

$$C_{\text{eff}} = \frac{P_n}{N_A V} \quad (5)$$

volume  $V$ , and  $N_A$  is Avogadro's number.

A serious difficulty arises in deciding what volume about the carbonyl group is reactive to hydrogen abstraction. On one hand one might presume that volume is defined by the shape of the  $n$  orbitals from which an electron is promoted in the  $n\pi^*$  excited state. There is some evidence to that effect in charge-transfer quenching of aliphatic ketone singlet states.<sup>34</sup> Under those circumstances only the "in-plane" hit sites should be included in the model for calculation of  $Z_0$ . We have carried out this calculation and find  $P_n$  reduced by somewhat less than one-third over the values in Figure 5. The problem is akin to the one raised several years ago by the question of "orbital steering".<sup>35</sup> It is no easy matter to define the orientation of reacting groups. Sisido took his reactive volume to be a sphere with its radius treated as an adjustable parameter.<sup>28</sup> This is not a weakness inherent in his calculation. Rather it represents the state of the art in understanding those details of organic chemical reaction mechanisms.

If, for simplicity, we take the reactive volume in 1 as spherical, with radius  $r$  in ångströms, and appropriate values are substituted into eq 5, then  $C_{\text{eff}} = 397P_n/r^3$ . This equation allows a quantitative comparison between the experimental data and the theoretical calculations, where  $r$  is the only adjustable parameter. Chemical intuition sets rather severe limits on  $r$ , and the equation describing  $C_{\text{eff}}$  is very sensitive to small changes in  $r$ . The dashed line in Figure 2 describes the effective concentration calculated from values of  $P_n$  with the reactive radius chosen to be 1.9 Å. For  $r = 2.1$  Å, the theoretical line passes through the experimental points for  $\text{CCl}_4$  as a solvent. This agreement for chemically reasonable values of  $r$  gives us confidence that the most

(34) N. J. Turro, J. C. Dalton, G. Garrington, M. Niemczyk, and D. M. Pond, *J. Am. Chem. Soc.*, **92**, 6978 (1970).

(35) (a) A. Dafforn and D. A. Koshland, *Biochem. Biophys. Res. Commun.*, **52**, 779 (1973), and references therein; (b) H. B. Burgi, and J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, **30**, 1563 (1974).

important physical features of molecule 1 have been incorporated into the theoretical model.

We can now begin to interpret the data in Figure 2 in terms of solvent effects on chain shape. Carbon tetrachloride is clearly the best solvent for hydrocarbon chains. In terms of our reference state, hydrocarbon chains in  $\text{CCl}_4$  best fit the assumptions of our model. Acetic acid, Freon 113, and the mixed solvents containing small amounts of water are equally poorer solvents than carbon tetrachloride, but not so bad as acetonitrile and 20% aqueous acetic acid, which seriously perturb chain shape and increase the cyclization probability.

The "goodness" of acetic acid as a solvent for hydrocarbon chains requires comment. Acetic acid exists in solution as a dimer. The dimer has a dielectric constant of 6, only slightly more polar than benzene. Addition of small amounts of water may disrupt some of the dimers, but our experimental results suggest that the chain remains solvated by the nonpolar dimer. Only when the mole fraction of water approaches 0.5 is the chain forced to interact with water and the polar acetic acid monomer.

The details of the conformational changes in 1 that occur in different solvents are not yet apparent. Polar and protic solvents increase the cyclization probability of the chain. Specific solvation effects are probably responsible. Repulsive solvent-chain interactions, which might locally disrupt favored solvent-solvent interactions, would serve to increase the fraction of chains in the environment of the chromophore.

*I wish to express my appreciation to the graduate students and postdoctoral fellows who carried out all the calculations and virtually all the experiments described here. Their labors and their ideas, along with the generous financial support of the Research Corporation and the National Research Council of Canada, brought this research to fruition. Professor S. G. Whittington has made many valuable contributions to this research. It is a pleasure to acknowledge his help on all aspects of our theoretical calculations. I also wish to thank Professor Herbert Morawetz for his critical comments on many aspects of this work.*

## Ylide Formation and Rearrangement in the Reaction of Carbene with Divalent Sulfur Compounds

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Sulfur ylides are being used increasingly in synthetic chemistry,<sup>1</sup> and some evidence is available suggesting their involvement in biochemical processes. One of the features of ylides which adds interest to their study is

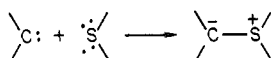
Wataru Ando was born in Shizuoka, Japan, in 1934. He worked for his Ph.D. degree under S. Oae (Osaka City University) and did postdoctoral work at UCLA with C. S. Foote and at Princeton University with M. Jones, Jr. From 1967 to 1974 he was associate professor at Gunma University, and from 1975 professor at the University of Tsukuba. His research has involved the study of the mechanism of reactive intermediates, such as carbene, nitrene, sulfur ylide, singlet oxygen, and silicon-carbon double bond, in hetero compounds, and photochemistry.

their unique molecular structure, involving as it does the question of multiple bonding between a carbanion and the onium atom.

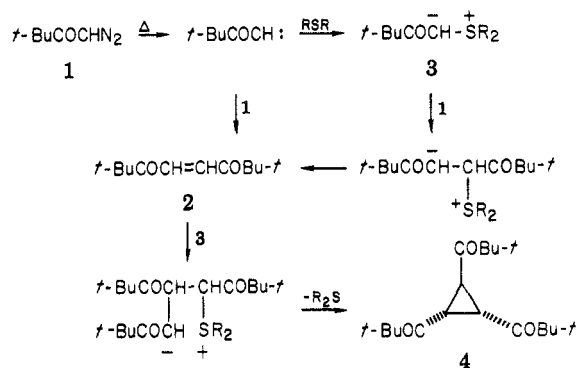
Two fundamentally distinct approaches to the generation of these ylides exist. The most widely employed method for the preparation of sulfur ylides is the so-called "salt method", whereby a sulfide effects a nucleophilic substitution on an alkyl halide to form a

(1) B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides", Academic Press, New York, N.Y., 1975.

sulfonium salt. A proton  $\alpha$  to the sulfur atom is subsequently removed by utilizing the appropriate bases to afford the ylide.<sup>2</sup> A less common but exceedingly useful approach involves the reaction of a sulfide with a carbene. Under either photochemical or thermal conditions, diazo compounds react with alkyl sulfides to expel molecular nitrogen and afford sulfur ylides in high yield. Our studies of ylide formation and rearrangement in the reaction of carbenes with molecules containing a heteroatom, especially a sulfur atom,<sup>3</sup> are the subject of this Account.

