# Decomposition of Dimethyl Diazomalonate in Allyl Compounds Containing Heteroatoms

**Wataru Ando,* Shuji Kondo, Keiji Nakayama, Keiji Ichibori, Hiromitsu Kohoda, Hideo Yamato, Isamu Imai, Setuko Nakaido, and Toshihiko Migita**

*Contribution from the Department of Chemistry, Gunma University, Kiryu, Gunma, Japan.* *Received April 16, 1971*

**Abstract:** Bis(methoxycarbonyl)carbene generated from the photolysis of dimethyl diazomalonate reacts with allyl sulfides giving allyl carbon–sulfur insertion products and adducts to the double bond. Similar insertion as well as addition were also observed in the reaction with allylic ethers, amines, and halides. The relative rates of insertion to addition were much reduced in the photosensitized reaction, which is presumed to produce the triplet carbene. It is concluded that the singlet state of bis(methoxycarbonyl)carbene attacks the heteroatoms of allylic compounds to give intermediate ylides, which rearrange to allyl carbon–heteroatom insertion products by 2,3-sigmatropic processes. Thermolysis of diazomalonate in the presence of copper sulfate gave insertion products almost exclusively, except the reaction with *tert*-butyl allyl sulfide and ether.

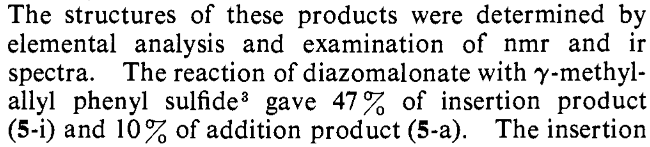
As shown in the previous paper,[1] bis(methoxycarbonyl)carbene generated from direct photolysis of diazomalonate reacts with alkyl and aryl sulfides to give sulfonium bis(methoxycarbonyl)methylides. Formation of sulfonium ylides was proposed to be the result of attack of the singlet carbene on a lone pair of a sulfur atom, which was found to proceed several times faster than attack on the $\pi$ bond of an olefin.[1]

Our work was extended to allyl compounds containing sulfur, oxygen, nitrogen and chlorine. This paper presents the data concerning formation and sigmatropic rearrangement of the intermediate ylides.

## Results and Discussion

**Photolysis of Dimethyl Diazomalonate in Allyl Sulfides.** The photolysis of diazomalonate in *n*-butyl allyl sulfide afforded the principal product (**1**-i) in 57% and the minor product (**1**-a) in 11% yield (Scheme I).

**Scheme I**



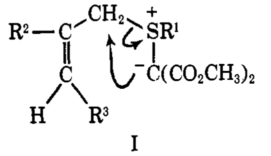
$$N_2C(CO_2CH_3)_2 + R^1SCH_2CR^2{=}CHR^3 \xrightarrow{h\nu} R^1SC(CO_2CH_3)_2CHR^3CR^2{=}CH_2 + R^1SCH_2CR^2\text{—}CHR^3\ (\text{with } C(CO_2CH_3)_2)$$

The product **1**-i was found to be an insertion product of bis(methoxycarbonyl)carbene into allyl carbon–sulfur bond and **1**-a to be an addition product of bis(methoxycarbonyl)carbene to the carbon–carbon double bond.[2] The structures of these products were determined by elemental analysis and examination of nmr and ir spectra. The reaction of diazomalonate with $\gamma$-methylallyl phenyl sulfide[3] gave 47% of insertion product (**5**-i) and 10% of addition product (**5**-a). The insertion product was identified as $\alpha$-(1-methyl-2-propenyl)-$\alpha$-phenylthiomalonate by spectral analysis. No trace of any isomer such as $\alpha$-(2-butenyl)-$\alpha$-phenylthiomalonate could be detected in the reaction products. Table **I** gives the yields of insertion and addition products in the direct photolysis of diazomalonate in various allyl sulfides.

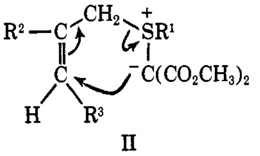
Table I. Yield of Products from Dimethyl Diazomalonate with Allyl Sulfides under Direct Photolysis

| Sulfide | Insertion (i), % | Addition (a), % |
|---|---|---|
| Allyl *n*-butyl (**1**) | 57 | 11 |
| Allyl *tert*-butyl (**2**) | 34 | 14 |
| $\beta$-Methylallyl *n*-butyl (**3**) | 54 | 12 |
| Allyl phenyl (**4**) | 32 | 7 |
| $\gamma$-Methylallyl phenyl (**5**) | 47 | 10 |

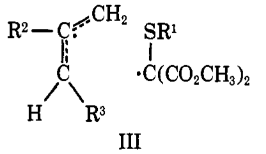
Since, as shown in the previous paper,[1] the carbene attacks a sulfur atom more rapidly than the carbon–carbon double bond, the major reaction of the carbene with allyl sulfide may be deduced to proceed by an attack of the carbene on the sulfur atom in allyl sulfide, although the expected sulfonium ylides were not isolated. Thus, a mechanism for the formation of insertion product may involve sulfonium ylide formation followed by intramolecular allylic rearrangement, as suggested by other workers.[4,5] Two types of rearrangement reactions involving intermediate allylic sulfonium ylides are known, namely, Stevens type and allylic rearrangements. These transformations could be either concerted reactions (I and II) or nonconcerted processes involving radical pair intermediate (III).



I



II



III

---

[1] W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969).

[2] W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *ibid.*, **91**, 5164 (1969).

[3] $\gamma$-Methylallyl phenyl sulfide contained 2% of isomeric $\alpha$-methylallyl phenyl sulfide by vpc analysis.

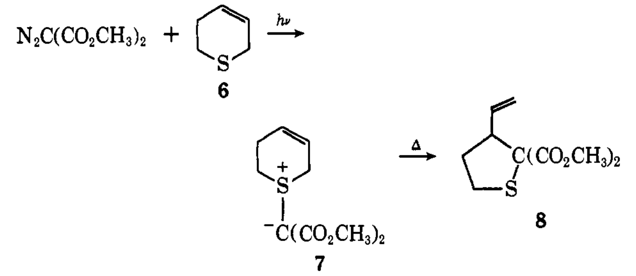
[4] W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964); 30, 728 (1965); **31**, 1694 (1966); W. E. Parham and J. R. Potoski, *ibid.*, **32**, 275, 278 (1967).

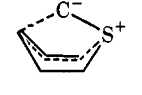
[5] W. Kirmse, M. Kapps, and R. B. Hanger, *Chem. Ber.*, **99**, 2855 (1966); W. Kirmse and M. Kapps, *ibid.*, **101**, 994, 1004, 1008 (1968).

Empirical extension of the Woodward–Hoffmann rules,[6] which have been applied to allylic and other sigmatropic rearrangement,[7–11] leads to a recognition that a concerted Stevens rearrangement (I) with retention of the configuration at the terminus of the migrating group is symmetry-forbidden, whereas the five-centered allylic rearrangement (II) is symmetry-allowed. The exclusive formation of the allylic rearranged insertion product suggests that the ylides derived from the reaction of bis(methoxycarbonyl)carbene with allyl sulfides rearrange by a concerted process under the reaction conditions.

