboalkoxycarbenes under thermal and photolytic conditions produced the C–S insertion products and some addition products to the olefin as a minor process[3,4] (eq 1 and 2). It was suggested that the reaction with allyl sul-

$$R^1SCH_2CR^2{=}CHR^3 \ + \ :C(CO_2R)_2$$

$$\longrightarrow \left[\begin{array}{c} R^1{-}\overset{+}{S}{-}CH_2CR^2{=}CHR^3 \\ \ \\ {}^-\!\overset{}{C}(CO_2R)_2 \end{array} \right]$$

not isolated

$$\longrightarrow \begin{array}{c} CO_2R \\ | \\ R^1S\overset{}{C}CHR^3CR^2{=}CH_2 \\ | \\ CO_2R \end{array} \quad (1)$$

major product

$$PhSCH{=}CR_2 \ + \ N_2CHCO_2Et \ \xrightarrow{\Delta} \ \begin{array}{c} PhSCH{-}CR_2 \\ \diagdown \diagup \\ CHCO_2Et \end{array} \quad (2)$$

major product

fide may involve a sulfur ylide intermediate followed by a 2,3-sigmatropic rearrangement, since the carbene attacks a sulfur atom more rapidly than a carbon–carbon double bond. On the other hand, in the thermolysis of ethyl diazoacetate in phenyl vinyl sulfide, Kaiser[5] reported only the formation of cyclopropane. In more recent studies, Parham[6,7] observed also the formation of cyclopropane as a major reaction product in the reaction of dichlorocarbene with several vinyl sulfides. The remarkable differences in behavior of these two olefins were attributed to the difference in nucleophilicity of the two double bonds relative to sulfur, since vinyl sulfides are known to be electron-rich olefins due to the M effect of the sulfur atom (eq 3 and 4). However, a contribution of the structure

$$RSCH{=}CHR' \ + \ :CCl_2 \ \longrightarrow \ \begin{array}{c} RSCH{-}CHR' \\ \diagdown \diagup \\ C \\ \diagup \diagdown \\ Cl \quad Cl \end{array} \quad (3)$$

$$\text{(cyclic sulfide)} \ + \ :CCl_2 \ \longrightarrow \ \text{(cyclopropane adduct)} \begin{array}{c} Cl \\ C \\ Cl \end{array} \quad (4)$$

of Ib is also possible owing to the capability of a sulfur atom to expand its valence shell. This contribution may enhance the reactivity of the sulfur atom toward electrophilic carbenes.
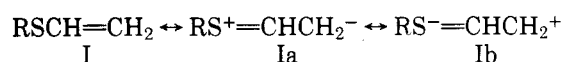
$$RSCH{=}CH_2 \leftrightarrow RS^+{=}CHCH_2^- \leftrightarrow RS^-{=}CHCH_2^+$$
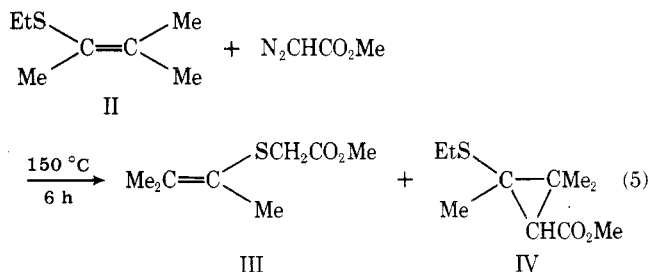$$\text{I} \qquad\qquad \text{Ia} \qquad\qquad \text{Ib}$$

In order to learn more about the generality and mechanism of these interesting transformations, an investigation of the reaction of vinyl sulfides and the reaction of unsaturated cyclic sulfides with various carbenes was carried out under the thermal and photochemical conditions. This paper presents the data concerning the isolation of intermediate sulfur ylides and the reactivities of unsaturated sulfides for the carbenes.

Results and Discussion

Thermolysis of Methyl Diazoacetate in Vinyl Sulfides.[8] Methyl diazoacetate (6.7 mmol) was dissolved in 30 mmol of trimethyl(ethylthio)ethylene (II) and heated at 150 °C for 6 h. Vapor-phase chromatographic analysis using several stationary phases detected two products III and IV formed in ca. 39 and 5% yields, respectively (eq 5). The product III proved

$$\begin{array}{c} EtS \\ \diagdown \\ C{=}C \\ \diagup \diagdown \\ Me Me \end{array} \begin{array}{c} Me \\ \diagup \\ \\ \diagdown \\ Me \end{array} \ + \ N_2CHCO_2Me$$

II

$$\xrightarrow[\text{6 h}]{150\,°C} \ \begin{array}{c} SCH_2CO_2Me \\ \diagup \\ Me_2C{=}C \\ \diagdown \\ Me \end{array} \ + \ \begin{array}{c} EtS \\ \diagdown \\ C{-}CMe_2 \\ \diagup\ \diagdown\ \diagup \\ Me CHCO_2Me \end{array} \quad (5)$$

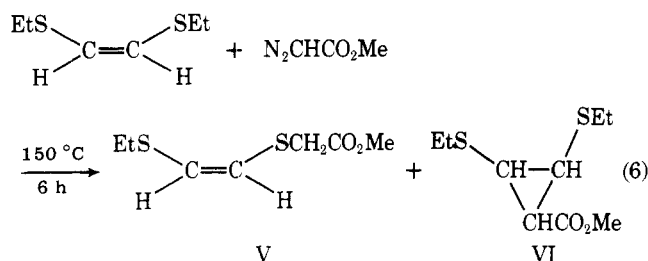$$\text{III}\text{IV}$$

to be methyl 1,2-dimethyl-1-propenylthioacetate, and the product IV was found to be the expected carbene addition product to the double bond. The structures of these products were determined by NMR and IR spectra and elemental analyses.

A study of methyl diazoacetate with *cis*-diethylthioethylene affords a 38% yield of the thioacetate V and 6% of the addition product of carbomethoxycarbene to the olefin (eq 6). The corresponding cyclopropane from the addition of carbene to the olefin is expected to form syn and anti forms, but this detail of structure could not be deduced from the spectral data.

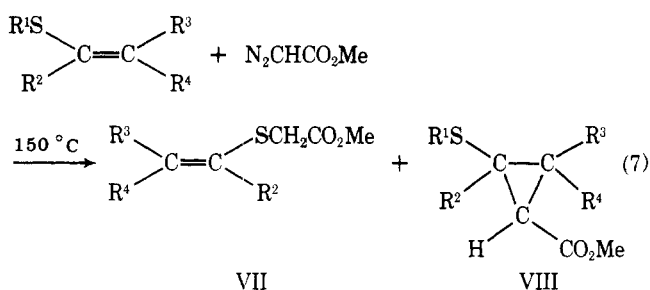A number of substituted vinyl sulfides gave rise to the

Table I. Yields of the Products from Vinyl Sulfides and Methyl Diazoacetate at 150 °C
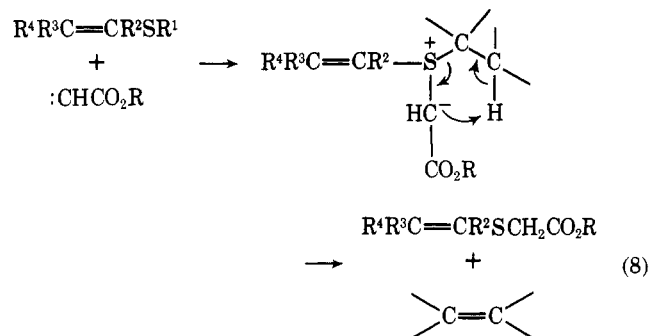
Product	R^1	R^2	R^3	R^4	VII, %	VIII, %
a	Me	H	Me	Me		12
b	Et	H	Me	Me	21	3
c	Et	Me	H	Me	29	5
d	Et	H	H	Me	25	18
e	i-Pr	H	Me	Me	32	15
f	i-Pr	Me	Me	H	36	Tr
g	t-Bu	H	Me	Me	37	10
h	Ph	H	H	H		58
i	Ph	H	Me	Me		15

Table II. Competitive Reaction for Cyclopropane Formation in the Reaction with Carbomethoxycarbene at 160 °C