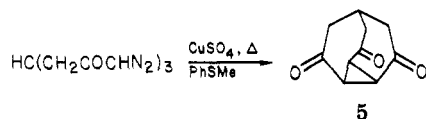


Some early examples of reactions of this type are noted below. Serratos and Quintana<sup>4</sup> found that pivaloyldiazomethane (1) thermally decomposed in the presence of copper-bronze to the olefin dimer, dipivaloylethylene (2), in 70% yield, probably via a

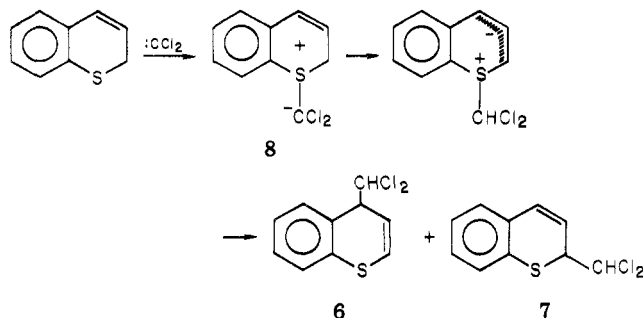


carbene intermediate. However, in the presence of sulfide, a cyclic trimer, tripivaloylcyclopropane (4), was formed in 90% yield, no trace of dimer being detected. It was proposed that an electrophilic carbene species and sulfide first formed the sulfur ylide 3, which then reacted with an additional carbene to form the dimer. Michael addition by the ylide on the dimer then completed the reaction.

A novel application of the use of a sulfide as a catalyst to effect trimerization of a diazoketo compound is the formation of bulvalenotriene (5).<sup>5</sup> A further example



is the reaction of dichlorocarbene with 1(2*H*)-benzothiapyran. Two insertion products, 6 and 7, are pro-



(2) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

(3) W. Ando, *Int. J. Sulfur Chem., Part B*, 7, 189 (1972).

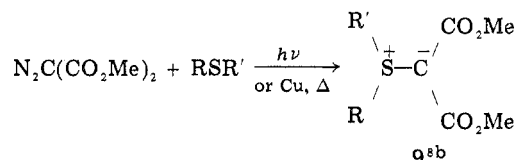
(4) F. Serratos and J. Quintana, *Tetrahedron Lett.*, 2249 (1967).

(5) J. Font, F. Lopez, and F. Serratos, *Tetrahedron Lett.*, 2589 (1972).

duced and are explicable on the basis of a sulfur ylide intermediate (8).<sup>6</sup>

### Stabilized Sulfur Ylides

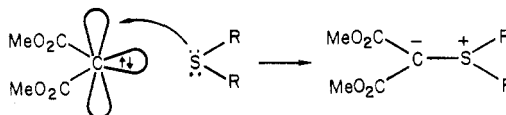
Although few stable sulfur ylides have been made from keto- or carboalkoxycarbene, many chemists have postulated such species as intermediates. We have isolated a series of stable sulfur ylides in the reaction of a series of sulfides with carbenes substituted by electron-withdrawing substituents.<sup>7</sup> Photolysis of dimethyl diazomalonate in alkyl and aryl sulfides forms a stable sulfonium biscarbomethoxymethylide. We



found that yields of the ylide vary considerably with the nucleophilicity and the steric hindrance of the sulfides.<sup>8a</sup> In phenyl or benzyl sulfides, copper (or copper salt) catalyzed thermal decomposition of diazo compound appears to be the most attractive synthetic technique; moreover, the thermal approach generates cleaner product mixture.

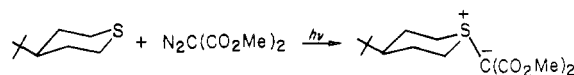
Repetition of the reaction with dimethyl sulfide in the presence of cyclohexene indicated that the sulfide was about six times as reactive as the olefin toward biscarbomethoxycarbene. Similar high reactivity of sulfides toward the carbene was also observed in other competitive experiments.<sup>7</sup>

The reactions are all assumed to occur by conversion of the diazo compound into an electrophilic singlet carbene, which attacks the nonbonding electron pair of a sulfur atom, giving a sulfur ylide. Thermolysis of a



diazocompound in the presence of a copper salt probably involves a carbene-copper complex.

In the reaction of dimethyl diazomalonate with cyclic sulfides, the corresponding sulfur ylides were also obtained, although yields varied depending on ring size.<sup>9</sup> High stereospecificity was observed with 4-*tert*-butylthiane.<sup>10</sup> With thietane, dimethyl diazomalonate



gave a ring expansion product, resulting from a facile rearrangement of the intermediate sulfur ylide.<sup>9</sup> With the three-membered ring 10, ethyl diazoacetate yielded

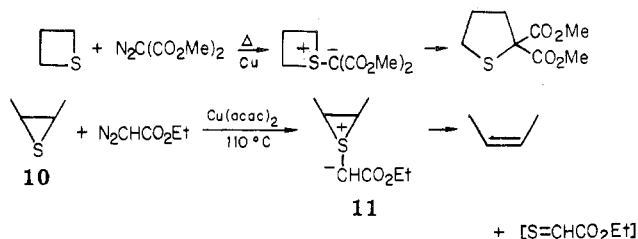
(6) W. E. Parham and P. Konros, *J. Am. Chem. Soc.*, 83, 4034 (1961); W. E. Parham and S. H. Gowen, *J. Org. Chem.*, 31, 1694 (1966).

(7) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Am. Chem. Soc.*, 91, 2786 (1969).

