over magnesium sulfate and decolorized with activated charcoal. Solvent removal gave the crude product.

2,4-Diphenyl-1-*p*-toluenesulfonylbut-1-en-3-yne (17c).—From **3a** (7.68 g, 0.02 mol) and cuprous phenylacetylide (3.29 g, 0.02 mol) there was obtained 1.05 g (15%) of **17c**, mp 117–118°.

Anal. Calcd for $C_{23}H_{18}O_2S$: C, 77.07; H, 5.06; S, 8.94. Found: C, 77.33; H, 5.00; S, 8.96.

2,4-Diphenyl-1-ethanesulfonylbut-1-en-3-yne (17b).—**5a** (6.44 g, 0.02 mol) and the acetylide (3.29 g, 0.02 mol) afforded 3.47 g (59%) of **17b**, mp 76–77°.

Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.99; H, 5.44; S, 10.82. Found: C, 73.08; H, 5.60; S, 10.58.

4-Phenyl-2-cyclohexyl-1-*p*-toluenesulfonylbut-1-en-3-yne (17a).—When **3c** (7.81 g, 0.02 mol) and the acetylide (3.29 g, 0.02 mol) were combined as before, a viscous yellow oil was obtained (5.84 g, 80%) which could not be induced to solidify. The ir and nmr spectra of this oil were identical with those obtained on the pure product (see the following). A portion of this oil was then chromatographed on a silica gel column using chloroform–hexane (1:1) as the eluent. Again, the same viscous, yellow oil was encountered and, after vacuum drying, it was analyzed as such.

Anal. Calcd for $C_{23}H_{24}O_2S$: C, 75.78; H, 6.64; S, 8.80. Found: C, 75.79; H, 6.83; S, 8.92.

Registry No.—**3a**, 22183-12-6; **3b**, 22214-91-1; **3c**, 22297-38-7; **3d**, 29038-88-8; **3e**, 28995-73-5; **3f**, 28995-74-6; **3g**, 28995-75-7; **3h**, 28995-76-8; **3i**, 28995-77-9; **3j**, 28995-78-0; *trans*-**3k**, 28995-79-1; *cis*-**3k**, 22214-90-0; **3l**, 22214-94-4; **3m**, 22214-93-3; **3n**, 22214-92-2; **4a**, 28995-82-6; **4b**, 28995-83-7; **5a**, 28995-84-8; **5b**, 28995-85-9; **6**, 28995-86-0; **7**, 28995-87-1; **8**, 28995-88-2; **9**, 28995-90-6; **10**, 28995-91-7; **11**, 28995-92-8; **12**, 24378-05-0; **15**, 28995-94-0; **17b**, 28995-95-1; **17c**, 28995-96-2; *cis*-1-cyclohexyl-2-*p*-toluenesulfonylethene, 28995-97-3.

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Reaction of Carbethoxycarbene with Aliphatic Sulfides and Allyl Compounds

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Reactions of carbethoxycarbene produced by photolysis of ethyl diazoacetate with dialkyl and alkyl allyl sulfides were investigated. Reactions in dialkyl sulfides bearing β-hydrogen atoms resulted in the formation of ethyl alkylmercaptoacetates. On the other hand, the reactions in alkyl allyl sulfides gave mixtures of 1-alkyl 1-alkylmercaptoacetates (C—S insertion) and cyclopropane derivatives (C=C addition). These product formations are explained by the mechanism involving ylide formation from the carbene and sulfides. Copper-catalyzed thermal decomposition of ethyl diazoacetate in these sulfides resulted in more selective reactions and gave high yields of the acetates, the formation of cyclopropane derivatives being drastically reduced. Allyl ethers and chlorides react less selectively with carbethoxycarbene to produce mixtures of insertion and addition products.

Although the reactions of carbenes with molecules containing heteroatoms have been extensively studied, little has been recorded of the photochemical and thermal reactions with aliphatic sulfides and allyl compounds containing sulfur, oxygen, and halides.[1] Some of the reactions of the allyl compounds have been reported with dichlorocarbene derived from the acid–base-catalyzed reaction of the halo ester[2] and with methylene produced by the decomposition of diazomethane with metal salts.[3] Kirmse has reported that the copper salt catalyzed thermal decomposition of diazomethane in allyl sulfides yields methylene insertion products into the carbon–sulfur bond as major products, together with some cyclopropane derivatives. In the allyl ethers and amines, however, the cyclopropane derivatives have been obtained as the major products. Furthermore, the addition products have been formed from allyl chlorides without substantial formation of insertion products. This is contrasted with the reaction in allyl bromide in which the insertion product has been obtained in about 80% yield. The formation of insertion products may be ascribed to ylide formation by the attack of the carbene on the lone-pair electrons of a heteroatom, followed by allylic rearrangement which is a thermally symmetry-allowed process. Similar results in the copper-catalyzed thermal decomposition of ethyl diazoacetate in allyl halides have been obtained. Thus, the addition of the carbene to the double bond in allyl chlorides competes effectively with insertion into the carbon–chlorine bond, whereas no cyclopropanes have been obtained from allyl bromides and iodides.[4,5] However, these reaction species have been known as carbenoids and should be significantly different in nature from the free carbenes formed by photolysis of the diazo compounds.[6–8]