Olefin	Product	Rate
$Me_2C=CHMe$	$Me_2C-CHMe$ / $CHCO_2Me$	1.0
$Me_2C=CHSEt$	$Me_2C-CHSEt$ / $CHCO_2Me$	1.9
$Me_2C=CHOEt$	$Me_2C-CHOEt$ / $CHCO_2Me$	4.3

$$EtS\diagdown C=C\diagup SEt \quad + \quad N_2CHCO_2Me$$
$$H\diagup \qquad \diagdown H$$

$$\xrightarrow[\text{6 h}]{150\ °C} \quad EtS\diagdown C=C\diagup SCH_2CO_2Me \quad + \quad EtS\diagdown CH-CH\diagup SEt \qquad (6)$$
$$\qquad\qquad H \qquad\qquad H \qquad\qquad CHCO_2Me$$
$$\qquad\qquad\qquad \text{V} \qquad\qquad\qquad\qquad \text{VI}$$

thioacetate as major product when treated with methyl diazoacetate as shown in eq 7 (see also Table I).

$$R^1S\diagdown C=C\diagup R^3 \quad + \quad N_2CHCO_2Me$$
$$R^2\diagup \qquad \diagdown R^4$$

$$\xrightarrow{150\ °C} \quad R^3\diagdown C=C\diagup SCH_2CO_2Me \quad + \quad R^1S\diagdown C-C\diagup R^3 \qquad (7)$$
$$R^4\diagup \qquad \diagdown R^2 \qquad\qquad R^2 \diagup C \diagdown R^4$$
$$\qquad\qquad\qquad\qquad H \diagup \diagdown CO_2Me$$
$$\qquad\qquad \text{VII} \qquad\qquad\qquad \text{VIII}$$

While we have not confirmed the existence of a sulfur ylide intermediate, we have been able to show that the formation of these thioacetates may be formulated as involving an attack of carbomethoxycarbene on the sulfur atom to form the vinylsulfonium ylide followed by a cyclic elimination of olefin, and that the sulfide sulfur inhibits the formation of carbene addition products[9] (eq 8). Data reveal that an attack of car-

$$R^4R^3C=CR^2SR^1$$
$$\qquad + \qquad \longrightarrow \quad R^4R^3C=CR^2-S\diagup C \diagdown C$$
$$\text{:CHCO}_2R \qquad\qquad\qquad\qquad HC\diagdown H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad CO_2R$$

$$R^4R^3C=CR^2SCH_2CO_2R$$
$$\longrightarrow \qquad + \qquad (8)$$
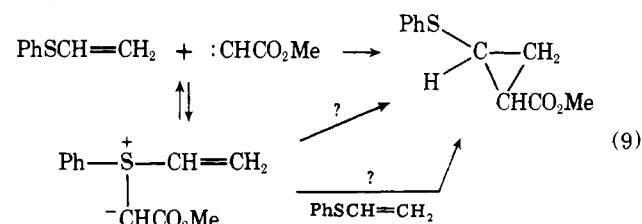$$\qquad\qquad \diagdown C=C\diagup$$

bomethoxycarbene on sulfur appears to be four to five times faster than addition on the double bond. 1-Phenyl-2-methyl-1-propene, which can form a sulfonium ylide that cannot undergo elimination of an olefin, apparently polymerizes to unknown compounds. On the other hand, the inhibiting effect of the sulfide sulfur on cyclopropane formation was not observed in the reaction of carbomethoxycarbene with phenyl vinyl sulfide. This may suggest that the intermediate sulfur ylide may react with either an intramolecular or intermolecular olefin to give the cyclopropane adduct (eq 9). An alternative explanation is that ylide formation is reversible, and when an intramolecular rearrangement is not possible,
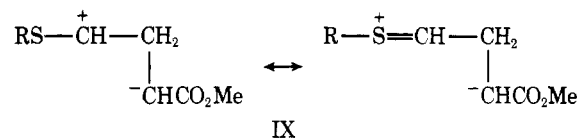
as it is not with phenyl or methyl, then the cyclopropane is ultimately formed by the addition of carbene on the double bond.

$$PhSCH=CH_2 \quad + \quad :CHCO_2Me \quad \longrightarrow \quad PhS\diagdown C-CH_2 \diagup$$
$$\qquad\qquad\qquad \updownarrow \qquad \qquad ? \nearrow \qquad H \diagdown CHCO_2Me$$
$$Ph-\overset{+}{S}-CH=CH_2 \qquad\qquad\qquad\qquad\qquad (9)$$
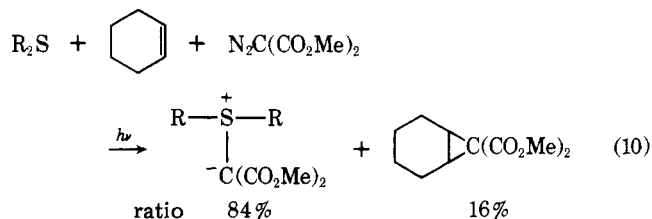$$^-CHCO_2Me \qquad\qquad PhSCH=CH_2$$

There are some electronic effects visible in the cyclopropane formation reactions. These can be evaluated from data on the competing reactivity of different olefins for the carbene formed on thermolysis of methyl diazoacetate at 160 °C (Table II). Data in Table II indicate the high reactivity of vinyl sulfide toward carbomethoxycarbene assuming the ylide is not sources of the cyclopropane. The double bond of vinyl sulfide is 1.9 times as reactive as that of trimethylethylene, but less reactive than of vinyl ether. A possible transition state for the carbene addition to vinyl sulfide may be IX, in which

$$RS-\overset{+}{C}H-CH_2 \qquad\qquad R-\overset{+}{S}=CH-CH_2$$
$$\qquad | \qquad\qquad \longleftrightarrow \qquad\qquad |$$
$$^-CHCO_2Me \qquad\qquad\qquad ^-CHCO_2Me$$
$$\qquad\qquad\qquad \text{IX}$$

the contribution of sulfur $2p-3p\pi$ is not as large as that of oxygen electrons $(2p-2p\pi)$.

The photolysis of methyl diazoacetate in 1-*tert*-butyl-thio-2-methyl-1-propene was also investigated. The vinyl thioacetate and cyclopropane were formed in only 1 and 9% yield, respectively; the major products of the reaction were observed, but not identified. In view of the low yield, the formation of the sulfur ylide in this case is uncertain. The reaction at low temperature has not provided much useful data to date.
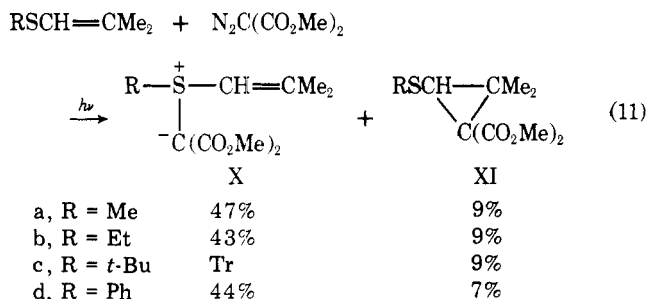
Reaction of Dimethyl Diazomalonate in Vinyl Sulfides. Biscarbomethoxycarbene generated from direct photolysis of dimethyl diazomalonate reacts with alkyl and aryl sulfides to give stable sulfonium biscarbomethoxymethylides[10,11] (eq 10). The formation of sulfonium ylides was proposed to be the

$$R_2S \quad + \quad \bigcirc \quad + \quad N_2C(CO_2Me)_2$$

$$\xrightarrow{h\nu} \quad R-\overset{+}{S}-R \quad + \quad \bigcirc C(CO_2Me)_2 \qquad (10)$$
$$\qquad\qquad ^-C(CO_2Me)_2$$
$$\text{ratio} \qquad 84\% \qquad\qquad\qquad 16\%$$

result of attack of the singlet carbene on a lone pair of the sulfur atom, which was found to proceed six times as fast as with double bond of cyclohexene.
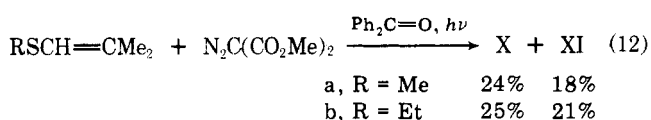
From this, we can expect that biscarbomethoxycarbene

might form stable sulfonium ylides in the reaction with vinyl sulfides. Irradiation of dimethyl diazomalonate in 1-methyl-thio-2-methyl-1-propene was carried out in a Pyrex tube with a high-pressure mercury lamp for 6 h until the evolution of N_2 gas ceased. The reaction products were analyzed by TLC and gas chromatography, and showed the formation of the principal product Xa in 47% yield and the minor product XIa in 9% yield, respectively (eq 11). The principal product Xa was

$$RSCH{=\!=}CMe_2 \quad + \quad N_2C(CO_2Me)_2$$

$$\xrightarrow{h\nu} \quad \begin{matrix} R{-\!\!\overset{+}{S}\!-}CH{=\!=}CMe_2 \\ | \\ {}^{-}C(CO_2Me)_2 \end{matrix} \quad + \quad \begin{matrix} RSCH{-\!\!-}CMe_2 \\ \diagdown\,\diagup \\ C(CO_2Me)_2 \end{matrix} \qquad (11)$$