(8) (a) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, 1929 (1969). (b) The NMR proton shift and IR carbonyl frequency of sulfur ylides suggest stabilization by participation of sulfur d orbitals and two carbonyl groups; e.g., 9 (R = R' = Me), NMR (CDCl<sub>3</sub>)  $\sigma$  3.71 (-CO<sub>2</sub>Me), 2.89 (-SMe); IR  $\nu_{\text{CO}}$  1625 and 1675 cm<sup>-1</sup>.

(9) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, 37, 1721 (1972).

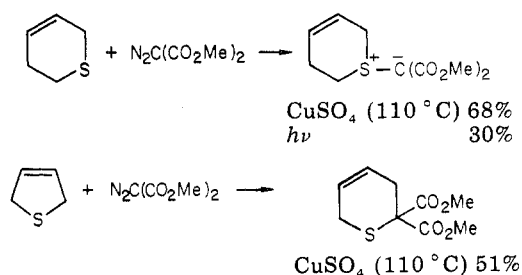
(10) D. C. Appleton, D. C. Bull, J. McKenna, and A. R. Walley, *J. Chem. Soc., Chem. Commun.*, 140 (1974).



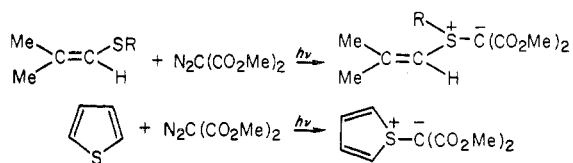
exclusively the cis olefin.<sup>11</sup> The episulfide probably formed ylide 11 as an initial intermediate and then decomposed stereospecifically by fragmentation into olefin and thioglyoxalic ester.

The effect of ring strain on the course of reactions of cyclic imines and ethers has also been reported.<sup>12</sup>

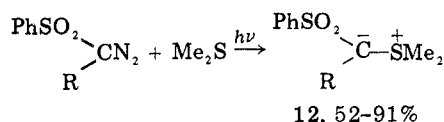
Although a six-membered olefinic sulfide gave a stable sulfur ylide, no stable sulfur ylide was isolated from the five-membered olefinic sulfide. Only ring-expansion product, resulting from a sulfur ylide intermediate,<sup>13</sup> was isolated.



Vinyl sulfides, thiophene, and dibenzothiophene, in which the lone pair of sulfur is highly delocalized, are efficient traps for the carbene and form stable sulfur

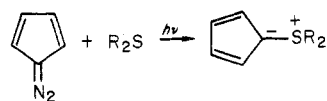


ylides.<sup>9,14</sup> Other stabilized sulfur ylides can be isolated by this technique. Benzenesulfonyldiazo compounds produce good to excellent yields of the corresponding sulfur ylides (12) when irradiated in neat dimethyl



sulfide.<sup>15</sup>

We have also found the photochemical reaction to be the most useful method to date for the preparation of sulfonium cyclopentadienylide (13) from diazocyclo-



(11) Y. Hata, M. Watanabe, S. Inoue, and S. Oae, *J. Am. Chem. Soc.*, **97**, 2553 (1975).

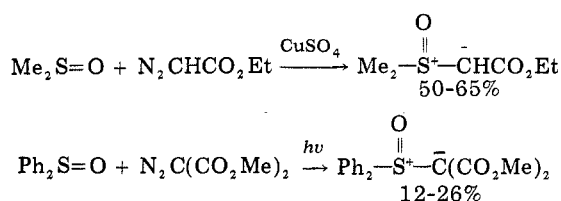
(12) H. Nozaki, H. Takaya, and R. Noyori, *Tetrahedron*, **22**, 3393 (1966).

(13) W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Am. Chem. Soc.*, **94**, 3870 (1972).

(14) W. Ando, H. Higuchi, and T. Migita, unpublished results.

(15) (a) J. Diekmann, *J. Org. Chem.*, **30**, 2272 (1965); (b) W. Illger, A. Leidhegener, and M. Regitz, *Justus Liebigs Ann. Chem.*, **760**, 1 (1972).

Scheme I

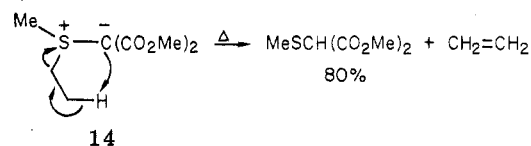


pentadiene and a variety of dialkyl sulfides.<sup>16,17</sup> Other cyclopentadienylides have proved to be readily obtainable by carbenic decomposition in sulfur compounds.<sup>18</sup>

Stabilized oxosulfonium ylides, unavailable by the direct condensation of sulfoxides and  $\alpha$ -halocarbonyl compounds, are especially suitable targets for the carbene approach<sup>8,19</sup> (Scheme I).

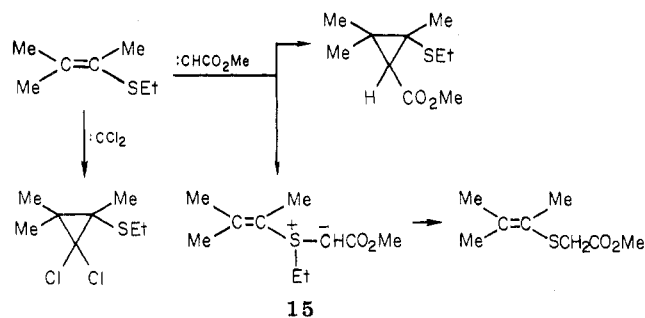
### $\alpha',\beta$ Elimination

Some sulfur ylides undergo intramolecular eliminations when warmed, especially those carrying large alkyl groups on sulfur. For example, ylide 14, having



a  $\beta$  hydrogen, underwent  $\alpha',\beta$  elimination at 150 °C to afford ethylene and dimethyl methylthiomalonate in high yield. The eliminative decomposition of sulfur ylides is probably a cis elimination proceeding through a five-membered cyclic transition state. The reaction of carboethoxycarbene with alkyl sulfides did not give any stable sulfur ylides, but afforded elimination products, alkene and  $\text{RSCH}_2\text{CO}_2\text{Et}$ .<sup>20</sup> Analogous elimination products were also observed, together with some Stevens-type product, in the reaction of diphenylcarbene with dialkyl sulfides.<sup>21</sup>

The use of olefinic sulfides afforded two competitive sites of attack by the carbene presumably formed from the diazo compound. Thermal decomposition of methyl diazoacetate with vinyl sulfide produced 5% of a cyclopropane derivative and 39% of a rearranged vinyl sulfide, resulting from carbene attack on the sulfur to form the sulfur ylide 15, followed by intramolecular



elimination of ethylene.<sup>22</sup> Reaction of dihalocarbene

(16) W. Ando, J. Suzuki, Y. Saiki, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 365 (1973).