Recently we reported that the photochemical reaction of dimethyl diazomalonate in aliphatic sulfides forms stable sulfonium ylides[9] and in allyl compounds forms the carbene insertion products into the carbon–sulfur, oxygen, and halogen bond.[10,11] We have sug-

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[1] (a) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (c) J. I. G. Cadogan and M. J. Perkins, "The Chemistry of Alkenes," Wiley-Interscience, New York, N. Y., 1964; (d) G. L. Closs in "Topics in Stereochemistry," Vol. 3, Wiley-Interscience, New York, N. Y., 1968.

[2] 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).

[3] W. Kirmse and M. Kapps, *Chem. Ber.*, **101**, 994, 1004 (1968); W. Kirmse and H. Arold, *ibid.*, **101**, 1008 (1968).

[4] I. A. Dykonov and N. B. Vinogradova, *Zh. Obshch. Khim.*, **22**, 1349 (1952); **23**, 66 (1953). I. A. Dyakonov and T. V. Domeareva, *ibid.*, **25**, 934, 1486 (1955).

[5] D. D. Philips, *J. Amer. Chem. Soc.*, **76**, 5385 (1956).

[6] G. L. Closs and R. A. Moss, *ibid.*, **86**, 4074 (1964).

[7] D. O. Cowab, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

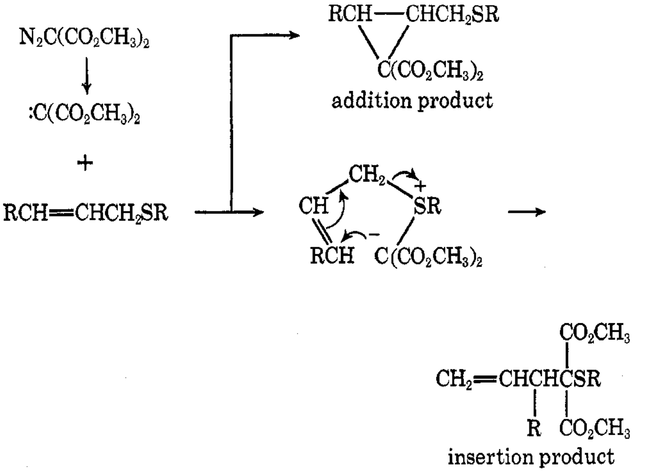
[8] S. H. Goh, L. E. Closs, and G. L. Closs, *ibid.*, **34**, 25 (1969).

[9] (a) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); (b) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, 1979 (1969).

[10] W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 5164 (1969).

[11] W. Ando, S. Kondo, and T. Migita, *ibid.*, **91**, 6516 (1969).

gested that the insertion products were formed as proceeding *via* [1,5] sigmatropic allylic rearrangement of intermediate ylides.



The study was extended to the photochemical reaction of diazoacetate, where the carbene formed by the photolysis is considered to be less electrophilic, and ylides formed by the reaction of the carbene with heteroatom-containing molecules are expected to be less resonance stabilized compared with the case of the reaction of diazomalonate.

Results

Irradiation of a solution of ethyl diazoacetate in a relevant substrate was carried out in a Pyrex tube with a high-pressure mercury lamp. The reaction mixture was analyzed by vpc, and the structures of the isolated products were determined on the basis of nmr and ir spectra and elemental analysis.