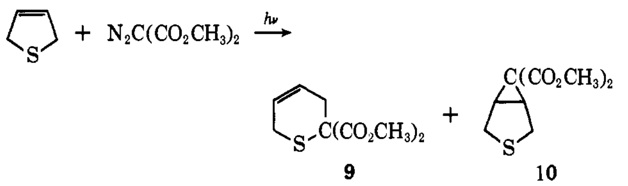
The studies on the reaction of carbenes with cyclic allyl sulfides gave particularly interesting results. The photolysis of dimethyl diazomalonate in $\Delta^3$-dihydrothiapyran (6) (Scheme II) gave a white solid which was characterized as sulfonium bis(methoxycarbonyl)methylide (7) from the analysis of its nmr and ir spectra. This ylide gave the rearranged product in 83% yield on heating at 180° for 30 min. These facts strongly support the mechanism by which the allylic rearranged insertion product are formed through the ylide intermediate in the reaction of the carbene with allyl sulfides. It is noteworthy that the ylide 7 was stable enough to be isolated, and rearranged only at higher temperature, while the ylides derived from the open chain allylic sulfides could not be isolated, perhaps being easily converted into rearranged products at room temperature. This lower or reduced susceptibility of the ylide 7 toward rearrangement is probably due to the transition state of the concerted allylic rearrangement requiring the unfavored "boat" form of the dihydrothiapyran ring bearing the $^-C(CO_2CH_3)_2$ group in "endo" position of the sulfur atom. It is also interesting to note that the reaction sequence observed here is quite different from that shown in the reaction of cyclic allyl sulfide with dichlorocarbene.[12]

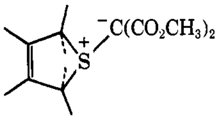
Scheme II





However, in contrast to the six-membered cyclic sulfide, 2,5-dihydrothiophene was found to give rise to 2,2-bis(methoxycarbonyl)thiapyran (9) and an adduct (10), but the corresponding sulfonium ylide 11 could not be isolated. The product 9 corresponds to a Stevens-type rearrangement product from the intermediate sulfonium ylide 11. The five-membered cyclic sulfonium ylide may be unstable and therefore undergo a Stevens-type rearrangement, because it would inevitably have an eclipsed conformation, and the interaction between the $^-C(CO_2CH_3)_2$ group and neighboring methylene carbon atom will promote C–S bond fission by either concerted or radical pair processes.





11

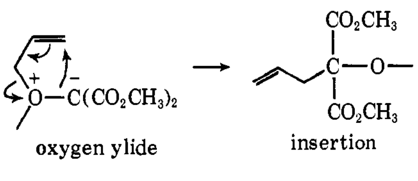
**Photolysis of Diazomalonate in Allyl Ethers, Amines, and Chlorides.** Dimethyl diazomalonate was photolyzed with the high-pressure mercury lamp in allyl methyl ether, allyl *tert*-butyl ether, allyl ethyl ether, γ-methylallyl methyl ether, and γ,γ-dimethylallyl methyl ether. These reactions were found to give also the rearranged "insertion" products and the adducts in yields shown in Table II. Some contrasting features can be seen compared with the reactions in the corresponding allyl sulfides. In the photolysis in allyl methyl ethers, the reactions led to both addition and insertion products, but in allyl *tert*-butyl ether only the formation of the addition product was observed. By analogy to reactions of allyl sulfides with bis(methoxycarbonyl)carbene, the obtained insertion products can be considered to form through the intermediate oxygen ylides by their allylic rearrangement (Scheme III). The

**Table II.** Yields of Products from the Photolysis of Dimethyl Diazomalonate in Allyl Ethers and Amines

| Allyl compound | Insertion (i), % | Addition (a), % |
|---|---|---|
| Allyl methyl ether (**12**) | 31 | 20 |
| γ-Methylallyl methyl ether (**13**) | 37 | 17 |
| γ-Methylallyl ethyl ether (**14**) | 15 | 38 |
| γ,γ-Dimethylallyl ethyl ether (**15**) | 16 | 25 |
| Allyl *tert*-butyl ether (**16**) | 0 | 39 |
| Allyldiethylamine (**17**)[a] | 9 | 6 |
| γ-Methylallyldiethylamine (**18**)[a] | 11 | 2 |

[a] Under the reaction conditions, the starting amines and its products were unstable. The main product from these reactions was dimethyl malonate.

Scheme III



---

(6) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

(7) A. Jeferson and S. Scheinmann, *Quart. Rev., Chem. Soc.*, 22, 391 (1968).

(8) J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

(9) G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith, and I. O. Sutherland, *Chem. Commun.*, 186 (1968).

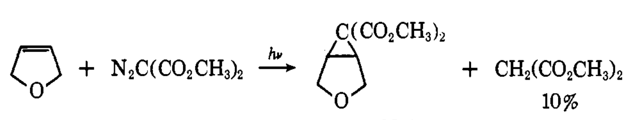
(10) R. W. C. Cose, A. M. Davies, W. D. Ollis, C. Smith, and I. O. Sutherland, *ibid.*, 293 (1969).

(11) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, 91, 3646 (1969); J. E. Baldwin, J. E. Brown, and R. W. Cordell, *J. Chem. Soc. D*, 31 (1970).

(12) W. E. Parham, L. H. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, 29, 2211 (1964).

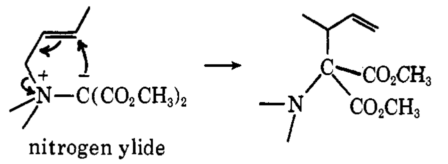
bulky *tert*-butyl group on the oxygen would interfere with the formation of the ylide, at the expense of which the yield of the addition product might have increased.

The difference observed between the reactions in allyl ethers and that in allyl sulfides may be due to the difference in the nucleophilicity between oxygen and sulfur, and in stability of their ylides. The intermediate sulfur ylides could be well stabilized by $d\pi$–$p\pi$ interaction [$R_2S^+—C^-R_2 \leftrightarrow R_2S{=}CR_2$], while such a contribution to stabilization can not be expected in the oxygen ylide. As a consequence, reactions proceeding through an oxygen ylide may be less favorable to occur than reactions proceeding through a sulfur ylide. In the reaction of 2,5-dihydrofuran with dimethyl diazomalonate, a 20% addition product **19** was obtained, but the ring expansion product could not be detected.