		X	XI
a,	R = Me	47%	9%
b,	R = Et	43%	9%
c,	R = t-Bu	Tr	9%
d,	R = Ph	44%	7%

found to be 2-methyl-1-propenylmethylsulfonium biscarbomethoxymethylide: ν (C=O) 1665 and 1635 cm^{-1}; NMR δ (CDCl$_3$) 1.91 (s, 3 H), 2.07 (s, 3 H), 2.90 (s, 3 H), 3.58 (s, 6 H), and 6.55 (s, 1 H). The proton shift of the >S$^+$–Me and the carbonyl shift in product Xa are analogous to those observed in dimethylsulfonium biscarbomethoxymethylide [ν (C=O) 1675 and 1625 cm^{-1}; NMR δ (CDCl$_3$) 2.89 for >S$^+$–Me and 3.71 for –CO$_2$Me). The product XIa was found to be a cyclopropane adduct.

Similar type of reactions in a variety of vinyl sulfides showed the formation of the corresponding alkyl vinylsulfonium biscarbomethoxymethylides as the major product. Reaction of *tert*-butylthio-2-methyl-1-propene with dimethyl diazomalonate did afford the corresponding sulfonium ylide, but in very low yield because of the steric effect of the *tert*-butyl group on the sulfur atom.

The most marked change in going from direct photolysis to sensitized photolysis is in the ratio of yield of the sulfonium ylide to cyclopropane derivatives. Benzophenone photosensitized decomposition of dimethyl diazomalonate in 1-methylthio-2-methyl-1-propene gave 24% of the corresponding sulfonium ylide and 18% of the cyclopropane derivative (eq 12). An appropriate control experiment showed that under

$$RSCH{=\!=}CMe_2 \quad + \quad N_2C(CO_2Me)_2 \xrightarrow{\;Ph_2C=O,\;h\nu\;} X \;+\; XI \qquad (12)$$

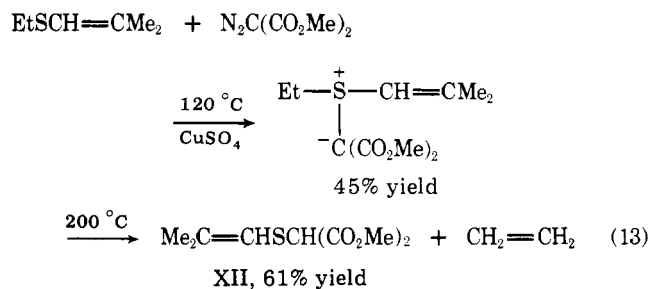|		X	XI
a,	R = Me	24%	18%
b,	R = Et	25%	21%

the reaction conditions the product neither isomerized nor was destroyed. One explanation is that the photosensitized reaction of dimethyl diazomalonate will give a triplet species which reacts selectively with a carbon–carbon double bond, but also that triplet species will equilibrate with the singlet species, which might react preferentially with the vinyl sulfide sulfur to give the sulfonium ylide.[12] However, there may be other plausible explanations for the formation of some sulfonium ylide in the photosensitized reaction. For instance, the charge-transfer complex which results from triplet benzophenone and sulfide may decrease the formation of the triplet carbene species.
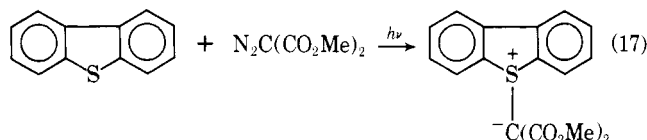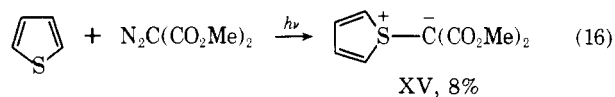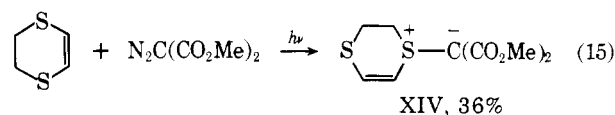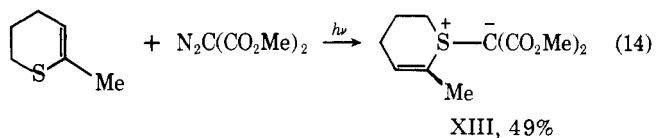
Thermal reaction of dimethyl diazomalonate in vinyl sulfides in the presence of copper sulfate at 120 °C gave the corresponding sulfonium ylide in 45–50% yields, and did not afford any cyclopropane derivatives by the addition of carbene to the double bond.

We have also examined the thermal behavior of the sulfonium biscarbomethoxymethylide. When ethyl 2-methyl-1-propenyl(ethyl)sulfonium biscarbomethoxymethylide was heated in sealed tube at a temperature above 200 °C for 1 h,

2-methyl-1-propenyl thiomalonate was obtained in 61% yield together with the formation of ethylene (eq 13). The elimi-

$$EtSCH{=\!=}CMe_2 \quad + \quad N_2C(CO_2Me)_2$$

$$\xrightarrow[\text{CuSO}_4]{120\ °C} \quad \begin{matrix} Et{-\!\!\overset{+}{S}\!-}CH{=\!=}CMe_2 \\ | \\ {}^{-}C(CO_2Me)_2 \end{matrix}$$

45% yield

$$\xrightarrow{200\ °C} \quad Me_2C{=\!=}CHSCH(CO_2Me)_2 \;+\; CH_2{=\!=}CH_2 \qquad (13)$$

XII, 61% yield

native decomposition of the sulfonium ylide is probably a cis elimination through a five-membered cyclic transition state.[9] Those observations give support to the proposed ylide mechanism in the reaction of carbomethoxycarbene with vinyl sulfide, which gave a vinylthioacetate together with the formation of olefin. In the reaction of dimethyl diazomalonate with unsaturated cyclic sulfides, the corresponding sulfonium ylides were also obtained as stable compounds (eq 14–17).

$$\text{(structure)} \quad + \quad N_2C(CO_2Me)_2 \xrightarrow{h\nu} \text{(structure)} \qquad (14)$$

XIII, 49%

$$\text{(structure)} \quad + \quad N_2C(CO_2Me)_2 \xrightarrow{h\nu} \text{(structure)} \qquad (15)$$

XIV, 36%

$$\text{(structure)} \quad + \quad N_2C(CO_2Me)_2 \xrightarrow{h\nu} \text{(structure)} \qquad (16)$$

XV, 8%

$$\text{(structure)} \quad + \quad N_2C(CO_2Me)_2 \xrightarrow{h\nu} \text{(structure)} \qquad (17)$$

Irradiation of dimethyl diazomalonate in 2,3-dihydro-6-methyl-4*H*-thiapyran gave the corresponding sulfonium ylide in 49% yield. The study of the reaction of carbene with conjugated vinyl sulfides is particularly interesting. Thiophene and dibenzothiophene,[12] in which the lone pair of sulfur is highly delocalized, are efficient traps for the carbene, and gave the corresponding sulfonium ylides in the reaction with dimethyl diazomalonate under either thermal or photochemical conditions. The stabilized thiophenium ylide showed: ν (C=O) at 1645 cm^{-1}; NMR δ (CDCl$_3$) at 3.67 (s, 6 H), 7.07 (br s, 2 H), and 7.27 (br s, 2 H); m/e 214.