Reactions with Aliphatic Sulfides.—Photochemical decomposition of ethyl diazoacetate in di-*tert*-butyl sulfide produced 23% ethyl *tert*-butylmercaptoacetate. Similarly, the reaction in diethyl sulfide gave ethyl ethylmercaptoacetate, although the yield was reduced. Each product was identified by comparison of its spectra with that of the authentic sample. On the other hand, the reaction in dimethyl sulfide gave only tarry materials and no product detectable by gas chromatographic analysis.

$$N_2CHCO_2C_2H_5 + tert\text{-}BuS\text{-}tert\text{-}Bu \longrightarrow \underset{23\%}{tert\text{-}BuSCH_2CO_2C_2H_5}$$

$$N_2CHCO_2B_2H_5 + EtSEt \longrightarrow \underset{7\%}{EtSCH_2CO_2C_2H_5}$$

$$N_2CHCO_2C_2H_5 + CH_3SCH_3 \longrightarrow \text{tarry materials}$$

Reactions with Allyl Sulfides.—Thermal and photochemical decomposition of ethyl diazoacetate in allyl sulfides produced insertion and addition products. The dependence of the yield on the reaction variables is summarized in Table I. The starting allyl sulfides and the products were stable under the conditions employed in the reactions and the analytical procedures.

In the reaction of I with carbethoxycarbene, no significant difference in the product distribution was observed between the thermal and photochemical decomposition, although thermolysis gave only 30% decomposition of ethyl diazoacetate under the conditions.

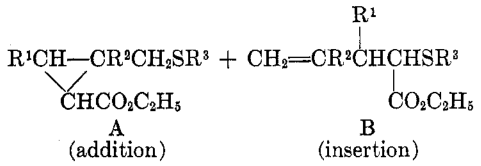
TABLE I
DEPENDENCE OF PRODUCT DISTRIBUTION ON REACTION VARIABLES

Sulfide	Diazoacetate, mmol	Mode of decompn	A (addition) (cis + trans), %	B (insertion), %
I	1.8	*hν*	6	23
I	1.9	*hν*	7	19
I	1.8	CuCl, 90° (2 min)		95
I	1.8	Cu, 90° (2 hr)		85
I	2.0	80°, 24 hr[a]	5	25
II	4.4	*hν*	10	15
III	4.4	*hν*	13	16
IV	4.4	*hν*	15	23

[a] 30% of diazoacetate was decomposed under these conditions.

On the other hand, the copper-catalyzed thermal decomposition was remarkable both in high reaction rate and in increased yields of insertion products. The structure of the insertion product obtained from I was established to be IB by the analysis of nmr and ir spectra. Absence of the nonrearranged insertion product in the reaction mixture was proved by gas chromatography. The elimination product, ethyl γ-methylallylmercaptoacetate, was also found not to be produced.

$$:CHCO_2C_2H_5 + R^1CH{=}CR^2CH_2SR^3 \longrightarrow$$



$$R^1CH—CR^2CH_2SR^3 + CH_2{=}CR^2\overset{R^1}{C}H\underset{CO_2C_2H_5}{C}HSR^3$$

I, $R^1 = CH_3$; $R^2 = H$; $R^3 = C_2H_5$
II, $R^1 = R^2 = H$; $R^3 = n\text{-}Bu$
III, $R^1 = R^2 = H$; $R^3 = tert\text{-}Bu$
IV, $R^1 = H$; $R^2 = CH_3$; $R^3 = n\text{-}Bu$

Reactions with Allyl Ethers.—Reaction products of carbethoxycarbene with allyl methyl ethers are tabulated in Table II. Analogous to the reactions with allyl sulfides, the insertion and addition products were mainly produced. However, the product distribution shows that the carbene attacked less favorably on oxygen atoms, compared with the reaction with allyl sulfides. It is noteworthy that, even in the copper salt catalyzed reaction, considerable amounts of addition products were formed.

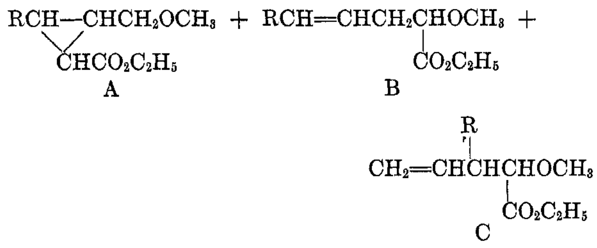
TABLE II
REACTIONS OF CARBETHOXYCARBENE WITH ALLYL METHYL ETHERS

Ether	Diazo-acetate, mmol	Mode of decompn	A[a] (addition), %	B (insertion), %	C (insertion), %
V	1.5	*hν*	19.5	19.5	
V	1.5	$CuSO_4$[b]	25.0	45.8	
VI	0.95	*hν*	15.2	4.5	21.8
VI	0.95	$CuSO_4$	10.4	2.7	32.0

[a] The mixture of cis and trans cyclopropanes. [b] Copper sulfate catalyzed thermal reaction was carried out at 105° for 5.5 hr.