**19**, 20%

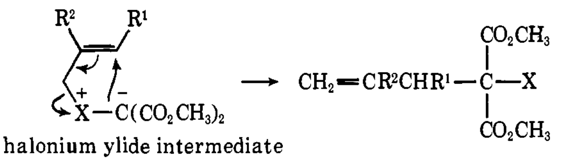
Also in the photoreactions of dimethyl diazomalonate with allyl amines, similar products, insertion and addition, were obtained, although in lower yields compared with the cases of allyl ethers and allyl sulfides (Table II). Formation of the insertion products may be expressed by



Photolysis of dimethyl diazomalonate in allylic chlorides also yielded both insertion and the addition products (Table III).[13] Again, the reaction with γ-methylallyl chloride gave a rearranged insertion product (**22**-i) and an addition product (**22**-a), but not 2-butenyl chloromalonate. The formation of **22**-i may be explained in terms of similar intramolecular 2,3-sigmatropic rearrangement of halonium ylide intermediate, as in the cases of the reaction of dimethyl diazomalonate with allyl sulfides, ethers, and amines.[14,15] It can be seen that in the reaction with allyl bromide, the insertion product was obtained in a fairly good yield, whereas only a small amount of addition product was formed.[16]

**Table III.** Photolysis of Dimethyl Diazomalonate in Allyl Halides

| Halide | Insertion (i), % | Addition (a), % |
|---|---|---|
| Allyl chloride (**20**) | 53 | 23 |
| β-Methylallyl chloride (**21**) | 25 | 22 |
| γ-Methylallyl chloride (**22**) | 38 | 15 |
| Allyl bromide (**23**) | 38 | 6 |



The relative rate of insertion to addition was about ~1–2.5 in the reaction of allyl chloride, but about 8 in allyl bromide. Since the reactivities of the double bonds toward the attacking carbene species are not considered to be very different in these two allylic substrates, the change in the above ratio may be due to the difference in the nucleophilicity between a chlorine and a bromine atom. This consideration is supported by the results of competitive experiments using pairs of allylic compounds.

Table IV shows the relative rates of insertion and addition of bis(methoxycarbonyl)carbene to allyl halides and ethyl allyl sulfide, the rate of addition to allyl chloride being taken as unity. The data indicate that the carbene attacks bromine and sulfur atoms more effectively than it attacks a chlorine atom, as is expected from the electrophilic nature of the attacking carbene. On the other hand, the carbene adds to the double bonds at almost equal rates regardless of the nature of the allylic substrate.

**Table IV.** Competitive Reactions of Dimethyl Diazomalonate to Allyl Compounds

| Allyl compound | Product[a] | Ratio |
|---|---|---|
| **20** | a | 1[b] |
|  | i | 2.3 |
| **23** | a | 1.0 |
|  | i | 8.5[c] |
| Allyl ethyl sulfide (**24**) | a | 1.2 |
|  | i | 6.3 |

[a] a = addition, i = insertion. [b] Standard. [c] The product was unstable to prolonged irradiation.

**Photosensitized Decomposition of Diazomalonate in Allyl Compounds.** The most marked change in going from direct to sensitized photolysis is in the relative ratio of the insertion to addition products produced by the reaction of dimethyl diazomalonate with allyl sulfides. The direct photolysis of diazomalonate in ethyl allyl sulfide gave 51% insertion and 10% of addition products. Contrastingly, the benzophenone photosensitized decomposition of diazomalonate gave 18% of insertion and 37% of addition products (Table V).[17] Appropriate control experiments showed that under the reaction conditions, the products were neither isomerized nor destroyed. The attractive mechanism is proposed in which the triplet carbene produced from the photosensitized reaction[18,19] adds to the olefin to give a diradical which undergoes intramolecular transfer of the thiyl group through the cyclic transition state, as well as cyclopropane ring formation. In the addition of the triplet carbene to olefin involving two bond

---

[13] W. Ando, S. Kondo, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 6516 (1969).

[14] W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 3959 (1968).

[15] W. H. Pirkle and G. F. Koser, *J. Amer. Chem. Soc.*, **90**, 3598 (1968).

[16] Under the reaction conditions, the insertion product is unstable and prolonged irradiation gave mainly dimethyl bromomalonate.

[17] Under the reaction conditions employed, the sensitizer absorbed *ca.* 98% of the incident light. The data are not corrected for the small amount of direct photolysis which must be occurring as the relative quantum yields of the two processes are not known.

[18] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 1015 (1962).

[19] M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Lett.*, 1391 (1967).

Table V. Photolysis of Dimethyl Diazomalonate in Allyl Sulfides

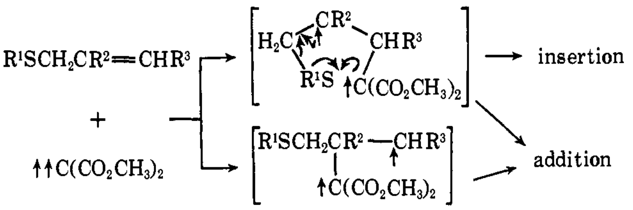
| Sulfide | Conditions | Insertion, % | Addition, % |
|---|---|---|---|
| Allyl ethyl (**24**) | $h\nu$ | 51 | 10 |
| | $h\nu + Ph_2CO$ | 18 | 37 |
| β-Methylallyl ethyl (**25**) | $h\nu$ | 46 | 12 |
| | $h\nu + Ph_2CO$ | 7 | 29 |
| γ-Methylallyl ethyl (**26**) | $h\nu$ | 53 | 7 |
| | $h\nu + Ph_2CO$ | 31 | 19 |
| γ,γ-Dimethylallyl ethyl (**27**) | $h\nu$ | 43 | 12 |
| | $h\nu + Ph_2CO$ | 19 | 27 |

forming processes, spin inversion is required in the intermediate step. During this step, internal rotations which gives the conformation leading to the cyclic structure illustrated in Scheme IV may occur. Similar radical attack on the double bond followed by C–S bond cleavage in allylic sulfide was observed in the reaction of the phenyl radical (from phenylazotriphenylmethane) with allyl ethyl sulfide giving allylbenzene.[20] These results also support the fact that in allyl sulfide,

$$Ph\cdot + CH_2{=}CHC(CH_3)_2{-}SEt \longrightarrow PhCH_2CH{=}C(CH_3)_2$$

triplet carbene could give the insertion product without sulfur ylide formation.

Scheme IV



Benzophenone sensitized photolysis of dimethyl diazomalonate in allyl ethers yielded mainly addition products and only negligible amounts of insertion products (see Table VI). This means that in contrast to the singlet carbene produced by direct photolysis, the triplet carbene produced by photosensitized reaction apparently almost exclusively adds to the double bond of allylic ethers. It is noteworthy that sulfide sulfur and ether oxygen show the remarkable difference in the course of reaction of the triplet carbene, that is, allyl ether does not give the insertion product, while allyl sulfide does. This can be explained by the difference in bond strength between C–O and C–S. In a biradical derived by attack of the carbene on the double bond, the migration of alkoxy group involving homolysis of a C–O bond would be much less easy than migration of thiyl group involving homolysis of a C–S bond. Indeed, the reaction of phenyl radical with allyl ether gives only a scanty amount of allylbenzene, contrasting to the reaction with allyl sulfide.[20]

Table VI. Photolysis of Dimethyl Diazomalonate in Allyl Ethers

| Ether | Conditions | Insertion, % | Addition, % |
|---|---|---|---|
| γ,γ-Dimethylallyl ethyl (**15**) | $h\nu$ | 16 | 25 |
| | $h\nu + Ph_2CO$ | Trace | 52 |
| β-Methylallyl ethyl (**28**) | $h\nu$ | 15 | 38 |
| | $h\nu + Ph_2CO$ | Trace | 62 |

Similar and more distinct tendencies in the ratio of insertion and addition products were also found in the reaction of diazomalonate in allyl chlorides. The direct photolysis of diazomalonate in allyl chloride gave a larger amount of the insertion product (53%) than addition product (23%) (see Table III), but the sensitized decomposition gave *ca.* 88% addition and only 5% insertion products (see Table VII). This contrast between direct and sensitized reactions was considered to arise for reasons similar to those described in allyl ethers.