Reaction of Acetylenic Sulfides with Diazoacetate and Diazomalonate.[2] Carbenes and carbenoids add to an acetylene less readily than to an olefin, while only a few cases are known of such carbene reactions with hetero-substituted acetylenes. Reactions are conveniently carried out in the absence of solvent at elevated temperature. Heating an equimolar mixture of methyl diazoacetate and phenylethylthioacetylene in the presence of a catalytic amount of anhydrous copper sulfate at 60 °C for 10 min gave a 35% yield (GLC) of compound XVIa (eq 18), in accord with the observed spectral data: ν (C=O) at 1745 cm^{-1}, and ν (C≡C) at 2180 cm^{-1}; NMR δ (CCl$_4$) 3.51 (s, 2 H), 3.77 (s, 3 H), and 7.2–7.5 (m, 5 H); m/e 206. Similar reactions of methyl diazoacetate with the acetylenic sulfides in the presence of copper sulfate lead to the formation of alkynylthioacetates. No cyclopropene derivative or rearranged products were obtained. By analogy with the reaction with alkyl sulfides and vinyl sulfides, the
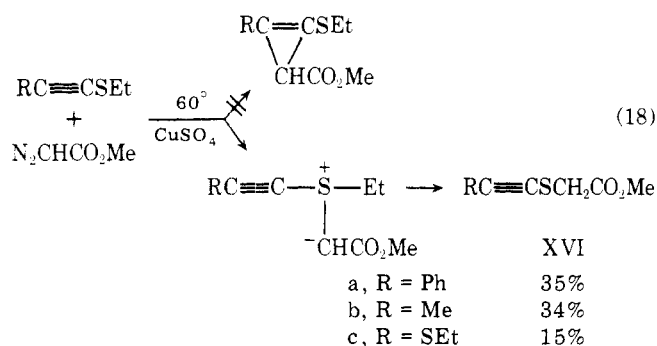
Table III. Competitive Reaction for Sulfur Atoms in the Reaction with Methyl Diazoacetate in Presence of CuSO$_4$ at 60 °C

Sulfide	Product	Rate
Et$_2$S	EtSCH$_2$CO$_2$Me	7.1
Me$_2$C=CHSEt	Me$_2$C=CHSCH$_2$CO$_2$Me	4.6
MeC≡CSEt	MeC≡CSCH$_2$CO$_2$Me	9.2
Me$_2$C=CHMe	Me$_2$C——CHMe 　　　\\/ 　　CHCO$_2$Me	1.0 (standard)

Table IV. Relative Ratio of Sulfur and Double Bond Attack in the Reaction of Arylcarbenes

Sulfide	:CPh$_2$	:CHPh
t-BuSCH=CMe$_2$	3.1	1.4
t-BuSCH$_2$CH=CH$_2$	7.3	4.7

formation of compound XVI may involve an attack of carbomethoxycarbene on the sulfur atom to form the acetylenic sulfonium ylide followed by cyclic elimination of olefin, although trapping of the acetylenic sulfonium ylide was not successful under the reaction conditions.

$$RC≡CSEt + N_2CHCO_2Me \xrightarrow[CuSO_4]{60°} \xcancel{\begin{array}{c} RC=CSEt \\ \backslash / \\ CHCO_2Me \end{array}} \quad (18)$$

$$RC≡C\overset{+}{\underset{\underset{\overline{C}HCO_2Me}{|}}{S}}Et \longrightarrow RC≡CSCH_2CO_2Me$$

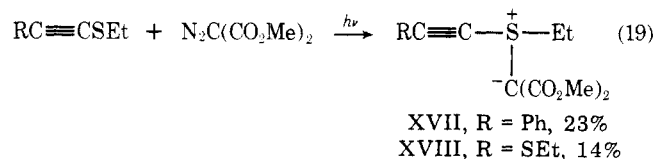|		XVI
a,	R = Ph	35%
b,	R = Me	34%
c,	R = SEt	15%

We have also examined the reactivity of the sulfur atoms of different unsaturated sulfides in the thermal reaction of methyl diazoacetate in the presence of copper sulfate. Table III shows the relative rates of carbenoid attack on divalent sulfur in the competing reaction with addition to trimethylethylene. The data indicate that the carbenoid attacks divalent sulfur more effectively than it attacks the double bond of trimethylethylene. On the other hand, the electrophilic carbenoid attacks the vinyl sulfide sulfur less efficiently in comparison with the attack on alkyl and acetylenic sulfide sulfurs. It could be argued that the electron density on the vinyl sulfide sulfur is decreased somewhat because the lone-pair electrons of the vinyl sulfide sulfur are delocalized to some extent through the overlap of 3p orbitals of sulfur with the carbon 2p orbitals.[13]

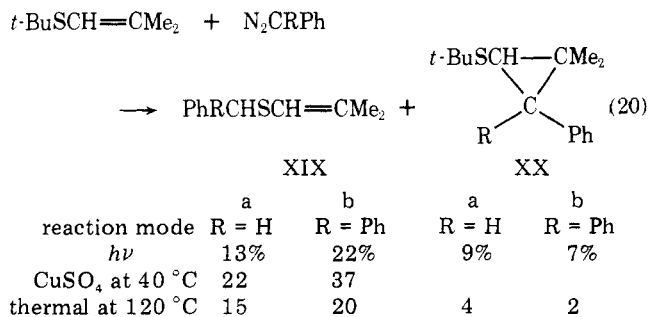$$R_2C=CHSR \leftrightarrow R_2C^-CH=S^+R$$
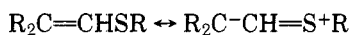
However, in the case of acetylenic sulfide, the electron density of the sulfur atom may be influenced by the inductive effect of the acetylene group, but not by its resonance effect.

The reactivity of acetylenic sulfide sulfur toward carbenes suggested the possibility of isolation of sulfonium ylides. Irradiating a mixture of methyl diazomalonate and the acetylenic sulfide (3 equiv) in a Pyrex tube for 21 h results in an isolated 23% yield of a pure acetylenic sulfonium ylide after preparative thin-layer chromatography (eq 19). The assigned
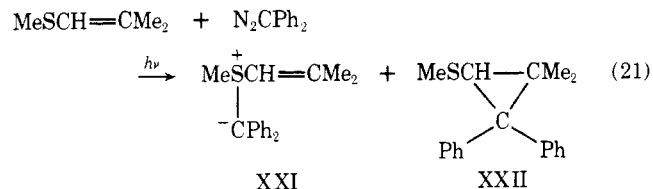
$$RC≡CSEt + N_2C(CO_2Me)_2 \xrightarrow{h\nu} RC≡C\overset{+}{\underset{\underset{\overline{C}(CO_2Me)_2}{|}}{S}}Et \quad (19)$$

XVII, R = Ph, 23%
XVIII, R = SEt, 14%

structure of sulfur ylide XVIII is in accord with the observed spectral data: ν (C=O) 1685 and 1650 cm^{-1}; NMR δ (CDCl$_3$) 1.40 (t, 3 H), 3.77 (s, 6 H), 3.80 (q, 2 H), and 7.48 (m, 5 H); *m/e* 292.

Photolysis of Phenyl- and Diphenyldiazomethanes in Vinyl Sulfides. The photolysis of phenyl- and diphenyldiazomethanes in vinyl sulfides was carried out in a Pyrex tube without degassing. The crude reaction mixture in the reaction of phenyldiazomethane and 1-*tert*-butylthio-2-methyl-1-propene did not show the formation of any sulfonium ylide as judged by the examination of either NMR or IR spectra. GLC analyses showed the formation of benzylthio-2-methyl-1-propene and the corresponding cyclopropane derivative together with some stilbene and benzalazine (eq 20).

$$t\text{-BuSCH=CMe}_2 + N_2CRPh$$

$$\longrightarrow PhRCHSCH=CMe_2 + \begin{array}{c} t\text{-BuSCH——CMe}_2 \\ \backslash / \\ C \\ / \backslash \\ R \quad Ph \end{array} \quad (20)$$

XIX　　　　　　XX

	a	b	a	b
reaction mode	R = H	R = Ph	R = H	R = Ph
$h\nu$	13%	22%	9%	7%
CuSO$_4$ at 40 °C	22	37		
thermal at 120 °C	15	20	4	2