Furthermore, a small percentage of the direct insertion product, namely VIB, was detected in the reaction mixture of VI. Although the possibility that this direct insertion product originates from α-methylallyl methyl ether, which exists in a small amount in the starting ether, might not be eliminated, at least a part of VIB should be considered to form from VI, since the yield of this acetate was much more than that expected from α-methylallyl methyl ether contaminating the starting material (less than 0.5%).

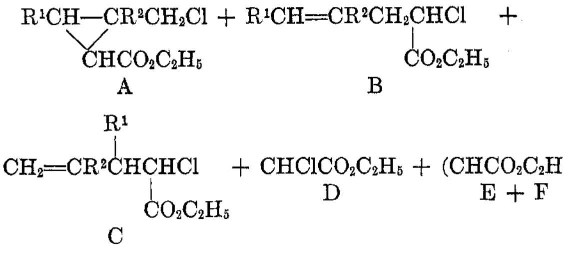
$:CHCO_2C_2H_5 + RCH{=}CHCH_2OCH_3 \longrightarrow$



V, R = H; VI, R = CH_3

Reactions with Allyl Chlorides.—Carbethoxycarbene produced by photolysis of ethyl diazoacetate reacted with allyl chloride to give 21% allyl chloroacetate and 18% cyclopropane derivatives. With IX, the formation of ethyl γ-methylallylchloroacetate (IXB), besides cyclopropane derivatives IXA and ethyl α-methylallylchloroacetate IXC, was observed contrasting to bis(carbomethoxy)carbene which did not give methyl α-methylallylchloromalonate. Since the starting IX, which contains less than 0.5% α-methyl allyl chloride, and the products were stable to the reaction conditions and to the analytical procedures, the direct insertion product (A) should be considered to actually form through the reaction of carbethoxycarbene with IX (Table III).

$:CHCO_2C_2H_5 + R^1CH{=}CR^2CH_2Cl \longrightarrow$



VII, $R^1 = R^2 = H$; VIII, $R^1 = H$, $R^2 = CH_3$; IX, $R^1 = CH_3$, $R^2 = H$

Discussion

In contrast to bis(carbomethoxy)carbene which reacts with a number of alkyl sulfides to give stable ylides,[9] carbethoxycarbene did not, but afforded the products which are considered to be produced by further reaction of the corresponding ylides. This may be partly due to less thermal stabilities of ylides formed by the reaction of carbethoxycarbene with sulfides, compared with those derived from bis(carbomethoxy)carbene.

Dimethylsulfonium carbethoxymethylide has been known as an isolable compound at low temperature.[12] Nevertheless, the isolation of the ylide was unsuccessful even when photochemical reaction of ethyl diazoacetate in dimethyl sulfide was carried out at low temperature. Perhaps a nascent ylide molecule, derived from sulfide and the carbene produced photochemically, has enough excess energy to allow a less stable ylide molecule to react.

Table III

Reaction of Ethyl Diazoacetate with Allyl Chlorides

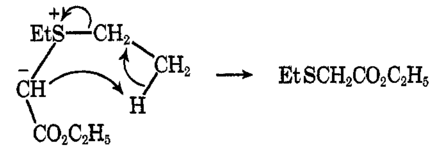
Chloride	Diazoacetate, mmol	Mode of decompn	Products, % A[a]	B	C	D	E[b]	F[c]
VII	1.8	hν	18	21		t[d]	t	t
VIII	1.8	hν	57	30		t	t	t
IX	1.8	hν	8	9	7	2	t	t
IX	1.9	CuCl, 80° (60 min)	2	1	8	4	40	22
IX	1.8	CuCl, 80° (9 min)	3	1	11	5	37	22
IX	1.9	Cu, 80° (60 min)	3	2	4	3	37	22

[a] The mixture of cis and trans cyclopropanes. [b] Ethyl fumarate. [c] Ethyl maleate. [d] t = trace amount.

The reactions with alkyl sulfides bearing β-hydrogen atoms gave β-elimination products (alkyl mercaptoacetate). These are considered to form by thermally induced intramolecular elimination. Although olefins were not detected, their formations may be almost certain, since similar eliminations involving cleavage of C–O or C–N bonds have been well known in the reactions of carbenes with ethyl ether, *n*-butyl ether, and trimethylamine.[1]

Furthermore, the intermediary formation of an ylide is supported by the fact that similar elimination actually occurs on the thermolysis of alkylsulfonium bis(carbomethoxy)methylide.[13]

$:CHCO_2C_2H_5 + EtSEt \longrightarrow$



The formation of rearranged insertion products in the reactions of the carbene with allylic compounds is also explained in terms of the ylide mechanism, as has been suggested for the similar reactions of dimethyl diazomalonate. The relative rate of insertion to addition can be seen to depend on nucleophilic characters of heteroatoms (S > O > Cl) of allylic compounds. This trend may be consistent with the idea that ylides are produced by electrophilic attack of the carbene on heteroatoms in the substrates. Copper-catalyzed reactions favored more selectively the insertion compared with photochemical reactions. This may be due to the fact that the attacking species in copper-catalyzed reactions are Cu-complexed carbenoid which are more selective and electrophilic than the free carbenes.