Table VII. Benzophenone Photosensitized Decomposition of Dimethyl Diazomalonate in Allyl Halides

| Halide | Insertion, % | Addition, % |
|---|---|---|
| **20** | 5 | 88 |
| **21** | Trace | 86 |
| **22** | Trace | 49 |
| **23** | 4 | 30 |

**Thermal Decomposition of Dimethyl Diazomalonate in the Presence of Copper Salts.** Considerable evidence supports the conclusion that reaction of diazoalkanes with metal salts generate carbenoid intermediates which show similar reactivity to that of a carbene.[21] This tendency was recognized in copper salt catalyzed reaction of diazomalonate. Thus, copper sulfate catalyzed thermal decomposition of diazomalonate in allyl sulfides yields insertion products in high yield. No addition product was obtained (Table VIII). These data are comparable with those of the reaction in the diazomethane copper system which has shown the formation of the insertion (83%) and addition (17%) products in a yield of 30–35%.[5] In our case, however, because of the excellent yields of the products and clearness of the reaction, these reactions may be quite useful for the preparation allyl alkylthiomalonates.

Table VIII. Thermal Decomposition of Dimethyl Diazomalonate in Allyl Sulfides

| Sulfide | Insertion, % | Addition, % |
|---|---|---|
| **1** | 93 | 0 |
| **2** | 13 | 0 |
| **3** | 100 | 0 |
| **4** | 90 | 0 |
| **5** | 92 | 0 |

The formation of the insertion products may be again considered to involve the symmetry-allowed 2,3-

---

(20) M. Kosugi, K. Takayama, Y. Nakagawa, and T. Migita, unpublished results.

(21) (a) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961); (b) E. Muller, G. Kesseler, H. Fricke, and W. Kiedaisch, *Justus Liebigs Ann. Chem.*, **675**, 63 (1964); (c) D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964); (d) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4074 (1964); (e) S. H. Goh, L. E. Closs, and G. L. Closs, *J. Org. Chem.*, **34**, 25 (1969).

sigmatropic rearrangement of the intermediate ylide. Thus, the reaction with $\gamma$-methylallyl phenyl sulfide gave the rearranged insertion product **5**-i in high yield; no trace of $\gamma$-methylallyl thiomalonate could be detected in the reaction mixture.

Since the reaction gave the insertion product exclusively and no addition product, it is thought that the carbenoid species derived in this reaction has more electrophilic nature than that generated in the photolysis. The possible structure of such a carbenoid might be represented by $X—Cu^-—C^+(CO_2CH_3)_2$.

Copper sulfate catalyzed thermal decomposition of dimethyl diazomalonate in allyl ethers and amines gave mainly the insertion products expected from the carbenoid attack on the oxygen or nitrogen atoms followed by 2,3-sigmatropic rearrangement. Predominant formation of insertion products, in all reactions studied, except with allyl *tert*-butyl ether, was observed as in the case with allyl sulfide system (Table IX). Interesting contrast can be seen between these data and those of copper-catalyzed reaction of diazomethane.[5] Kirmse has found that the reaction of diazomethane with allyl methyl ethers favored addition over insertion (9:1). This difference in behavior between methylenoid and bis(methoxycarbonyl)methylenoid may be interpreted in terms of the difference in hardness between these two species. Owing to the electron-withdrawing effect of carbomethoxy groups, bis(methoxycarbonyl)methylenoid can be considered to be a harder acid than methylenoid and tends to react with a hard base, the oxygen atom in allyl ether, more easily than methylenoid does.

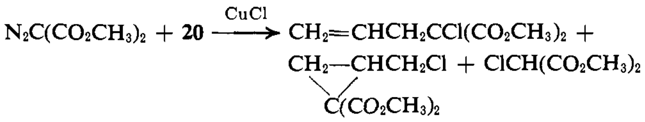
Table IX. Copper Sulfate Catalyzed Thermal Reactions of Diazomalonate in Allyl Ethers, Amines, and Chlorides (110°)

| Allyl compound | Insertion, % | Addition, % | $HClC(CO_2CH_3)_2$, % |
|---|---|---|---|
| **12** | 60 | 20 | |
| **13** | 75 | Trace | |
| **16** | 0 | 50 | |
| **17** | 40 | Trace | |
| **18** | 27 | Trace | |
| **20**[a] | 32 | 3 | 10 |
| **21**[a] | 35 | 4 | 10 |
| **22**[a] | 35 | Trace | 24 |

[a] CuCl-catalyzed reactions at 110°.

Exclusive formation of adduct in the reaction with allyl *tert*-butyl ether, as well as the poor yield of insertion product in the reaction with allyl *tert*-butyl sulfide, can be considered to be due to steric hindrance to carbenoid attack on heteroatoms.

Similary, the copper chloride catalyzed thermal decomposition of dimethyl diazomalonate in allyl chloride gave 35% of insertion product and less than 4% of addition product (Table IX). These are contrasted to the copper-catalyzed thermal reaction of diazomethane in allyl chloride, which gives mainly addition product and a trace of insertion product. However, under the reaction conditions, a significant decomposition of the insertion product into dimethyl chloromalonate was observed. From the reaction of diazomalonate with **21**, 1-chloro-2-methyl-3-butene-1,1-dicarboxylate was the only insertion product. This is in contrast with the reaction of allyl halides with ethyl diazoacetate which gave both insertion products derived by Stevens and allylic rearrangements of the intermediate ylide.[22]



$$N_2C(CO_2CH_3)_2 + \mathbf{20} \xrightarrow{CuCl} CH_2{=}CHCH_2CCl(CO_2CH_3)_2 + \underset{C(CO_2CH_3)_2}{CH_2—CHCH_2Cl} + ClCH(CO_2CH_3)_2$$

## Conclusions

The results discussed show that direct photolysis of dimethyl diazomalonate produces bis(methoxycarbonyl)carbene which predominantly attacks a heteroatom in allyl sulfides, allyl ethers, allylamines, or allyl chlorides. On the other hand, the triplet carbene generated by benzophenone sensitized photolysis of diazomalonate adds to the olefinic double bond. Copper salts catalyzed thermal reaction of diazomalonate produces a carbenoid species which attacks a heteroatom almost exclusively.

## Experimental Section

**General.** Vapor-phase chromatographic analyses were carried out on an Ohkura gas chromatographic instrument, using a 5-ft column packed with 10% Carbowax on Firebrick. Infrared spectra were taken with a Japan Spectroscopic Co. LTD DS-21 instrument in chloroform or carbon tetrachloride. Photolyses and thermolyses were carried out with the system previously described.[1] Yields were determined gas chromatographically and were not corrected for thermal conductivities.