The structure of these products was determined by spectral and elemental analyses. The reactions were also carried out under various other conditions. The results indicate that arylcarbenes prefer to attack the sulfur atom over the double bond; the copper carbenoid exclusively attacks the sulfur atom. Under the photolytic conditions, the relative rate of XIX and XX was about 3.1 in the reaction of diphenylcarbene and 1.4 in the reaction of phenylcarbene. Since the reactivity of the *tert*-butyl allylic sulfide sulfur to the double bond in the allylic sulfide is 7.3 in the diphenylcarbene reaction and 4.7 in the phenylcarbene reaction (Table IV),[14] the change in the ratio may be due to the difference in nucleophilicity between vinyl sulfide sulfur and allylic sulfide sulfur, owing to donation of the 3pπ electron of sulfur to the double bond in vinyl sulfide.
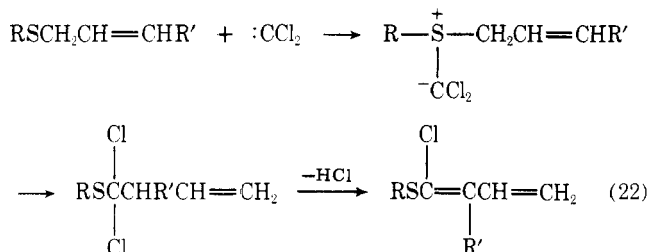
We have also examined the reaction of diphenylcarbene with vinyl sulfide, in which the sulfur bears an alkyl group not containing a β hydrogen. The photolysis of 2.34 mmol of diphenyl diazomethane in 22.7 mmol of 1-methylthio-2-methyl-1-propene was carried out in a Pyrex tube with a high-pressure mercury lamp for 2 h. The reaction products were anlayzed by column chromatography with silica gel and chloroform, ether, and methanol as solvents. Two main products, XXI and XXII, were found in 5 and 13% yield, respectively, together with some diphenylazine and benzophenone (eq 21). Product XXI showed NMR spectra δ (CDCl$_3$)
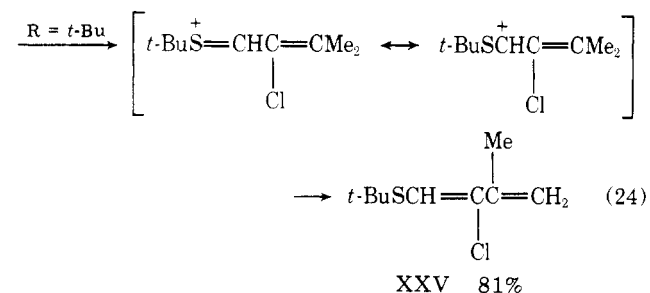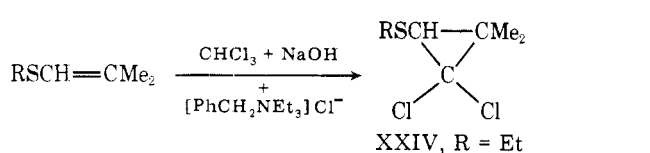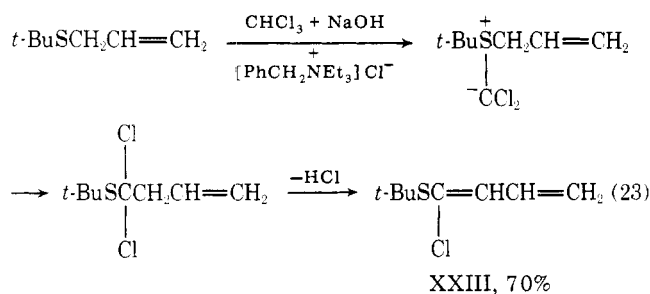
$$MeSCH=CMe_2 + N_2CPh_2$$

$$\xrightarrow{h\nu} Me\overset{+}{\underset{\underset{\overline{C}Ph_2}{|}}{S}}CH=CMe_2 + \begin{array}{c} MeSCH——CMe_2 \\ \backslash / \\ C \\ / \backslash \\ Ph \quad Ph \end{array} \quad (21)$$

XXI　　　　　　XXII

1.93 (s, 3 H), 2.03 (s, 3 H), 2.63 (s, 3 H), 6.12 (s, 1 H), and 7.28 (m, 10 H); *m/e* 268. The signal at δ 2.63 is especially interesting; it is tentatively assigned to the methyl protons of the corresponding sulfonium ylide. The IR spectra would not be expected to have any special band characteristic of sulfonium ylide. The product XXII was found to be the addition product of the carbene on the double bond from the NMR and IR spectral analyses.

Reactions of Vinyl Sulfides with Dichlorocarbene. The

reaction of dichlorocarbene with noncyclic allyl sulfides leads to the formation of 1-chloro-1-substituted mercaptobutadienes in high yields, together with some olefins derived by addition of hydrogen chloride to the butadienes. An attractive mechanism for the formation of mercaptobutadienes involves sulfonium ylide formation followed by intramolecular allylic rearrangement[15] (eq 22). It was also shown that the sulfide

$$RSCH_2CH{=}CHR' + :CCl_2 \longrightarrow R{-}\overset{+}{S}{-}CH_2CH{=}CHR' \atop {-}CCl_2$$

$$\longrightarrow \underset{Cl}{\overset{Cl}{RS\overset{|}{C}CHR'CH}}{=}CH_2 \xrightarrow{-HCl} \underset{R'}{\overset{Cl}{RS\overset{|}{C}}{=}CCH}{=}CH_2 \quad (22)$$
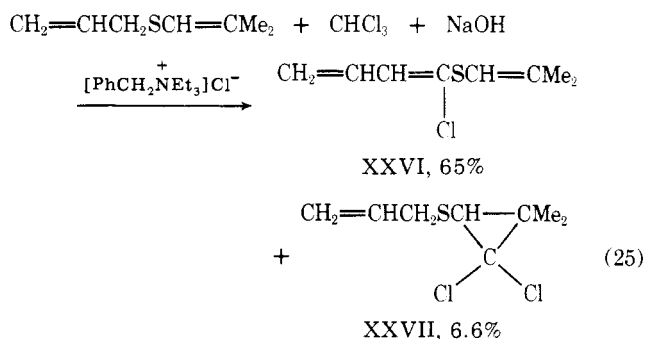
sulfur inhibits the formation of dichlorocyclopropyl adducts from the double bond. On the other hand, it was reported that the reaction of vinyl sulfide with dichlorocarbene gave the corresponding cyclopropane adducts in high yields. The remarkable difference in behavior of these olefins was explained by the difference in nucleophilicity of two double bonds relative to sulfur.[6,7] In order to learn more about the generality and mechanism of these interesting transformations, an investigation of the reaction of vinyl sulfides and allyl vinyl sulfides was undertaken using chloroform and sodium hydroxide mixtures in the presence of an ammonium salt. The reaction of *tert*-butyl allyl sulfide with chloroform was carried out in benzene–water solvent using conditions described by Makosza[16] (eq 23). A high yield of 1-chloro-1-*tert*-butyl-

$$t{-}BuSCH_2CH{=}CH_2 \xrightarrow[\text{[PhCH}_2\text{NEt}_3]\text{Cl}^-]{\text{CHCl}_3 + \text{NaOH}} t{-}BuS\overset{+}{C}H_2CH{=}CH_2 \atop {-}CCl_2$$

$$\longrightarrow \underset{Cl}{\overset{Cl}{t{-}BuS\overset{|}{C}CH_2CH}}{=}CH_2 \xrightarrow{-HCl} \underset{Cl}{\overset{}{t{-}BuS\overset{}{C}}{=}CHCH}{=}CH_2 \quad (23)$$

$$\text{XXIII, 70\%}$$

$$RSCH{=}CMe_2 \xrightarrow[\text{[PhCH}_2\text{NEt}_3]\text{Cl}^-]{\text{CHCl}_3 + \text{NaOH}} \underset{Cl}{\overset{RSCH{-}CMe_2}{\underset{}{\overset{\diagdown}{C}}{\diagup}}} Cl$$

$$\text{XXIV, R = Et}$$

$$\xrightarrow{R = t{-}Bu} \left[t{-}Bu\overset{+}{S}{=}CHC{=}CMe_2 \atop Cl \leftrightarrow t{-}Bu\overset{+}{S}CHC{=}CMe_2 \atop Cl \right]$$

$$\longrightarrow \underset{Cl}{\overset{Me}{t{-}BuSCH}{=}CC}{=}CH_2 \quad (24)$$

$$\text{XXV } 81\%$$

mercaptobutadiene (XXIII) was obtained as the product from the transformation of intermediate sulfur ylide. The addition product of dichlorocarbene to the double bond was not observed under the reaction conditions. On the other hand, the reactions of 1-ethyl- or 1-*tert*-butylthio-2-methyl-1-propenes with CHCl₃ and NaOH were carried out in benzene–water using conditions previously described for allyl sulfide (eq 24). In each case high yields of either the corresponding cyclopropane or butadiene derivatives were obtained (81–92%). The
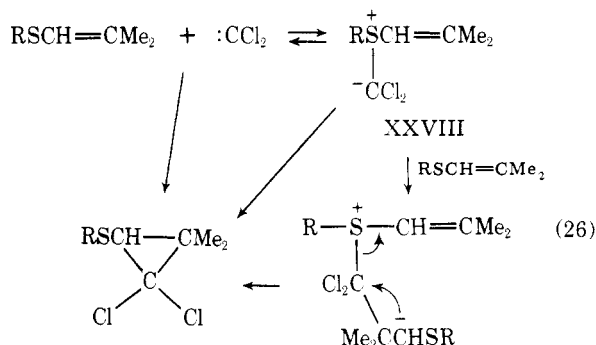
dichlorocyclopropane and butadiene derivatives were characterized by their composition and spectra.