(17) W. Ando, Y. Saiki, and T. Migita, *Tetrahedron*, **29**, 3511 (1973).

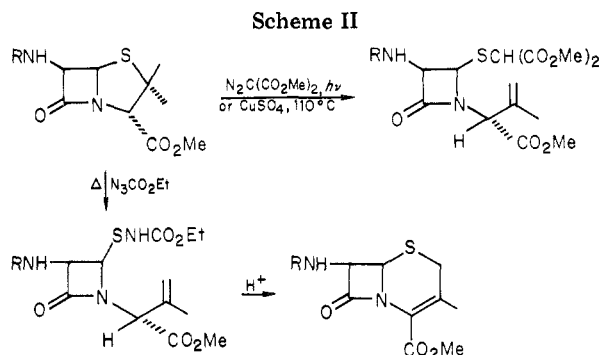
(18) D. Loyed and M. I. C. Singer, *Chem. Ind. (London)*, 118 (1967).

(19) F. Dost and J. Gosselek, *Tetrahedron Lett.*, 1933 (1969).

(20) W. Ando, T. Yagihara, S. Kondo, K. Nakayama, H. Yamato, S. Nakaido, and T. Migita, *J. Org. Chem.*, **36**, 1732 (1971).

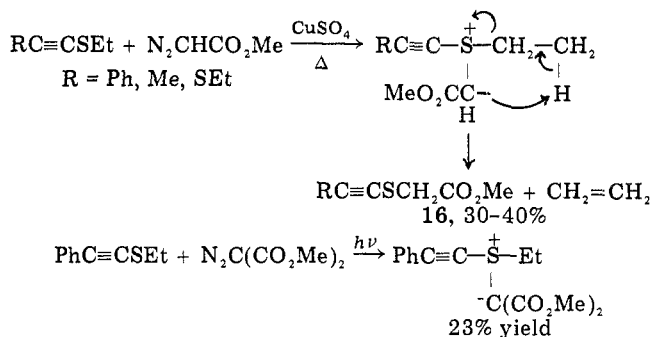
(21) W. Ando, M. Yamada, E. Matsuzaki, and T. Migita, *J. Org. Chem.*, **37**, 3791 (1972).

(22) W. Ando, H. Fujii, T. Takeuchi, H. Higuchi, Y. Saiki, and T. Migita, *Tetrahedron Lett.*, 2117 (1974).



with vinyl sulfide produced only addition product.

Copper-catalyzed thermal reaction of methyl diazoacetate with acetylenic sulfides gave thioacetate 16,

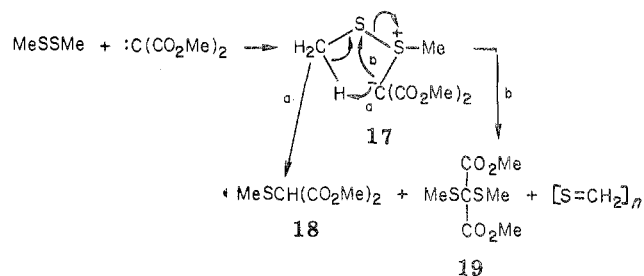


which may arise from attack of carbomethoxycarbene on the sulfur atom to form the acetylenic sulfur ylide, followed by cyclic elimination of olefin, although trapping of the acetylenic sulfur ylide was not successful. However, photolysis of dimethyl diazomalonate in phenylethylthioacetylene gave a stable sulfur ylide at room temperature.<sup>23</sup>

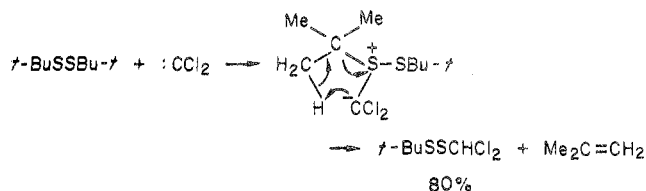
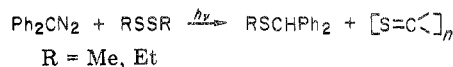
The reactivity of the sulfur atom in acetylenic sulfides compared with various other sulfides was investigated by competitive reactions with trimethylethylene. The results show that the acetylenic sulfide sulfur is about 9 times as reactive as the trimethylethylene double bond, and vinyl sulfide sulfur reacts 4.6 times faster than the double bond of trimethylethylene.

The application of the carbene approach to the ylidic intermediate for  $\alpha',\beta$  elimination has been most fruitful in the penicillin system.<sup>24</sup> Treatment of penicillin V methyl ester with dimethyl diazomalonate in the presence of copper sulfate at 110 °C afforded 2-azetidone in 46% yield. In a similar manner penicillin V methyl ester was heated with ethyl azidoformate at 90-100 °C, and resulted in the formation of the 2-azetidone derivative, in 12% yield, which cyclized to a desacetoxycephalosporin when treated with diethylamine hydrochloride (Scheme II).