**Materials.** The reagents, allyl, $\beta$-methylallyl, and $\gamma$-methylallyl chlorides, were purified before use by distilling commercial materials. Most of the allyl sulfides, ethers, and amines were prepared by treatment of the corresponding alkyl and aryl halides with alkyl mercaptans, alcohols, and amines. For example, allyl *tert*-butyl sulfide was prepared as follows. A mixture of *tert*-butyl mercaptan (25 g), ethyl alcohol (10 ml), and sodium hydroxide (11 g) was heated on a steam bath with stirring until the sodium hydroxide had dissolved. After the solution was cooled, allyl chloride (21 g) was added dropwise with stirring, and the mixture was refluxed for 20 min. After removal of alcohol by distillation at atmospheric pressure, the residue was diluted with 500 ml of water. The aqueous layer was extracted with 3 × 400 ml portions of ether. The water insoluble layer and the ether extracts were combined, washed with water repeatedly until the water layer was neutral, and dried. After removal of the solvent, the residue was distilled *in vacuo*. The yield was 18 g (50%), by 138–140° (lit.[23] 139–140°). All other allyl sulfides were prepared by the same method. Allyl *tert*-butyl ether was prepared in the following ways. Sodium (1 g-atom) was gradually added to a solution of 1 mol of *tert*-butyl alcohol in 200 ml of xylene. Then, the solution was heated to 115°. After the sodium melted, the solution was cooled to room temperature, and an equimolar amount of allyl chloride was gradually added to the mixture through a separatory funnel. When the entire amount of allyl chloride was added, the bath temperature was raised to 110° and kept at this temperature for 5 hr. The mixture was then washed with water, dried, and distilled to give the product. All other ethers were prepared in the same manner. Allyldiethylamine was prepared from diethylamine and allyl bromide by the method of Cope and Towle.[24]

$\Delta^3$-Dihydrothiapyran was prepared by the method described in ref 12. 2,5-Dihydrothiophene was obtained by reducing thiophene with sodium–liquid ammonia–methanol.[25]

2,5-Dihydrofuran was obtained commercially and purified before use. Dimethyl diazomalonate was prepared by the method previously described.[26]

**Photolysis of Dimethyl Diazomalonate in Allyl *n*-Butyl Sulfide (1).** Irradiation of a cooled solution of 0.245 g (1.5 mmol) of dimethyl

---

[22] D. D. Philips, *J. Amer. Chem. Soc.*, **76**, 5385 (1954).

[23] D. S. Tarbell and W. F. Lovett, *ibid.*, **78**, 2259 (1956).

[24] A. C. Cope and P. H. Towle, *ibid.*, **71**, 3423 (1949).

[25] S. F. Birch and D. T. McAllan, *J. Chem. Soc.*, 2556 (1951).

[26] W. Ando, S. Kondo, and T. Migita, *Bull. Chem. Soc. Jap.*, **44**, 571 (1971).

diazomalonate in 1 ml of **1** contained in a Pyrex vessel resulted in the evolution of nitrogen gas. After the infrared spectrum of the reaction mixture showed no diazo band, the reaction products were isolated by glpc method. Infrared bands and nmr signals, and the results of elemental analysis, on which determination of the structures of the products were based, are described here. The yields given previously were determined by glpc analysis using an internal standard. Dimethyl (α-allyl-α-*n*-butylthio)malonate (**1**-i) showed ir 920, 1638, and 1725 cm$^{-1}$; nmr 0.92 (t, 3 H), 1.44 (m, 4 H), 2.56 (t, 2 H), 2.73 (d, 2 H), 3.70 (s, 6 H), 4.96 (m, 1 H), 5.17 (m, 1 H), and 5.71 ppm (m, 1 H). *Anal.* Calcd for $C_{12}H_{20}O_4S$: C, 55.38; H, 7.69. Found: C, 55.30; H, 7.48. Substituted 1,1-dicarbomethoxycyclopropane (**1**-a) showed ir 1735 cm$^{-1}$; nmr 0.92 (broad t, 4 H), 1.45 (m, 6 H), 2.55 (m, 4 H), 3.70 ppm (s, 6 H). *Anal.* Calcd for $C_{12}H_{20}O_4S$: C, 55.38; H, 7.69. Found: C, 55.51; H, 7.53.

**Photolysis of Dimethyl Diazomalonate in Allyl *tert*-Butyl Sulfide (2).** A solution of 0.239 g (1.5 mmol) of diazomalonate in 1 ml of allyl *tert*-butyl sulfide (**2**) was irradiated. The reaction mixture was analyzed directly by gas chromatography. The two main products were collected and identified as dimethyl (α-allyl-α-*tert*-butylthio)-malonate (**2**-i) [ir 925, 1645, and 1740 cm$^{-1}$; nmr 1.32 (s, 9 H), 2.80 (d, 2 H), 3.70 (s, 6 H), 4.90 (m, 1 H), 5.12 (m, 1 H), and 5.74 ppm (m, 1 H). *Anal.* Calcd for $C_{12}H_{20}O_4S$: C, 55.37; H, 7.75. Found: C, 55.27; H, 7.65.] and the cyclopropane derivative (**2**-a) [ir 1735 cm$^{-1}$; nmr 1.29 (s, 9 H), 1.45 (m, 1 H), 2.04 (m, 2 H), 2.49 (d, 2 H), 3.68 (s, 3 H), and 3.69 ppm (s, 3 H). *Anal.* Calcd for $C_{12}H_{20}O_4S$: C, 55.37; H, 7.75. Found: C, 55.36; H, 7.54.].

**Photolysis of Dimethyl Diazomalonate in β-Methylallyl *n*-Butyl Sulfide (3).** A solution of 0.214 g (1.3 mmol) of diazomalonate in 1 ml of **3** was irradiated in a cooled Pyrex vessel with the high-pressure mercury lamp as described before. After 10 hr, no starting diazo compound remained. Two reaction products were obtained by gas chromatography: **3**-i [ir 900, 1645, and 1735 cm$^{-1}$; nmr 0.92 (t, 3 H), 1.44 (m, 4 H), 1.73 (s, 3 H), 2.56 (t, 2 H), 2.78 (s, 2 H), 3.70 (s, 6 H), and 4.78 ppm (m, 2 H). *Anal.* Calcd for $C_{13}H_{22}O_4S$: C, 56.91; H, 8.08. Found: C, 57.46; H, 8.19.] and the product **3**-a [ir 1740 cm$^{-1}$; nmr 0.92 (t, 3 H), 1.26 (s, 3 H), 1.44 (m, 6 H), 2.45 (t, 2 H), 2.75 (d, 2 H), and 3.70 ppm (s, 6 H). *Anal.* Calcd for $C_{13}H_{22}O_4S$: C, 56.91; H, 8.08. Found: C, 56.96; H, 7.94].

**Photolysis of Dimethyl Diazomalonate in γ-Methylallyl Phenyl Sulfide (5).** Photolysis of a solution of 0.200 g (1.3 mmol) of diazomalonate in 1 ml of **5** gave **5**-i [ir 920, 1645, and 1740 cm$^{-1}$; nmr 1.24 (d, 3 H), 2.95 (q, 1 H), 3.62 (s, 6 H), 5.02 (m, 2 H), 6.01 (m, 1 H), and 7.39 ppm (m, 5 H). *Anal.* Calcd for $C_{15}H_{18}O_4S$: C, 61.21; H, 6.17. Found: C, 61.87; H, 6.47.] and **5**-a [ir 1740 cm$^{-1}$; nmr 0.98 (d, 3 H), 1.78 (m, 2 H), 2.91 (d, 2 H), 3.69 (s, 6 H), and 7.26 ppm (m, 5 H). *Anal.* Calcd for $C_{15}H_{18}O_4S$: C, 61.21; H, 6.17. Found: C, 61.20; H, 6.35.].