A study of the reaction of allyl vinyl sulfide with dichlorocarbene was of particular interest in view of the reactivity relationship of these olefins and the sulfur atom with allyl sulfide and vinyl sulfide. Allyl vinyl sulfide reacted readily with dichlorocarbene to give chlorobutadienylthio-1-methyl-1-propene (XXVI) in 65% and the addition product to the vinyl group XXVII in 6.6% yield (eq 25). The formation

$$CH_2{=}CHCH_2SCH{=}CMe_2 + CHCl_3 + NaOH$$

$$\xrightarrow{[PhCH_2NEt_3]Cl^-} \underset{Cl}{\overset{CH_2{=}CHCH{=}CSCH{=}CMe_2}{\overset{|}{}}}$$

$$\text{XXVI, 65\%}$$

$$+ \quad \underset{Cl \quad Cl}{\overset{CH_2{=}CHCH_2SCH{-}CMe_2}{\underset{}{\overset{\diagdown}{C}}{\diagup}}} \quad (25)$$

$$\text{XXVII, 6.6\%}$$

of XXVI is consistent with the expected course of intermediate sulfur ylide rearrangement. The formation of an intermediate sulfur ylide is reasonable in view of the nucleophilic character of sulfide sulfur. Also it can be readily seen that the dichlorocarbene reacts with the vinyl double bond, because of the difference in nucleophilicity. However, one should emphasize that *vinylic sulfide sulfur is more sensitive to electrophilic species than the vinylic double bond.*

An attractive mechanism for the formation of cyclopropane from vinyl sulfide may involve direct carbene attack on the sulfur to form sulfonium ylide XXVIII followed by either intramolecular cyclization or intermolecular reaction with the double bond of another vinyl sulfide molecule (eq 26). How-

$$RSCH{=}CMe_2 + :CCl_2 \rightleftarrows \underset{{-}CCl_2}{\overset{+}{RSCH{=}CMe_2}}$$

$$\text{XXVIII}$$

$$\downarrow RSCH{=}CMe_2$$

$$\underset{Cl \quad Cl}{\overset{RSCH{-}CMe_2}{\underset{}{\overset{\diagdown}{C}}{\diagup}}} \quad \underset{Me_2\overset{}{C}CHSR}{\overset{R{-}\overset{+}{S}{-}CH{=}CMe_2}{\underset{Cl_2C}{}}} \quad (26)$$

ever, one can not rule out the direct carbene addition on the double bond via reversible carbene formation from intermediate sulfur ylide XXVIII.

Experimental Section

Materials. Methyl diazoacetate,[17] dimethyl diazomalonate,[11] phenyldiazomethane,[18] and diphenyldiazomethane[19] were prepared by known procedures as referenced. The vinyl sulfides, 1-ethylthio-1,2-dimethyl-1-propene (bp 154–156 °C), 1-ethylthio-1-methyl-1-propene (bp 136–138 °C), 1-ethylthio-1-propene (bp 121–123 °C), 1-ethylthio-2-methyl-1-propene (bp 132–133 °C), 1-isopropylthio-2-methyl-1-propene (bp 147 °C), 1-*tert*-butylthio-2-methyl-1-propene [bp 98 °C (118 mmHg)], 1-phenylthio-2-methyl-1-propene [bp 122 °C (48 mmHg)], and 1-*sec*-butylthio-2-methyl-1-propene [bp 103–104 °C (99 mmHg)] were prepared in 30–80% yield by the method of Boostra et al.[20] Phenyl vinyl sulfide[21] was prepared as described by Ford-Moore et al.,[21] giving the product in 64% yield, bp 87–91 °C (25 mmHg). 1-Methylthio-2-methyl-1-propene was prepared as described for the mixture of isobutylaldehyde and methyl mercaptan using zinc chloride. Distillation of the crude product gave 28% yield of the product, bp 120–125 °C.[21,22] 2,3-Dihydro-6-methyl-4H-thiapyran was prepared as described by Cohen and Steele.[23] 1,4-Dithiene[24] was prepared by the Parham method. 1-Allylthio-2-

Table V. Analytical Data of the Products Obtained from Vinyl Sulfides and Diazoacetate

Product	Registry no.	IR, cm^{-1} (main peaks)	NMR, ppm downfield from Me$_4$Si	Calcd, %		Found, %	
				C	H	C	H
III	42954-21-2	2980, 2950, 1740, 1438, 1278, 1130	1.79 (s, 3 H), 1.96 (s, 6 H), 3.21 (s, 2 H), 3.63 (s, 3 H)	55.14	8.10	54.99	8.11
IV	42954-25-6	2930, 1730, 1432, 1376, 1185, 1165, 1140, 1108	1.23 (t, 3 H), 1.28 (s, 3 H), 1.42 (s, 3 H), 1.56 (s, 3 H), 1.94 (s, 1 H), 2.60 (q, 2 H), 3.60 (s, 3 H)	59.32	8.97	59.55	8.90
V	63196-70-3	2930, 1740, 1275, 1150	1.31 (t, 3 H), 2.70 (q, 2 H), 3.22 (s, 2 H), 3.70 (s, 3 H), 5.99 (2, 1 H), 6.30 (s, 1 H)	43.72	6.29	43.86	6.20
VIIb	42954-22-3	2950, 1740, 1435, 1280, 1133	1.75, (s, 3 H), 1.78 (s, 3 H), 3.18 (s, 2 H), 3.68 (s, 3 H), 5.69 (s, 1 H)	52.47	7.55	52.42	7.61
VIIc	42954-23-4	2950, 1740, 1433, 1275, 1130	1.70 (d, 3 H), 1.90 (s, 3 H), 3.27 (s, 2 H), 3.67 (s, 3 H), 5.60 (q, 1 H)	52.42	7.55	52.38	7.49
VIId	63196-71-4	2980, 1740, 1277, 1130	1.72 (d, 3 H), 3.21 (s, 2 H), 3.70 (s, 3 H), 5.50–5.98 (m, 2 H)	49.29	6.89	49.08	7.01
VIIIa	63196-72-5	2930, 1740, 1440, 1210, 1160	1.23 (s, 3 H), 1.33 (s, 3 H), 1.63 (d, 1 H), 2.05 (s, 3 H), 2.18 (d, 1 H), 3.63 (s, 3 H)	55.14	8.10	55.02	8.16
VIIIb	42954-26-7	2930, 1732, 1440, 1220, 1170	1.26 (t, 3 H), 1.30 (s, 6 H), 1.77 (d, 1 H), 2.40 (d, 1 H), 2.53 (d, 2 H), 3.63 (s, 3 H)	57.41	8.57	57.92	8.72
VIIIc	42954-27-8	2930, 1735, 1430, 1265, 1155	1.22 (t, 3 H), 1.47 (s, 6 H), 1.6–1.9 (m 2 H), 2.53 (q, 2 H), 3.63 (s, 3 H)	57.41	8.57	57.56	8.39
VIIId	63196-73-6	2950, 1735, 1430, 1155	1.23 (t, 3 H), 1.28 (d, 3 H), 1.3–2.0 (m, 3 H), 2.47 (q, 2 H), 3.65 (s, 3 H)	51.58	7.58	52.01	7.51
VIIIe	63196-74-7	2960, 1735, 1440, 1220, 1170	1.26 (d, 6 H), 1.27 (s, 6 H), 1.42 (d, 1 H), 2.36 (d, 1 H), 2.92 (m, 1 H), 3.65 (s, 3 H)	59.32	8.97	58.86	8.70
VIIIg	63196-75-8	2960, 1733, 1440, 1280, 1215, 1165	1.23 (s, 6 H), 1.28 (s, 9 H), 1.65 (d, 1 H), 2.05 (d, 1 H), 3.58 (s, 3 H)	61.07	9.32	61.18	9.29
VIIIh	63196-76-9	3050, 2950, 1730, 1485, 1435, 1260, 1200, 1170	1.21 (m, 1 H), 1.77 (m, 2 H), 2.71 (m, 1 H), 3.70 (s, 3 H), 7.23 (m, 5 H)	63.43	5.81	63.59	5.75