This insertion accompanying allylic rearrangement may be essentially a [1,5] sigmatropic rearrangement of an ylide which is expected to occur quite smoothly, since the process is orbital symmetry allowed in thermal reaction. Indeed, a number of examples of such rearrangements of unstable ylides have been reported.[14,15]

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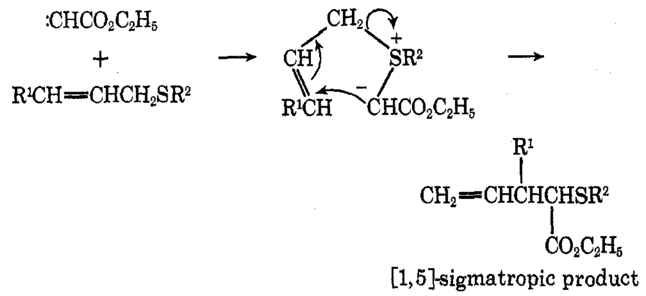
[12] A. J. Speziale, C. C. Tung, K. W. Ratts, and A. Yao, *J. Amer. Chem. Soc.*, **87**, 3460 (1965).

[13] W. Ando, T. Yagihara, and T. Migita, *Tetrahedron Lett.*, 1975 (1969).

[14] J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, 3646 (1969), and references cited therein.

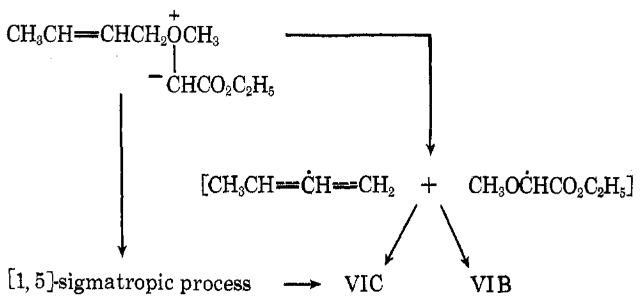
[15] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965), and references cited therein.

The reaction of carbethoxycarbene with I gave this [1,5] sigmatropic product but not the β-elimination product. This is in accord with the fact that bis(carbomethoxy)carbene did not give any isolable ylides in the reaction with allylic sulfides,[10] contrasting with the reaction with saturated aliphatic sulfides, and indicates that [1,5] sigmatropic rearrangement of the ylide occurs much more smoothly than intramolecular elimination.

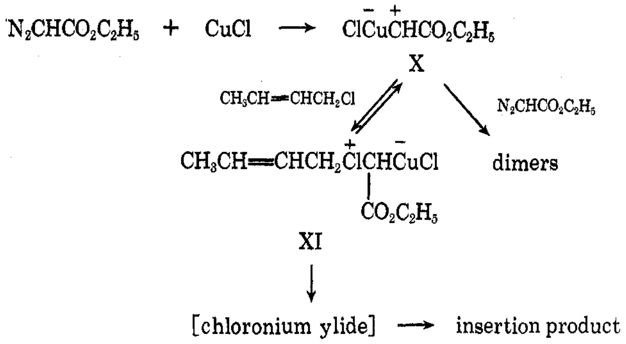


A notable feature of the reactions of carbethoxycarbene with allylic ether or chloride is the formation of nonrearranged insertion products, which were observed neither in the reactions with allylic sulfides nor in the reactions of bis(carbomethoxy)carbene with allylic sulfides and ethers.