**Photolysis of Dimethyl Diazomalonate in $\Delta^3$-Dihydrothiapyran (6).** Irradiation of a solution of 0.5 g of dimethyl diazomalonate in 2 ml of **6** was carried out in a Pyrex vessel with the high-pressure mercury lamp. Sulfonium ylide (**7**) was isolated as a pure white solid in 46% yield by adding petroleum ether, cooling at 0°, and then washing the solid with petroleum ether again, mp 103–104°. *Anal.* Calcd for $C_{10}H_{14}O_4S$: C, 52.17; H, 6.13. Found: C, 52.06; H, 6.01. This product showed nmr spectrum at 2.68 (m, 2 H), 3.05 (m, 1 H), 3.35 (m, 1 H), 3.70 (s, 6 H), 4.70 (m, 2 H), and 5.87 ppm (m, 1 H); ir absorption maxima at 1635 and 1685 cm$^{-1}$. This product was soluble in water and chloroform, but not in carbon tetrachloride or acetone.

**Thermal Decomposition of Sulfonium Ylide 7.** Sulfonium ylide **7** (0.5 g) was sealed in 8 × 10 mm Pyrex tubes without degassing. The sample was heated at 180° for 30 min in an oil bath. The reaction mixture was analyzed directly by gas chromatography and found to contain the compound **8**: ir 920, 985, and 1740 cm$^{-1}$; nmr 2.35 (m, 2 H), 3.01 (m, 2 H), 3.35 (m, 1 H), 3.65 (s, 3 H), 3.75 (s, 3 H), 5.12 (m, 2 H), and 5.67 ppm (m, 1 H). *Anal.* Calcd for $C_{10}H_{14}O_4S$: C, 52.17; H, 6.13. Found: C, 52.34; H, 6.24.

**Photolysis of Dimethyl Diazomalonate in 2,5-Dihydrothiophene.** A solution of 0.247 g (1.55 mmol) of dimethyl diazomalonate in 0.661 g of 2,5-dihydrothiophene was irradiated in Pyrex vessels. The infrared spectrum of the reaction mixture did not show the carbonyl shift observed in the sulfonium ylide. Thus, the reaction mixture was analyzed directly by gas chromatography to show two main products, **9** and **10**. The product **9** showed an ir band at 1735 cm$^{-1}$; nmr 2.71 (m, 2 H), 3.14 (m, 2 H), 3.73 (s, 6 H), and 5.78 ppm (m, 2 H). *Anal.* Calcd for $C_9H_{12}O_4S$: C, 50.00; H, 5.60. Found: C, 50.09; H, 5.39. The product **10** showed ir 1735 cm$^{-1}$; nmr 2.40 (m, 2 H), 3.17 (m, 4 H), 3.71 (s, 3 H), and 3.75 ppm (s, 3 H). *Anal.* Calcd for $C_9H_{12}O_4S$: C, 50.00; H, 5.60. Found: C, 49.81; H, 5.76.

**Reaction of Dimethyl Diazomalonate in Allyl Ethers.** In 1 ml of allyl methyl ether (**12**) was dissolved 0.462 g (2.9 mmol) of diazomalonate. The solution was then irradiated for 20 hr using the high-pressure mercury lamp as described before. From the analysis by gas chromatography, two main products were found: one of them was identified as α-allyl-α-methoxymalonate (**12**-i) [ir 916, 995, 1645, and 1750 cm$^{-1}$; nmr 2.71 (d, 2 H), 3.40 (s, 3 H), 3.76 (s, 6 H), 4.97 (m, 1 H), 5.18 (m, 1 H), and 5.75 ppm (m, 1 H). *Anal.* Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.48; H, 7.05.] and the other as an addition product (**12**-a) [ir 1735 cm$^{-1}$; nmr 1.38 (m, 2 H), 2.10 (m, 1 H), 3.26 (s, 3 H), 3.40 (d, 2 H), and 3.75 ppm (s, 6 H). *Anal.* Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.15; H, 7.12.] from the analytical and spectroscopic data.

The reaction of diazomalonate in allyl *tert*-butyl ether (**16**) gave only the bis(carbomethoxy)cyclopropane (**16**-a): ir 1734 cm$^{-1}$; nmr 1.08 (s, 9 H), 1.36 (m, 2 H), 2.04 (m, 1 H), 3.35 (m, 2 H), and 3.70 ppm (s, 6 H). *Anal.* Calcd for $C_{12}H_{20}O_5$: C, 58.98; H, 8.18. Found: C, 58.99; H, 8.36.

The reaction of diazomalonate in γ-methylallyl methyl ether (**13**) gave **13**-i, **13**-a, and **13**-a′. **13**-i showed ir 917, 1642, 1740, and 1755 cm$^{-1}$; nmr 1.00 (d, 3 H), 2.85 (m, 1 H), 3.41 (s, 3 H), 3.68 (s, 6 H), 4.80 (m, 1 H), and 5.75 ppm (m, 1 H). *Anal.* Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 56.02; H, 7.61. **13**-a and **13**-a′ showed very similar spectra, which probably are those of stereo isomer. **13**-a showed ir 1735 cm$^{-1}$; nmr 1.10 (d, 3 H), 1.93 (m, 2 H), 3.23 (s, 3 H), 3.38 (d, 2 H), 3.66 (s, 3 H), and 3.71 ppm (s, 3 H). *Anal.* Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.63; H, 7.67. Photolysis of dimethyl diazomalonate in 2,5-dihydrofuran was carried out in the same scale described in allyl methyl ether, and found to give dimethyl malonate and **19**: ir 1740 cm$^{-1}$; nmr 2.30 (m, 2 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 3.75 (d, 2 H), and 4.05 ppm (d, 2 H). *Anal.* Calcd for $C_9H_{12}O_5$: C, 53.99; H, 6.04. Found: C, 54.45; H, 6.12.

**Reaction of Dimethyl Diazomalonate in Allylamines.** Photolysis and copper sulfate thermal decomposition of diazomalonate in allyldiethylamine (**17**), according to the procedure mentioned above, gave α-allyl-α-diethylaminomalonate (**17**-i) and the addition product (**17**-a). **17**-i showed ir 918, 1642, 1740, and 1750 cm$^{-1}$; nmr 1.00 (t, 6 H), 2.64 (m, 6 H), 3.64 (s, 6 H), 4.86 (m, 1 H), 5.10 (m, 1 H), and 5.60 ppm (m, 1 H). *Anal.* Calcd for $C_{12}H_{21}O_4N$: C, 59.24; H, 8.70. Found: C, 59.56; H, 8.71. **17**-a showed ir 1740 cm$^{-1}$; nmr 0.93 (t, 6 H), 1.37 (m, 2 H), 1.95 (m, 1 H), 2.45 (m, 6 H), and 3.64 ppm (s, 6 H). *Anal.* Calcd for $C_{12}H_{21}O_4S$: C, 59.24; H, 8.70. Found: C, 59.38; H, 8.87. The reaction of diazomalonate in γ-methylallyldiethylamine (**18**) gave two products. One of them is **18**-i: ir 910, 1640, and 1733 cm$^{-1}$; nmr 0.99 (d, 3 H), 1.05 (t, 6 H), 2.50 (q, 4 H), 3.05 (m, 1 H), 3.64 (s, 3 H), 3.69 (s, 3 H), 4.80 (m, 1 H), 5.02 (m, 1 H), and 5.90 ppm (m, 1 H). *Anal.* Calcd for $C_{13}H_{23}O_4N$: C, 60.68; H, 9.01. Found: C, 60.20; H, 8.87. The other product is **18**-a: ir 1735 cm$^{-1}$; nmr 0.95 (d, 6 H), 1.07 (d, 3 H), 1.78 (m, 2 H), 2.45 (m, 6 H), 3.66 (s, 3 H), and 3.72 ppm (s, 3 H). *Anal.* Calcd for $C_{13}H_{23}O_4N$: C, 60.68; H, 9.01; N, 5.44. Found: C, 60.42; H, 8.87; N, 5.83.