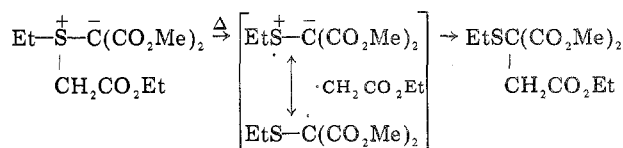
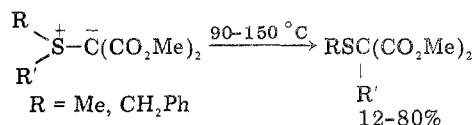
A similar elimination reaction occurs between bis-carbomethoxycarbene and dialkyl disulfides. Thus, the reaction with dimethyl disulfide afforded dimethyl methylthiomalonate (18), thioketal via S-S insertion (19), and thioketone via a sulfur ylide intermediate (17). Cleavage of the sulfur-sulfur bond has been observed in the reaction of phenyl- and diphenylcarbenes with disulfides as the principal reaction pathway<sup>21</sup> (Scheme



**Scheme III**



**Scheme IV**



III). The reaction of *t*-butyl disulfide with dichlorocarbene affords dichloromethyl disulfide in 80% yield.<sup>25</sup>

### Stevens Rearrangement

The first Stevens rearrangement of sulfur ylides was reported by Stevens in 1932 and involved the conversion of phenacylmethylbenzylsulfonium bromide in methanolic sodium to  $\alpha$ -thiomethyl- $\beta$ -phenylpropionophenone, presumably via an ylide intermediate.<sup>26</sup> Stabilized ester sulfur ylides can undergo Stevens rearrangement on heating.<sup>27</sup> Migration preference is shown when one group on sulfur is especially stabilized. On the basis of kinetic analysis and CIDNP NMR spectroscopy, it was claimed that the reaction proceeded through a homolytic dissociation and 1,3 migration of an ester group or a benzyl group<sup>9</sup> (Scheme IV). The details of the earlier work on the Stevens rearrangement of sulfur ylides have now been published by Schöllkopf et al.<sup>28</sup>

The Stevens rearrangement of sulfur ylides has some limited application. However, the reaction of silyldiazoacetate stands as a spectacular illustration of its potential. The photolysis of ethyl trimethylsilyldiazoacetate (20) with dimethyl and diethyl sulfides at room temperature gave an insertion product of the carbene into the C-S bond as a major product, whereas at lower temperatures the stable sulfur ylide (21) was formed.<sup>29</sup> The sulfur ylide did not give any C-S in-

(25) S. Searles, Jr., and R. E. Wann, *Tetrahedron Lett.*, 4387 (1965).

(26) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932).

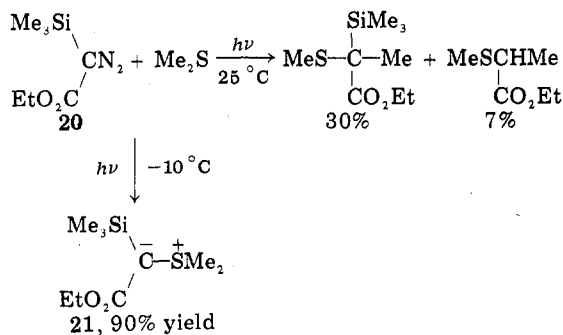
(27) W. Ando, T. Yagihara, and T. Migita, *Tetrahedron Lett.*, 1425 (1969).

(28) U. Schöllkopf, J. Schossig, and G. Ostermann, *Justus Liebigs Ann. Chem.*, 737, 158 (1970).

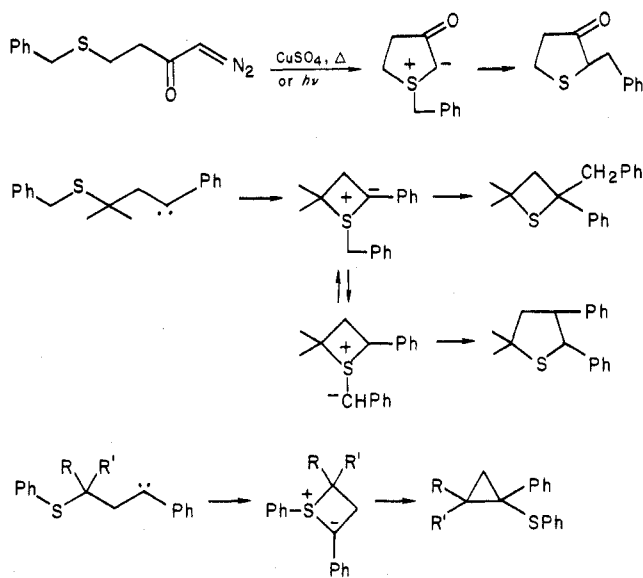
(29) W. Ando, T. Hagiwara, and T. Migita, *Tetrahedron Lett.*, 1425 (1974).

(23) W. Ando, H. Higuchi, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 523 (1974).

(24) (a) M. Numata, Y. Imahashi, I. Minamida, and M. Yamaoka, *Tetrahedron Lett.*, 5097 (1972); (b) M. Yoshimoto, S. Ishihara, E. Nakayama, E. Shoji, H. Kuwano, and N. Soma, *Tetrahedron Lett.*, 4387 (1972).



Scheme V

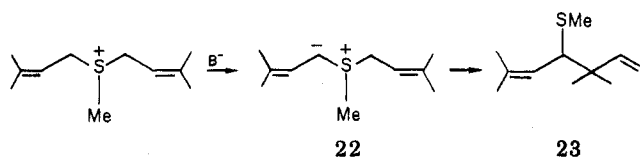


sersion product under photolytic or thermal conditions.

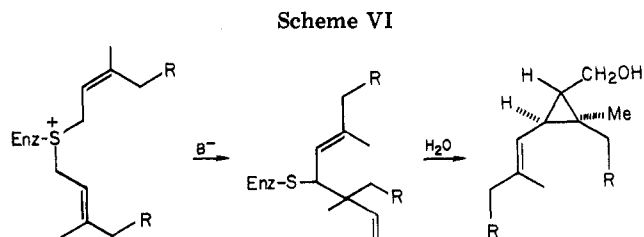
Although the intramolecular version of the sulfide-carbene reaction did not give any stable sulfur ylides, the products clearly arose from Stevens rearrangements of cyclic sulfur ylides<sup>30</sup> (Scheme V).