One of the tentative mechanisms for the formation of these nonrearranged products seems to be a dissociation–recombination process, since the concerted mechanism of such a [1,3] sigmatropic rearrangement of ylide is orbital symmetry forbidden in thermal reactions. Although we have no experimental evidence which is useful in distinguishing whether the dissociation is heterolytic or homolytic, the homolytic process seems to be more likely, since several chemically induced dynamic nuclear polarization (CIDNP) observations have been reported on the formation of [1,3] sigmatropic products in the thermal rearrangement of a sulfonium ylide formed from a sulfonium salt and base.[16] As mentioned above, an ylide molecule is considered to have excess energy at a moment of the formation from a carbene and heteroatomic molecule. If this excess energy is enough for the dissociation of ylide, and if the dissociation is fast enough to compete with collisional deactivation of the ylide molecule, the [1,3] sigmatropic rearrangement will become a possible pathway involving a radical-pair intermediate. On the other hand, if the activation energy of the dissociation exceeds the excess energy, the [1,3] sigmatropic process would not occur. Sulfonium ylides are resonance stabilized by pπ–dπ conjugation, and the negative charge of bis(carbomethoxy)methylide is stabilized by the resonance effect of two carbomethoxy groups. Dissociation of these relatively highly stabilized ylides will require high activation energy. On the other hand, the relatively unstable oxonium and chloronium carbethoxymethylides will dissociate with less activation energy, converting to [1,3] sigmatropic products by recombination of a radical pair.



The copper-catalyzed thermal reaction of ethyl diazoacetate with allyl chloride gave the carbene dimers as major products in contrast to no formation of carbene dimers in the reaction with allyl sulfides and ethers. A possible pathway is proposed involving the decomposition of the Cu-complexed chloronium compound XI to the carbenoid X rather than the formation of the chloronium ylide, followed by the reaction of X with ethyl diazoacetate leading to the dimers.



Experimental Section

General.—Infrared spectra were determined on a Japan spectroscopic Co., Ltd., DS-21 instrument in carbon tetrachloride solution or neat. The nmr spectra were recorded on Varian A-60D spectrometer using carbon tetrachloride solutions containing tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per million (ppm) downfield from TMS, designating the multiplicity of the signals: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Samples of ethyl diazoacetate were added to clean 10 × 100 mm Pyrex tubes. The tubes were then corked (nondegassed) and placed in a water-cooled bath for irradiation. The light source was a 400-W Rikosha high-pressure mercury lamp having the maximum output at 3650–3660 Å with the minor output at 3125 Å. Photolyses were carried out until the disappearance of diazo band in the infrared spectra. The solutions were analyzed on an Ohkura gas–liquid partition chromatograph with a calibrated 5 ft × 0.25 in. stainless steel column of 10% DC-710 or Carbowax 20M on C-22 firebrick. Hydrogen was used as a carrier gas. Absolute yields were estimated from the relative area of peaks of products to known amounts of appropriate internal standards.

Materials.—Research grade reagents of dimethyl sulfide and di-*tert*-butyl sulfide (Tokyo Kasei), allyl chloride, β-methylallyl chloride, and γ-methylallyl chloride (Wako Fine Chemicals) were used without further purification. Diethyl sulfide was prepared by the addition of ethyl bromide to an ethyl alcohol solution of sodium metal and ethyl mercaptan. The fraction boiling at 92–93° was collected for use. All of the allyl sulfides and ethers were prepared by standard procedures.[17,18] Ethyl diazoacetate[19] was prepared by treating ethyl glycinate hydrochloride with sodium nitrile, bp 36–36.5° (9 mm).

General Procedure of Photochemical Reactions of Ethyl Diazoacetate.—Photolysis of 0.32 g (2.8 mmol) of ethyl diazo-

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[16] (a) U. Schöllkopf, G. Ostermann, and J. Schossing, *Tetrahedron Lett.*, 2619 (1969); (b) A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 1237 (1969); **91**, 1237 (1969); (c) R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1226 (1969); (d) D. G. Morris, *ibid.*, 1345 (1969).

[17] A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Amer. Chem. Soc.*, **84**, 3897 (1962).

[18] W. H. Watanabe, L. E. Conlon, and J. C. H. Hwa, *J. Org. Chem.*, **23**, 1666 (1958).

[19] N. E. Searle "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 424.

acetate in 3 ml of a substrate was carried out with a high-pressure mercury lamp. After the diazo band disappeared from the reaction mixture, a known amount of an internal standard (phenyltriethylsilane) was added to the reaction mixture, which was then analyzed by gas chromatography. The structure of the isolated product was determined on the basis of nmr and ir spectra data and elemental analysis. The cyclopropane derivatives obtained from the reaction with the allyl system consist of two geometrical isomers. Their configurations were not assigned. Analytical data are summarized (A-1 and A-2 are stereoisomers of cyclopropane products).

IA-1: nmr 1.25 (m, 12 H), 2.48 (m, 4 H), 4.10 (q, 2 H); ir 1725 cm^{-1}. *Anal.* Calcd for $C_{10}H_{18}O_2S$: C, 59.38; H, 8.97. Found: C, 58.67; H, 8.81.