**Reaction of Dimethyl Diazomalonate in Allyl Halides.** In a typical run, 0.218 g (1.3 mmol) of diazomalonate in 1 ml of allyl chloride (**20**) was irradiated in a cooled Pyrex tube with high-pressure mercury lamp as described before and after 10 hr, no starting diazo compound remained. α-Allyl-α-chloromalonate (**20**-i) [ir 950, 1645, and 1752 cm$^{-1}$; nmr 1.92 (d, 2 H), 3.78 (s, 6 H), and 5.24 ppm (m, 3 H). *Anal.* Calcd for $C_8H_{11}O_4Cl$: C, 46.48; H, 5.32. Found: C, 46.71; H, 5.49.] and 1,1-dicarbomethoxy-2-chloromethylcyclopropane (**20**-a) [ir 1725 cm$^{-1}$; nmr 1.43 (d, 1 H), 1.55 (s, 1 H), 2.12 (m, 1 H), 3.50 (d, 2 H), 3.71 (s, 3 H), and 3.75 ppm (s, 3 H). *Anal.* Calcd for $C_8H_{11}O_4Cl$: C, 46.48; H, 5.32. Found: C, 46.49; H, 5.43.] were detected as major products in the analysis by gas chromatography.

The reaction of diazomalonate in γ-methylallyl chloride gave two products. One of them is **22**-i: ir 950, 1645, and 1752 cm$^{-1}$; nmr 1.18 (d, 3 H), 3.18 (d, 1 H), 3.75 (s, 3 H), 3.78 (s, 3 H), and 5.12 ppm (m, 3 H). *Anal.* Calcd for $C_9H_{13}O_4Cl$: C, 48.97; H, 5.89. Found: C, 48.87; H, 6.06. The other product is **20**-a: ir 1728 cm$^{-1}$; nmr 1.10 (d, 3 H), 2.16 (m, 2 H), 3.50 (m, 2 H), and 3.74 ppm (s, 6 H). *Anal.* Calcd for $C_9H_{13}O_4Cl$: C, 48.97; H, 5.89. Found: C, 48.73; H, 6.15.

The photolysis of diazomalonate in β-methylallyl chloride (**21**) gave two products: **21**-i [ir 905, 1645, and 1750 cm$^{-1}$; nmr 1.75

**Table X.** Relative Ratios of Products by Photodecomposition of Diazomalonate in Allyl Ethyl Sulfide Containing Benzophenone

| Molar ratio | | | Product ratio |
|---|---|---|---|
| Diazo | Sulfide | Benzophenone | **24**-i:**24**-a |
| 1 | 5 | 2.6 | 0.48 |
| 1 | 5 | 4 | 0.49 |
| 1 | 5 | 5.5 | 0.59 |
| 1 | 5 | 10 | 0.57 |

(d, 3 H), 2.95 (d, 2 H), 3.78 (s, 6 H), and 4.84 ppm (m, 2 H). *Anal.* Calcd for $C_9H_{13}O_4Cl$: C, 48.97; H, 5.89. Found: C, 49.06; H, 6.20.] and **21**-a [ir 1735 cm$^{-1}$; nmr 1.31 (s, 3 H), 1.54 (m, 2 H), 3.71 (m, 2 H), and 3.74 ppm (s, 6 H). *Anal.* Calcd for $C_9H_{13}O_4Cl$: C, 48.97; H, 5.89. Found: C, 49.26; H, 6.02.]. From the reaction of diazomalonate and allyl bromide, α-allyl-α-bromomalonate (**23**-i) [ir 950, 1645, and 1752 cm$^{-1}$; nmr 2.96 (d, 2 H), 3.78 (s, 6 H), and 5.32 ppm (m, 3 H). *Anal.* Calcd for $C_8H_{11}O_4Br$: C, 38.24; H, 4.38. Found: C, 38.52; H, 4.59.] and 1,1-dicarbomethoxy-2-bromomethylcyclopropane (**23**-a) [ir 1725 cm$^{-1}$; nmr 1.43 (d, 1 H), 1.60 (s, 1 H), 2.38 (m, 1 H), 3.38 (m, 2 H), 3.73 (s, 3 H), and 3.77 ppm (s, 3 H). *Anal.* Calcd for $C_8H_{11}O_4Br$: C, 38.24; H, 4.38. Found: C, 38.12; H, 4.27.] were obtained.

**Relative Rate of Reaction of Dimethyl Diazomalonate in Allyl Compounds.** A solution of 0.25 g (1.6 mmol) of diazomalonate in a mixture of 1.22 g (16 mmol) of allyl chloride and an equivalent amount of competing allyl compound was irradiated with the high-pressure mercury lamp. Irradiation was stopped at 10–20% decomposition of diazomalonate. The reaction mixture was then analyzed by gas chromatography. A stainless steel column with 4 ft × 0.25 in. 10% Carbowax 20M on Celite 22 was used. The products were stable under the short irradiation and the vpc conditions. Relative reactivities reported in Table IV were calculated from the molar ratios of the products.

**Photosensitized Decomposition of Dimethyl Diazomalonate in Allyl Sulfides.** A solution of 1.8 g of benzophenone and 0.25 g of dimethyl diazomalonate in 3 ml of γ-methylallyl ethyl sulfide (**26**) was irradiated in a Pyrex vessel at room temperature for 40–60 hr. The gas evolution had ceased and ir showed no diazo band at 2140 cm$^{-1}$. After irradiation, the solution was injected directly into the gas chromatograph. The insertion product (**26**-i) [ir 915 and 1715 cm$^{-1}$; nmr 1.15 (d, 3 H), 1.21 (t, 3 H), 2.63 (q, 2 H), 2.84 (m, 1 H), 3.70 (s, 6 H), 5.00 (center of multiplet, 2 H), and 5.84 ppm (m, 1 H). *Anal.* Calcd for $C_{11}H_{18}O_4S$: C, 53.65; H, 7.37. Found: C, 53.60; H, 7.39.] of the carbene into allyl carbon–sulfur bond was isolated together with the addition product (**26**-a) [ir 1715 cm$^{-1}$; nmr 1.21 (t + d, 6 H), 1.80 (m, 2 H), 2.50 (m, 4 H), and 3.71 ppm (s, 6 H). *Anal.* Calcd for $C_{11}H_{18}O_4S$: C, 53.65; H, 7.37. Found: C, 53.57; H, 7.37.]. The yields were estimated by gas chromatography using biphenyl as an internal standard.