Table VI. Reaction Products from Vinyl Sulfides and Dimethyl Diazomalonate

Product	Registry no.	IR, cm^{-1} (main peaks)	NMR, ppm downfield from Me$_4$Si	Calcd, %		Found, %	
				C	H	C	H
Xa	63196-77-0	1665, 1630, 1320, 1070	1.91 (s, 3 H), 2.07 (s, 3 H), 2.90 (s, 3 H), 3.58 (s, 6 H), 6.55 (s, 1 H)	51.70	6.94	51.92	6.79
Xb	63196-78-1	1690, 1630, 1440, 1320, 1080	1.25 (t, 3 H), 1.96 (t, 3 H), 2.08 (s, 3 H), 3.53 (m, 2 H), 3.65 (s, 6 H), 6.48 (s, 1 H)	53.63	7.37	53.69	7.30
Xc	63196-79-2	2950, 1650, 1440, 1330, 1240, 1080	1.27 (s, 9 H), 1.95 (s, 3 H), 2.07 (s, 3 H), 3.72 (s, 6 H), 6.45 (s, 1 H)	56.91	8.08	57.04	7.98
Xd	63196-80-5	1680, 1640, 1430, 1325, 1080	2.03 (s, 3 H), 2.15 (s, 3 H), 3.65 (s, 6 H), 6.35 (s, 1 H), 7.48 (m, 5 H)	61.20	6.16	61.23	6.19
XII	63196-81-6	1760, 1740, 1430, 1300, 1265, 1145	1.82 (s, 6 H), 3.75 (s, 6 H), 4.07 (s, 1 H), 5.80 (s, 1 H)	49.52	6.48	49.80	6.62
XIII	63196-82-7	1680, 1640, 1430, 1330, 1080, 915	1.90 (s, 3 H), 2.1–2.4 (m, 4 H), 3.0–3.3 (m, 2 H), 3.67 (s, 6 H), 6.20 (s, 1 H)	54.08	6.60	54.57	6.38
XIV	63196-83-8	3000, 1680, 1645, 1435, 1330, 1080	3.5–4.2 (m, 4 H), 3.68 (s, 6 H), 5.95, (d, 1 H), 6.93 (d, 1 H)	43.53	4.87	43.98	4.86
XV	63196-84-9	3090, 1645, 1440, 1245, 1080	3.67 (s, 6 H), 7.07 (s, 2 H), 7.27 (s, 2 H)	50.45	4.71	50.38	4.91
XVIa	36814-62-7	3075, 1745, 1490, 1445, 1440, 1300, 1280, 1170, 1135	3.51 (s, 2 H), 3.77 (s, 3 H), 7.2–7.5 (m, 5 H)	64.06	4.89	63.75	5.13
XVIb	54045-22-6	1745, 1440, 1280, 1160, 1135	1.97 (s, 3 H), 3.37 (s, 2 H), 3.75 (s, 3 H)	49.98	5.59	50.23	5.72
XVIc	54045-23-7	2950, 1745, 1440, 1300, 1265, 1145	1.46 (t, 3 H), 2.70 (q, 2 H), 3.42 (s, 2 H), 3.75 (s, 3 H)	44.18	5.30	44.21	5.29
XVII	63196-85-0	1685, 1650, 1440, 1335, 1245, 1085, 910	1.40 (t, 3 H), 3.77 (s, 6 H), 3.80 (q, 2 H), 7.48 (m, 5 H)	61.62	5.52	61.73	5.59
XVIII	63196-86-1	1675, 1640, 1435, 1330, 1240, 1085	1.35 (t, 3 H), 1.45 (t, 3 H), 2.87 (q, 2 H), 3.68 (q, 2 H), 3.73 (s, 6 H)	47.08	5.84	47.11	5.83

methyl-1-propene was prepared by the addition of allyl mercaptan to isobutylaldehyde in a manner described for 1-ethylthio-1,2-dimethyl-1-propene in 50% yield, bp 80–82 °C (90 mmHg). Phenylethylthioacetylene was prepared as described by Brandsma[25] in 36% yield, bp 108–113 °C (11 mmHg). Methylethylthioacetylene and 1,2-bis(ethylthio)acetylene were prepared in the method described for phenylethylthioacetylene.

General Procedure of Thermal and Photochemical Reactions of Methyl Diazoacetate in Vinyl Sulfides. Thermal or photochemical reactions of 5 mmol of methyl diazoacetate in 30–50 mmol of vinyl sulfides were carried out in Pyrex sealed tube without degassing at >160 °C or with a high-pressure mercury lamp. After the diazo band disappeared from the IR spectrum of the reaction mixture, a known amount of an internal standard was added to the reaction mixture, which was then analyzed by gas chromatography. The

structure of the isolated products was determined on the basis of NMR and IR spectra and elemental analysis. The cyclopropane derivatives obtained from the reaction consist of two geometrical isomers. Their configurations were not assigned. The analytical data are reported in Table V.

Reactions of Dimethyl Diazomalonate in Vinyl Sulfides. Most of the vinylsulfonium biscarbomethoxymethylides were prepared by the photolysis of dimethyl diazomalonate in vinyl sulfides. For example, the sulfur ylide, 2-methyl-1-propenylethylsulfonium biscarbomethoxymethylide (Xb) was prepared in 43% yield by photolysis of 0.52 g (3.3 mmol) of dimethyl diazomalonate in 3 mL of 1-ethylthio-2-methyl-1-propene. In 80% decomposition of the diazomalonate, the excess vinyl sulfide was distilled off under reduced pressure. The residue was analyzed by a silica gel column with chloroform, acetone, or methanol. The sulfur ylide Xb was isolated as an oily product,

Table VII. Reaction Products from Vinyl Sulfides and Phenyl- and Diphenyldiazomethanes

Prod-uct	Registry no.	IR, cm⁻¹ (main peaks)	NMR, ppm downfield from Me₄Si	Calcd, % C	H	Found, % C	H
XIXa	63196-87-2	3050, 2950, 2900, 1500, 1455, 1375, 790, 770	1.70 (s, 6 H), 3.72 (s, 2 H), 5.54 (s, 1 H), 7.22 (m, 5 H)	74.10	7.91	74.21	7.95
XIXb	63196-88-3	3040, 2950, 1660, 1600, 1490, 1450, 1370, 1320	1.70 (s, 3 H), 1.77 (s, 3 H), 5.15 (s, 1 H), 5.47 (s, 1 H), 7.1–7.4 (m, 10 H)	80.27	7.13	80.34	7.06
XXa	63196-89-4	3000, 2940, 1450, 1360, 1160	0.9–2.2 (m, 17 H), 7.17 (m, 5 H)	76.86	9.46	76.45	9.40
XXb	63196-90-7	3030, 2920, 1480, 1440	1.27 (s, 9 H), 1.30 (s, 6 H), 1.70 (s, 1 H), 7.0–7.4 (m, 10 H)	81.21	8.44	81.39	8.38

Table VIII. Reaction Products from Dichlorocarbene with Vinyl and Allylic Sulfides

Prod-uct	Registry no.	IR, cm⁻¹ (main peaks)	NMR, ppm downfield from Me₄Si	Calcd, % C	H	Found, % C	H
XXIII	63196-91-8	2970, 1365, 1165, 990	1.42 (s, 9 H), 5.0–5.6 (m, 2 H), 6.4–7.2 (m, 2 H)	54.38	7.41	54.59	7.58
XXV	63196-92-9	2950, 2905, 1445, 1365, 1160	1.42 (s, 9 H), 2.00 (s, 3 H), 4.95 (s, 1 H), 5.37 (s, 1 H), 6.50 (s, 1 H)	56.68	7.94	56.25	7.48
XXVI	63196-93-0	2900, 1615, 1170, 900, 785	1.83 (s, 6 H), 5.1–5.4 (m, 2 H), 5.84 (s, 1 H), 6.4–7.0 (m, 2 H)	55.01	6.35	55.23	6.31
XXVII	63196-94-1	3100, 3000, 2950, 1620, 1465, 1380, 1235, 1120, 1010, 920, 850, 740	1.30 (s, 3 H), 1.43 (s, 3 H), 2.18 (s, 1 H), 3.25 (d, 2 H), 5.0–6.5 (m, 3 H)	45.72	5.75	45.46	5.94

which was easily dissolved in water and chloroform, but not in carbon tetrachloride. The vinylsulfonium biscarbomethoxymethylides were often prepared with copper or cupric sulfate catalyzed thermal decomposition of dimethyl diazomalonate in the corresponding vinyl sulfides. For example, the stable sulfonium ylide Xb was obtained when a solution of 1.0 g (6.6 mmol) of dimethyl diazomalonate in 5 mL of ethylthio-2-methyl-1-propene was heated at 120 °C for 2 h in the presence of anhydrous cupric sulfate (20 mg). Chloroform was added and the undissolved materials were separated from the reaction mixture. After the chloroform and excess vinyl sulfide were distilled off, the residue was chromatographed on a silica gel column with chloroform or acetone solvents to give Xb in 45% yield. The NMR and IR spectra and other physical properties are recorded in Table VI.