IA-2: nmr 1.25 (m, 11 H), 1.68 (m, 1 H), 2.50 (q, 2 H), 2.70 (m, 2 H), 4.10 (q, 2 H); ir 1725 cm^{-1}. *Anal.* Calcd for $C_{10}H_{18}O_2S$: C, 59.38; H, 8.97. Found: C, 59.91, H, 8.92.

IB: nmr 1.18 (m, 9 H), 2.55 (q, 2 H), 2.66 (m, 1 H), 2.96 (d, 1 H), 4.13 (q, 2 H), 5.01 (broad m, 2 H), 5.66 (m, 1 H); ir 930, 980, 1635, 1750 cm^{-1}. *Anal.* Calcd for $C_{10}H_{18}O_2S$: C, 59.38; H, 8.97. Found: C, 59.55; H, 9.17.

IIA: nmr 1.25 (m, 14 H), 2.42 (m, 2 H), 4.03 (q, 2 H); ir 1725, 1746 cm^{-1}. *Anal.* Calcd for $C_{22}H_{20}O_2S$: C, 61.09; H, 9.32. Found: C, 61.55; H, 9.35.

IIB: nmr 0.92 (t, 3 H), 1.26 (t, 3 H), 1.44 (m, 4 H), 2.51 (t, 2 H), 3.10 (m, 3 H), 4.13 (q, 2 H), 5.03 (broad d, 2 H), 5.80 (m, 1 H); ir 920, 1645, 1735 cm^{-1}. *Anal.* Calcd for $C_{11}H_{20}O_2S$: C, 61.09; H, 9.32. Found: C, 61.39; H, 9.56.

IIIA-1: nmr 1.25 (m, 7 H), 1.29 (s, 9 H), 2.50 (center of two d, 2 H), 4.05 (q, 2 H); ir 1725 cm^{-1}. *Anal.* Calcd for $C_{11}H_{20}O_2S$: C, 61.09; H, 9.32. Found: C, 60.86; H, 8.95.

IIIA-2: nmr 1.28 (m, 7 H), 1.29 (s, 9 H), 2.70 (center of two d, 2 H), 4.10 (q, 2 H); ir 1725 cm^{-1}. *Anal.* Calcd for $C_{11}H_{20}O_2S$: C, 61.09; H, 9.32. Found: C, 60.96; H, 8.95.

IIIB: nmr 1.25 (t, 3 H), 1.34 (s, 9 H), 2.40 (m, 2 H), 3.18 (center of two d, 1 H), 4.12 (q, 2 H), 5.02 (broad d, 2 H), 5.72 (m, 1 H); ir 925, 1645, 1730 cm^{-1}. *Anal.* Calcd for $C_{11}H_{20}O_2S$: C, 61.09; H, 9.32. Found: C, 61.07; H, 9.14.

IVA: nmr 0.97 (m, 3 H), 1.23 (s, 3 H), 1.26 (t, 3 H), 1.58 (m, 7 H), 2.45 (m, 2 H), 2.70 (s, 2 H), 4.10 (q, 2 H); ir, 1716 cm^{-1}. *Anal.* Calcd for $C_{12}H_{22}O_2S$: C, 62.58; H, 9.63. Found: C, 62.63; H, 9.51.

IVB: nmr 0.95 (t, 3 H), 1.25 (t, 3 H), 1.50 (m, 4 H), 1.73 (s, 3 H), 2.50 (m, 4 H), 3.28 (center of two d, 1 H), 4.11 (q, 2 H), 4.72 (m, 2 H); ir 895, 1655, 1725, 1745 cm^{-1}. *Anal.* Calcd for $C_{12}H_{22}O_2S$: C, 62.58; H, 9.63. Found: C, 62.84; H, 9.61.

VA: nmr 1.25 (t, 3 H), 1.53 (m, 4 H), 3.26 (s, 3 H), 3.28 (m, 2 H), 4.08 (q, 2 H); ir 1730 cm^{-1}. *Anal.* Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.77; H, 9.06.

VB: nmr 1.30 (t, 3 H), 2.41 (m, 2 H), 3.33 (s, 3 H), 3.66 (t, 1 H), 4.15 (q, 2 H), 4.98 (broad d, 2 H), 5.55 (m, 1 H); ir 916, 1643, 1740, 1755 cm^{-1}. *Anal.* Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.98; H, 8.86.

VIA-1: nmr 1.27 (m + t, 9 H), 3.20 (s, 3 H), 3.45 (m, 2 H), 4.06 (q, 2 H); ir 1725 cm^{-1}. *Anal.* Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 63.09; H, 9.42.