### 2,3-Sigmatropic Rearrangement

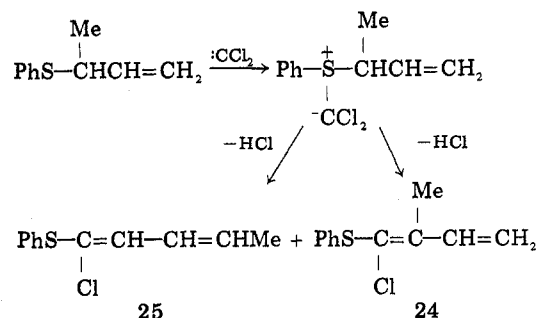
In addition to elimination and Stevens rearrangement, the other major alternative for ylide rearrangement, especially in the presence of unsaturation in the molecule, is a cyclic 2,3-sigmatropic rearrangement. The sigmatropic ylide rearrangement proceeds with complete allylic inversion as demanded by orbital symmetry control. Methylbis( $\gamma,\gamma$ -dimethylallyl)-sulfonium tetrafluoroborate was treated with base to generate ylide **22** which rearranged to the thioether **23**.<sup>31</sup>



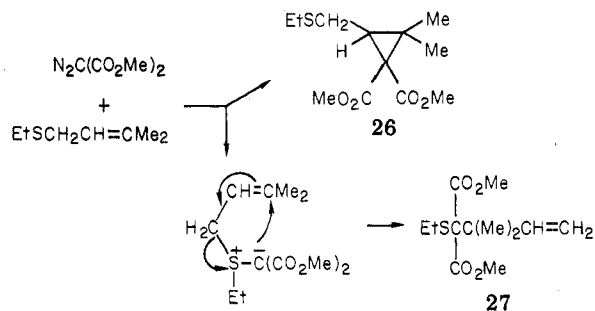
Trost has attempted to use the 2,3-sigmatropic rearrangement as a means of transferring chirality.<sup>32</sup> Very high optical induction probably could be achieved in an enzymatic environment, and this type of reaction could serve as a hypothetical model for the biosynthesis of presqualene<sup>32</sup> (Scheme VI).



The application of the carbene approach to the production of sulfur ylide intermediates for 2,3-sigmatropic rearrangement has been most fruitful, and a number of communications on this topic have appeared in the past 10 years. Parham and Groen found that treatment of an allylic sulfide with sodium trichloroacetate, a source of dichlorocarbene, resulted in the formation of two products, **24** and **25**.<sup>33</sup> **24** was



probably formed via initial ylide formation, then a Stevens rearrangement, and finally elimination of HCl. **25** was probably formed via initial ylide formation followed by 2,3-sigmatropic rearrangement. Under photochemical conditions, methyl diazomalonate reacted with allyl *n*-butyl sulfide to afford an 11% yield of the addition products and a 57% yield of the insertion product, resulting from initial ylide formation followed by 2,3-sigmatropic rearrangement.<sup>34</sup> Under thermal conditions in the presence of cupric sulfate, the only insertion product was obtained in 93% yield. Thus, the carbene or carbene-copper complex is more discriminating between sulfide sulfur and double bond as a nucleophile. The photochemical reaction between  $\gamma,\gamma$ -dimethylallyl ethyl sulfide and dimethyl diazomalonate afforded a 43% yield of the insertion product and 12% of the addition product, but repetition of the



Reaction mode	26	27
$h\nu$	12%	43%
$h\nu + \text{sens}$	27%	19%
$\text{CuSO}_4, 110^\circ\text{C}$	0	95%

(33) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964); **30**, 728 (1965).

(34) W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *J. Am. Chem. Soc.*, **91**, 5164 (1969); W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, S. Imai, S. Nakaido, and T. Migita, *J. Am. Chem. Soc.*, **94**, 3870 (1972).

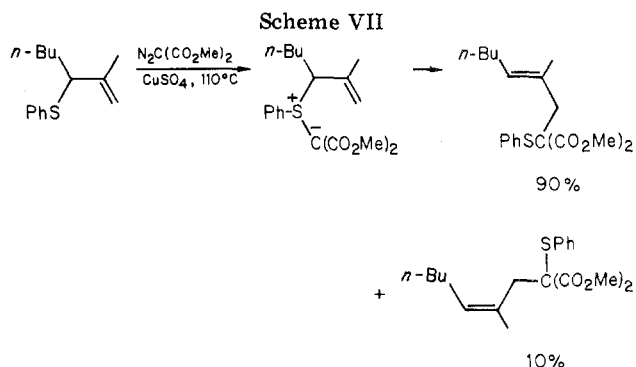
(30) K. Kondo and I. Ojima, *J. Chem. Soc., Chem. Commun.*, 860 (1972).

(31) J. E. Baldwin and R. E. Hackler, *J. Am. Chem. Soc.*, **91**, 3646 (1969).

(32) (a) B. M. Trost and W. G. Biddlecon, *J. Org. Chem.*, **38**, 3438 (1973);

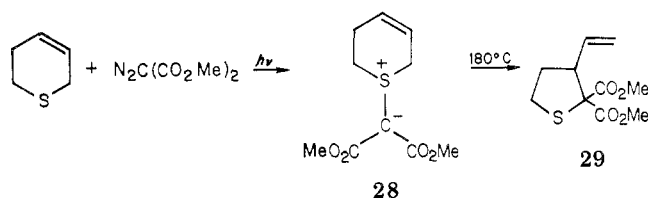
(b) B. M. Trost and R. F. Hammen, *J. Am. Chem. Soc.*, **95**, 962 (1973);

(c) B. M. Trost and M. J. Bogdanowicz, *ibid.*, **95**, 5298 (1973).



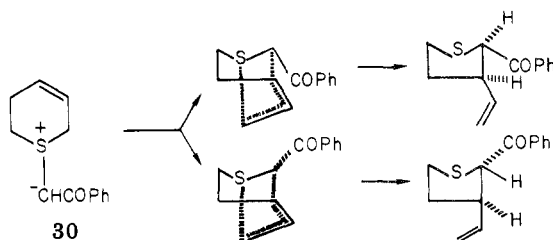
reaction in the presence of benzophenone sensitizer gave 19% of the insertion product and 27% of addition products.<sup>34</sup>

Introduction of a bulky group at the  $\alpha$  position led to preferential formation of the trans isomer at the newly created double bond<sup>35</sup> (Scheme VII). The photolysis of dimethyl diazomalonate with the cyclic olefin thiopyran gave the stable sulfur ylide **28**. When