Photochemical Reactions of Phenyl- and Diphenyldiazomethanes. The photolysis of 0.4–2 mmol of phenyl- or diphenyldiazomethanes in 5–20 mmol of a substrate was carried out with a high-pressure mercury lamp in Pyrex tubes without degassing. After the diazo band disappeared from the IR spectrum of the reaction mixture, the reaction mixture was directly analyzed by gas chromatography. In the reaction of diphenyldiazomethane (0.445 g) in 1-methylthio-2-methyl-1-propene (2.31 g), the reaction mixture was analyzed by column chromatography on silica gel. The one of isolated fraction showed NMR spectrum at δ 2.63 which corresponds to >S⁺–Me protons.

General Procedure of Cupric Sulfate Catalyzed Thermal Reactions. Thermal reactions were carried out for 0.4–2 mmol of phenyl- and diphenyldiazomethanes in 5–15 mmol of a substrate in the presence of 20 mg of cupric sulfate. Samples were kept at room temperature or at 70 °C for 30 min. The results obtained are independent of the reaction conditions and shown in Table VII.

General Procedure of Thermal Reactions of Aryldiazomethanes. A similar reaction on the same scale was carried out without cupric sulfate. More violent conditions are required to complete the reactions. Samples of phenyldiazomethane were heated at 100 °C and of diphenyldiazomethane at 160 °C for 1 h. The products were examined by GLC.

Catalytic Decomposition of Methyl Diazoacetate in Acetylene Sulfides. A solution of 1 mmol of methyl diazoacetate in 5 mmol of acetylene sulfides with 20 mg of anhydrous cupric sulfate was sealed in Pyrex tubes and heated at 60 °C for 10 min. The reaction mixture was directly analyzed by gas chromatography.

Photolysis of Dimethyl Diazomalonate in Acetylene Sulfides. A solution of 1.2 mmol of dimethyl diazomalonate in 4 mmol of acetylene sulfide was irradiated. The reaction was 60% complete after 21 h. After the excess sulfide and diazomalonate were distilled off under the reduced pressure, the residue was analyzed by thin-layer chromatography. The major fraction was isolated and characterized by NMR and IR spectra and mass spectrum. The results were shown in Table VI.

Reaction of Dichlorocarbene with Vinyl Sulfides and Allylic Sulfides. A solution of 5 mL of 50% sodium hydroxide, 5 mL of ben-zene, 7 mL of chloroform, and 10 mmol of the corresponding sulfides was stirred rapidly in the presence of 0.2 g of benzyltriethylammonium chloride for 6 h. The reaction was completed when the solution became a strong brown color. The solution was diluted with water and acidified and extracted with petroleum ether. After the solution was dried and the solvent distilled off, the residue was directly analyzed by gas chromatography. The structures of the isolated products were determined by NMR and IR spectra and elemental analysis. The data are shown in Table VIII.

References and Notes

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Synthesis of 1,2,3,5-Oxathiadiazole 2-Oxides from Amidoximes and Thionyl Chloride and the Mechanism of Their Thermally Induced Fragmentation and Rearrangement to Carbodiimides[1]

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3,4-Disubstituted 1,2,3,5-oxathiadiazole 2-oxides **2** are prepared in good yields by cyclization of *N*-alkyl- and *N*-arylamidoximes **1** with thionyl chloride in the presence of triethylamine. The reaction provides a convenient route to heterocycles **2** as an alternative to the cycloaddition of *N*-sulfinylamines to nitrile oxides. 4-Aryl substituted heterocycles **2** decompose under mild thermal conditions to sulfur dioxide and carbodiimides **3**. Kinetic evidence as well as the failure to detect unstable intermediates by trapping experiments suggests that the conversion of **2** into **3** is a one-step process where the fragmentation and rearrangement occur concertedly via a single transition state.

The synthesis of 3,4-disubstituted 1,2,3,5-oxathiadiazole 2-oxides **2**, heterocycles of some interest as fungicides[3] and precursors of carbodiimides **3**, has been described by 1,3-dipolar cycloaddition of *N*-sulfinylamines to nitrile oxides[3,4] (route 1). Of the alternative entry to heterocycles **2** from amidoximes **1** and thionyl chloride in the presence of a tertiary
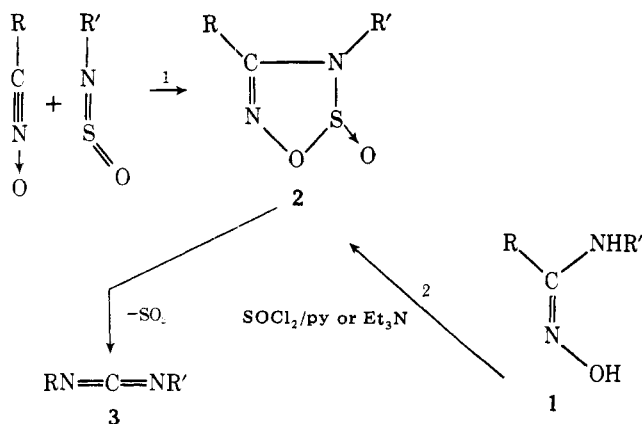
amine (route 2), a single example has been so far described[4b] in order to confirm the structure of the product **2** (R = *p*-NO$_2$C$_6$H$_4$, R′ = *p*-MeC$_6$H$_4$) obtained from the cycloaddition reaction.

As route 2 appeared a promising alternative to route 1, we have examined the cyclization of a number of *N*-alkyl- and *N*-arylamidoximes with thionyl chloride in order to define the scope and limitations of this reaction. We have then employed the easy thermal fragmentation of various oxathiadiazole 2-oxides for the preparation of carbodiimides and investigated the kinetics of the reaction as well as attempted trapping experiments in order to gain some insight into its mechanism.

Results and Discussion

Synthesis of Heterocycles 2. The cyclization of amidoximes **1a–r** with thionyl chloride in the presence of triethyl-

amine occurred readily in methylene chloride below room temperature to give the corresponding 3,4-disubstituted 1,2,3,5-oxathiadiazole 2-oxides (**2a–r**) (Table I). Structural proof of new compounds was based on spectral data (IR, NMR,[5] and MS). Compounds **2a–k** and **2q** were isolated in good yields (70–90%), whereas other products were obtained in much lower yields or could not be isolated. For **2m–p** this can be explained by the observation (IR at 2140 cm^{-1}) that these compounds rearranged into the corresponding carbodiimides when the reaction mixture was allowed to warm up to room temperature. The low yield of **2l** was due to both its partial conversion to *N*-*tert*-butyl-*N*′-phenylcarbodiimide (**3g**) and to some reluctance of *N*-*tert*-butylbenzamidoxime (**1l**) to undergo the cyclization (see footnote *j* of Table I). Also **2r** was obtained in very low yield from *N*-*tert*-butyltrimethylacetamidoxime (**1r**) under the standard conditions (−15 or 0 °C, 1 h at room temperature), but its thermal stability allowed the reaction temperature to be raised to 10 °C, and the yield increased to an acceptable value (60%).

The yields were not optimized nor were the effects of changing solvent or the tertiary amine investigated in detail. However, it was observed that almost identical results were obtained when the cyclization of *N*-phenylbenzamidoxime (**1i**) was carried out in benzene solvent instead of methylene chloride and/or by using pyridine in place of Et$_3$N (Table I, footnote *h*).

From the examples reported in Table I it appears that the cyclization of amidoximes with thionyl chloride can be conveniently employed for the synthesis of heterocycles **2** in a number of cases. This reaction offers several advantages with respect to the nitrile oxide–*N*-sulfinylamine cycloaddition (route 1), since: (i) it circumvents the preparation of *N*-sulfinylamines; (ii) it does not suffer from side reactions[4c] such as dimerization and isomerization of nitrile oxides,[6] and decomposition of *N*-sulfinylamines by moisture and air[7]; (iii) it occurs at low temperature, which is an important factor in view of the thermal instability of heterocycles **2**; (iv) it employes stable and easily available starting materials: *N*-sub-