VIA-2: nmr 1.27 (m + t, 9 H), 3.25 (m + s, 5 H), 4.08 (q, 2 H); ir 1725 cm^{-1}. *Anal.* Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.33; H, 9.09.

VIB: nmr 1.27 (t, 3 H), 1.73 (d, 3 H), 2.33 (center of two d, 2 H), 3.24 (d, 3 H), 3.53 (m, 1 H), 4.08 (q, 2 H), 5.45 (m, 2 H); ir 966, 1675, 1742 cm^{-1}. *Anal.* Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.89; H, 9.55.

VIC: nmr 1.03 (d, 3 H), 1.28 (t, 3 H), 2.50 (m, 1 H), 3.30 (s, 3 H), 3.48 (d, 1 H), 4.15 (q, 2 H), 4.91 (broad d, 2 H), 5.65 (m, 1 H); ir 915, 1640, 1735, 1754 cm^{-1}. *Anal.* Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 63.08; H, 9.52.

VIIA-1: nmr 1.13 (m, 2 H), 1.28 (t, 3 H), 1.80 (m, 2 H), 3.72 (center of two d, 2 H), 4.12 (q, 2 H). *Anal.* Calcd for $C_7H_{11}ClO_2$: C, 51.69; H, 6.76. Found: C, 51.37; H, 6.72.

VIIA-2: nmr 1.26 (t + m, 5 H), 1.58 (m, 2 H), 3.45 (s, 2 H), 4.10 (q, 2 H). *Anal.* Calcd for $C_7H_{11}ClO_2$: C, 51.69; H, 6.76. Found: C, 51.56; H, 6.98.

VIIB,C: nmr 1.30 (t, 3 H), 2.67 (m, 2 H), 4.21 (q + t, 3 H), 5.12 (broad d, 2 H), 5.68 (m, 1 H). *Anal.* Calcd for $C_7H_{11}ClO_2$: C, 51.69; H, 6.76. Found: C, 51.75; H, 7.12.

IXA-1: nmr 1.26 (t + d + m, 9 H), 3.72 (center of two d, 2 H), 4.10 (q, 2 H); ir 1730 cm^{-1}. *Anal.* Calcd for $C_8H_{13}ClO_2$: C, 54.36; H, 7.36. Found: C, 54.90; H, 7.40.

IXA-2: nmr 1.26 (t + d, 6 H), 1.54 (m, 3 H), 3.45 (d, 2 H), 4.10 (q, 2 H); ir 1730 cm^{-1}. *Anal.* Calcd for $C_8H_{13}ClO_2$: C, 54.36; H, 7.36. Found: C, 54.09; H, 7.55.

IXB: nmr 1.30 (t, 3 H), 1.68 (d, 3 H), 2.60 (m, 2 H), 4.10 (t, 1 H), 4.18 (q, 2 H), 5.54 (m, 2 H); ir 965, 1745 cm^{-1}. *Anal.* Calcd for $C_8H_{13}ClO_2$: C, 54.36; H, 7.36. Found: C, 53.78; H, 7.23.

IXC: nmr 1.18 (t, 3 H), 1.28 (t, 3 H), 2.75 (m, 1 H), 3.96 (d, 1 H), 4.16 (q, 2 H), 5.09 (broad d, 2 H), 5.70 (m, 1 H); ir 940, 975, 1745 cm^{-1}. *Anal.* Calcd for $C_8H_{13}ClO_2$: C, 54.36; H, 7.36. Found: C, 54.77; H, 7.76.

General Procedure of Copper Salt Catalyzed Thermal Reactions.—Thermal reactions were carried out for 0.17 g (1.5 mmol) of ethyl diazoacetate in 2 ml of a substrate in the presence of 20 mg of copper salt. Samples were sealed in Pyrex tubes under vacuum and heated at 100° for the appropriate time.

Registry No.—IA, 29123-96-4; IB, 29123-97-5; IIA, 29123-98-6; IIB, 29123-99-7; IIIA-1, 29119-66-2; IIIA-2, 29199-37-9; IIIB, 29124-00-3; IVA, 29124-01-4; IVB, 29124-02-5; VA, 29124-03-6; VB, 29124-04-7; VIA, 29124-05-8; VIB, 29119-67-3; VIC, 29119-68-4; VIIA, 29119-69-5; VIIB, 29119-70-8; IXA, 29119-71-9; IXB, 29119-72-0; IXC, 29119-38-0; carbethoxycarbene, 3315-61-5.