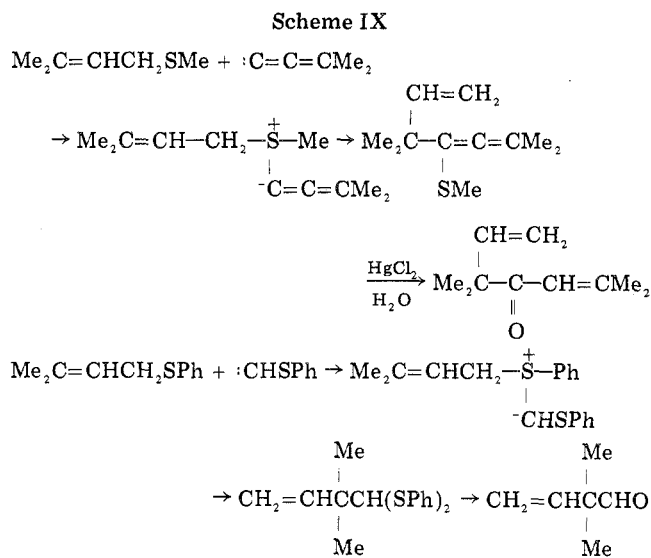
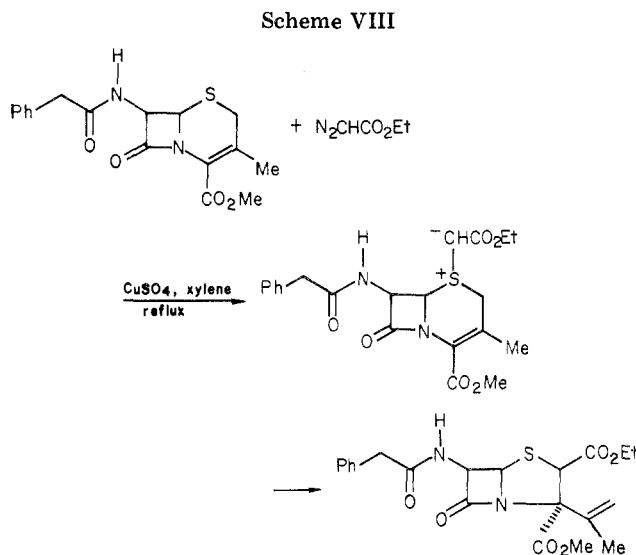
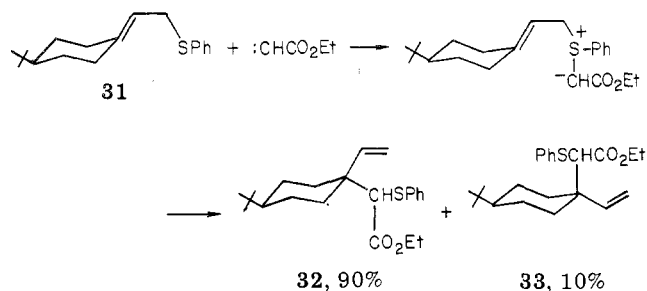
**28** was heated, it underwent a sigmatropic rearrangement to produce the insertion type product **29**.<sup>13</sup>

A clear preference for the exo orientation was also seen in the rearrangement of the sulfur ylide **30**.<sup>36</sup>



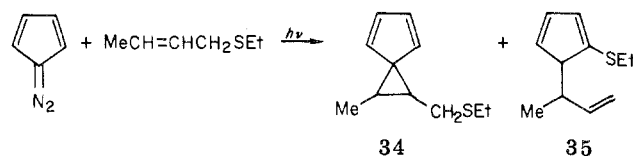
A novel conversion of the cephalosporin nucleus to the penicillin nucleus illustrates some of the potential of the method<sup>37</sup> (Scheme VIII).

The reaction of ethyl diazoacetate with allylic sulfide **31** afforded an intermediate ylide, which spontaneously rearranged in 59% yield to a 91:9 ratio of the products **32** and **33**.<sup>38</sup> The reaction of dichlorocarbene proceeded



analogously, indicating that the carbanion portion of the ylide preferred to attack the exocyclic bond so as to enter the ring in an equatorial position.

With diazocyclopentadiene,  $\gamma$ -methylallyl ethyl sulfide gave a 7% yield of the addition product **34** and



23% of insertion product **35**, resulting from initial ylide formation followed by a sigmatropic rearrangement.<sup>17</sup>

A novel and potentially useful method in the synthesis of artemisia ketone having a carboxyaldehyde equivalent at an allylic position has been developed<sup>39,40</sup> (Scheme IX). Replacement of the double bond by allene and triple bonds led to a successful reaction<sup>41</sup> (Scheme X). Allenyl phenyl sulfide afforded the homologous alkynyl sulfide when treated with diazomethane and cuprous chloride.<sup>42</sup>

(35) P. A. Grieco, D. Boxler, and K. Hiroi, *J. Org. Chem.*, **38**, 2572 (1973).

(36) S. Magewaren, W. D. Ollis, and I. Osutherland, *J. Chem. Soc., Chem. Commun.*, 656 (1973).

(37) M. Koshimoto, S. Ishihara, E. Nakayama, and N. Soma, *J. Chem. Soc., Tetrahedron Lett.*, 2923 (1972).

(38) G. Andrews and D. A. Evans, *Tetrahedron Lett.*, 5121 (1972).

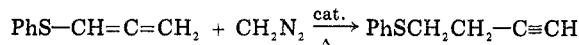
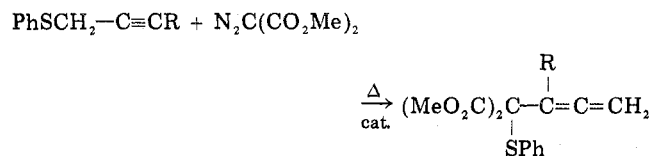
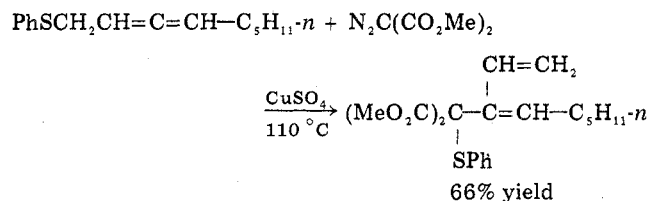
(39) D. Michelot, G. Linstrumelle, and S. Julia, *J. Chem. Soc., Chem. Commun.*, 10 (1974).