The reaction of dimethyl diazomalonate in allyl ethyl sulfide (**24**) containing benzophenone gave **24**-i and **24**-a. Table X shows the product ratios from the reactions in the presence of various concentrations of benzophenone.

From the reaction of dimethyl diazomalonate in **25** containing benzophenone, **25**-i [ir 900 and 1725 cm$^{-1}$; nmr 1.20 (t, 3 H), 1.73 (s, 3 H), 2.69 (q, 2 H), 2.70 (s, 2 H), 3.72 (s, 6 H), and 4.79 ppm (m, 2 H). *Anal.* Calcd for $C_{11}H_{18}O_4S$: C, 53.65; H, 7.37. Found: C, 53.92; H, 7.26] and **25**-a [ir 1730 cm$^{-1}$; nmr 1.28 (s + t, 6 H), 1.47 (d, 2 H), 2.50 (q, 2 H), 2.77 (d, 2 H), and 3.72 ppm (s, 6 H). *Anal.* Calcd for $C_{11}H_{18}O_4S$: C, 53.65; H, 7.37. Found C, 53.75; H, 7.45.] were obtained as major products.

The reaction of diazomalonate in **27** gave **27**-i [ir 915 and 1710 cm$^{-1}$; nmr 1.19 (t, 3 H), 1.28 (s, 6 H), 2.58 (q, 2 H), 3.70 (s, 6 H), 4.95 (m, 2 H), and 6.28 ppm (m, 1 H). *Anal.* Calcd for $C_{12}H_{20}O_4S$: C, 55.37; H, 7.75. Found: C, 55.61; H, 7.91.] and **27**-a [ir 1715 cm$^{-1}$; nmr 1.20 (s, 3 H), 1.27 (s + t, 6 H), 1.82 (d, 1 H), 2.56 (m, 4 H), 3.67 (s, 3 H), and 3.68 ppm (s, 3 H). *Anal.* Calcd for $C_{12}H_{20}O_4S$: C, 55.37; H, 7.75. Found: C, 55.14; H, 8.08.].

**Photosensitized Decomposition of Dimethyl Diazomalonate in Allyl Ethers.** Experimental procedures were the same as those for the corresponding reaction in sulfides. The vapor-phase chromatogram of the reaction mixture in an γ,γ-dimethylallyl ethyl ether (**15**) solution of diazomalonate and benzophenone showed one large peak after one small peak. The major product was identified as **15**-a on the basis of nmr and ir spectra. The other minor product was present in too small quantities to be isolated. The retention time corresponded to that of **15**-i obtained from direct photolysis. The yield of addition product was higher than that in direct photolysis. A similar type of reaction was applied to a β-methylallyl ethyl ether (**28**), and spectral properties of resulting products are shown in Table XI.

**Table XI.** Spectral Data of the Products Obtained from Allyl Ethers and Dimethyl Diazomalonate

| Product | Ir (principal band), cm$^{-1}$ | Nmr (ppm downfield from TMS) |
|---|---|---|
| **15**-i | 915, 1640, 1750 | 1.16 (s, 6 H), 1.20 (t, 3 H), 3.51 (q, 2 H), 3.68 (s, 6 H), 4.90 (d, 2 H), 6.10 (m, 1 H) |
| **15**-a | 1732 | 1.16 (t, 3 H), 1.22 (s, 3 H), 1.27 (s, 3 H), 1.88 (d, 1 H), 3.48 (m, 4 H), 3.63 (s, 3 H), 3.67 (s, 3 H) |
| **28**-i | 900, 980, 1650, 1750 | 1.19 (t, 3 H), 1.74 (s, 3 H), 2.65 (s, 2 H), 3.54 (q, 2 H), 3.69 (s, 6 H), 4.70 (m, 2 H) |
| **28**-a | 1730 | 1.14 (t, 3 H), 1.24 (s, 3 H), 1.42 (d, 2 H), 3.42 (m, 4 H), 3.64 (s, 3 H), 3.70 (s, 3 H) |

**Photosensitized Decomposition of Diazomalonate in Allyl Chlorides.** Irradiation of allyl chloride solutions of dimethyl diazomalonate and benzophenone in Pyrex tubes with the high-pressure mercury lamp resulted in the formation of addition products as major products and of some insertion products. These products were identified on the basis of their retention time and infrared spectrum.

**Cupric Sulfate Catalyzed Thermal Decomposition of Dimethyl Diazomalonate in Allyl *n*-Butyl Sulfide (1).** A solution of 0.325 g (2.1 mmol) of diazomalonate in 1 ml of allyl *n*-butyl sulfide was heated in 50-ml test tubes at 90–100° in the presence of 20 mg of anhydrous cupric sulfate. After 15 hr, the gas evolution had ceased. The gas chromatographic analysis showed the formation of **1**-i in 93% yield, and **1**-a was not detected.

**Thermal Decomposition of Dimethyl Diazomalonate in Allyl *tert*-Butyl Sulfide (2).** A solution of 0.221 g (1.4 mmol) of diazomalonate in 1 ml of allyl *tert*-butyl sulfide (**2**) was heated at 90–100° for 5 hr in the presence of 20 mg of cupric sulfate. The infrared spectrum of the reaction mixture did not show a diazo band at 2140 cm$^{-1}$. The yield of **2**-i was 10–15%, and **2**-a was not detected.

**Thermal Decomposition of Dimethyl Diazomalonate in β-Methylallyl *n*-Butyl Sulfide (3).** Using the same procedure as for the thermal decompositions above, a solution of 0.225 g (1.4 mmol) of diazomalonate in 1 ml of β-methylallyl *n*-butyl sulfide (**3**) was heated at 90–100° for 4 hr. Complete decomposition of diazomalonate was observed from the infrared spectrum. The product **3**-i was found in 100% yield as measured by the internal standard techniques. The addition product to olefin was not detected.

**Thermal Decomposition of Dimethyl Diazomalonate in γ-Methylallyl Phenyl Sulfide (5).** Using the same procedure as for the thermal reaction above, a solution of 0.212 g (1.4 mmol) of diazomalonate in 1 ml of γ-methylallyl phenyl sulfide (**5**) was heated in a test tube at 90–100° for 5 hr. The infrared spectrum of the crude reaction mixture did not show a diazo band. The analysis by gas chromatography showed only one peak which on collection proved to be **5**-i in the yield shown in Table VIII.

**Decomposition of Diazomalonate in Allyl Ethers and Chlorides Catalyzed by Cupric Salts.** The cupric sulfate catalyzed thermal decomposition described below is typical. A solution of 0.28 g of diazomalonate in 2 ml of allyl methyl ether was heated at 105° for 12 hr in the presence of 0.05 g of anhydrous cupric sulfate. After the reaction was completed, the reaction mixture was analyzed directly by gas chromatography. Products obtained were identical with those of photolysis. Analogous experiments were carried out in allyl chloride solutions containing diazomalonate and a catalytic amount of cupric chloride. Addition products as minor product and the insertion product as major product were obtained.

**Acknowledgment.** The authors wish to thank Professor Maitland Jones, Jr., Princeton University, for helpful discussions.