(40) S. Julia, C. Huynh, and D. Michelot, *Tetrahedron Lett.*, 3587 (1972).

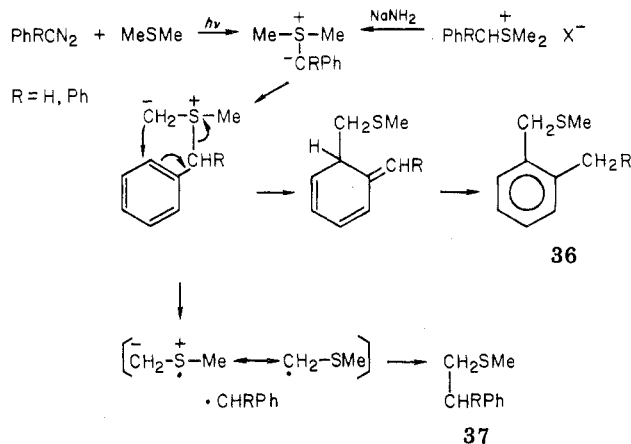
(41) P. A. Grieco, M. Meyers, and R. S. Finkellor, *J. Org. Chem.*, **39**, 1198 (1974).

(42) L. Veniard and G. Pourcelot, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **275**, 1190 (1971).

## Scheme X



Although allylic sulfur ylides invariably react by the 2,3-sigmatropic pathway, inclusion of an allylic portion in an aromatic ring may dramatically alter the course of the reaction. The photolysis of diphenyldiazomethane in dimethyl sulfide led to the formation of *o*-benzylbenzyl methyl sulfide (36) and 1,1-diphenyl-2-methylthioethane (37) in 10 and 40% yields, respectively. Diphenylcarbene might react with sulfide sulfur to form an unstable sulfur ylide which rearranges by a net 1,2 shift (Stevens rearrangement) to yield 37 and by a sigmatropic rearrangement to yield 36.<sup>21</sup> The ratio of the two products 36 and 37 can be controlled by solvent; it is 0.3 in benzene and 3.2 in acetone for 36/37. The striking result is the formation of a normal sigmatropic rearrangement product in polar solvents, whereas in nonpolar solvents a Stevens-type process (orbital-symmetry-forbidden process) predominates. A possible explanation relates to the stabilization of the intermediate sulfur ylide in solvent.

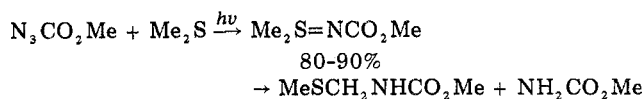


## Reaction of Nitrene with Sulfides

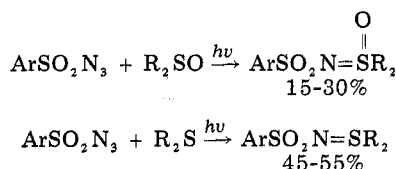
Our studies also extended to the sulfur imines. There has been considerable interest in the chemistry of iminosulfuranes in the past few years. Various sulfur imines are isoelectronic with sulfur ylides, oxosulfonium ylides, sulfoxides, or sulfones. *N*-Methoxycarbonyliminodimethylsulfurane was obtained as a pale yellow liquid in 80–90% yield when methyl azidoformate was decomposed in dimethyl sulfide.<sup>43</sup> It was suggested that the reaction involves electrophilic singlet nitrene which attacks the sulfur atom. Prolonged irradiation of the reaction mixture resulted in a Stevens-type re-

(43) W. Ando, N. Ogino, and T. Migita, *Bull. Chem. Soc. Jpn.*, **44**, 2278 (1971).

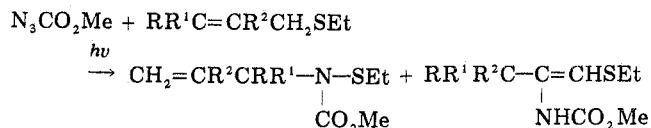
## Scheme XI



## Scheme XII



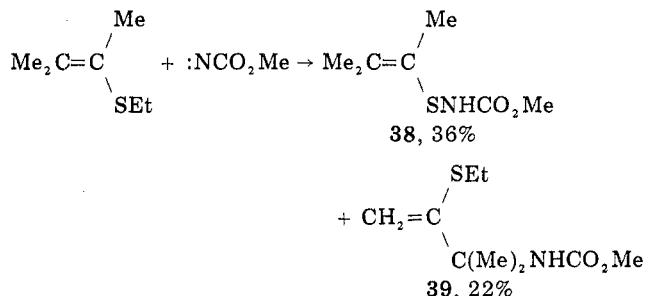
## Scheme XIII



arrangement product and some methyl carbamate (Scheme XI).

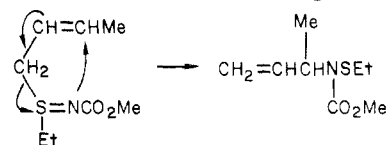
Horner<sup>44</sup> has reported the formation of *N*-arylsulfonylsulfoximides in the photolysis of an arene-sulfonyl azide in a sulfoxide solvent. Better yields are obtained in sulfide solvents, the products being *N*-arylsulfimides (Scheme XII).

Thermolysis of methyl azidoformate in trimethyl-(ethylthio)ethylene at 100 °C gave two products, 38 and 39, in 36 and 22% yields, respectively. Attack of



carbomethoxynitrene on the sulfur atom forming iminosulfurane, followed by five-membered cyclic elimination, would lead to the formation of 38.

Thermal and photochemical decomposition of methyl azidoformate in allylic sulfides produced the product of insertion of the nitrene into the allyl carbon-sulfur bond and the enamine as a minor product<sup>45,46</sup> (Scheme XIII). The notable selectivity of attack on the C-S bond suggests that an electrophilic singlet nitrene is the reacting entity, so that the attack on the sulfur atom overshadows the unstable iminosulfurane formation followed by 2,3-sigmatropic rearrangement.



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(44) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

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(46) W. Ando, H. Fujii, I. Nakamura, N. Ogino, and T. Migita, *Int. J. Sulfur Chem.*, **8**, 13 (1973).