cm^{-1} (per cent absorbance): 700 (90), 755 (65), 810 (50), 1350 (50), 1450 (55), 1490 (60), 1520 (80), 1615 (65).

The nmr spectrum ($CDCl_3$) for the solid with mp 178° (**5**) showed a broadened singlet at δ 2.37 (8 H), a singlet at 2.90 (6 H), a doublet at 6.67 and 6.58 (2 H), and a multiplet at 7–7.4 (17 H). The doublet at δ 6.67 and 6.58 corresponds to the two aromatic hydrogens ortho to the dimethylamino group. The semisolid shows two broad bands at δ 0.90–1.05 (~2 H), and 1.25–1.40 (~2 H), which may be due to solvent impurities, as well as an extra methyl singlet at δ 2.83 and methylene absorbance at δ 2.25. Assuming that these latter are due to **6**, the ratio of **5** to **6** is about 3:1.

The mass spectral data are summarized in Table III. The observed ratio of parent peak (P_{419} = 100) to P + 1 = 34.3 and P + 2 = 5.6 is in good agreement with the ratios calculated from isotope abundances of 100:34.4:5.7.

Registry No.—**2**, 28278-49-1; **3**, 34347-83-6; **4**, 34347-84-7; **5**, 34347-85-8; **6**, 34347-86-9.

The Reactions of Dimethyl Diazomalonate with Divalent Sulfides

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Biscarbomethoxycarbene, generated photochemically from dimethyl diazomalonate, reacts with alkyl and aryl sulfides to form stable sulfonium biscarbomethoxymethylides. The reaction of the carbene with alkyl disulfides forms alkylthiomalonate as the major product instead of the sulfonium ylides. The triplet carbene, generated from benzophenone-photosensitized decomposition of the diazomalonate, also reacts with dimethyl sulfide to produce the sulfonium ylide. This ylide formation is considered to involve the fast intersystem crossing from the triplet to the singlet carbene in the presence of dimethyl sulfide. Copper salt catalyzed thermal decomposition of diazomalonate in alkyl or aryl sulfides produces sulfonium ylides in high yields.

Photochemically induced reactions of diazo compounds with various types of compounds containing heteroatoms have been studied extensively.[1-4] Most of these reactions have been proposed to proceed through ylide formation by reactions of carbenes derived from diazo compounds and this has been supported by the recent synthesis of sulfonium ylides by the reaction of highly electrophilic carbenes with alkyl sulfides.[5-7]

Previously, we reported in preliminary form that the photolysis and copper salt catalyzed thermal decomposition of dimethyl diazomalonate in neat dimethyl sulfide gave dimethylsulfonium biscarbomethoxymethylide, and we showed that the reaction may be useful for synthesis of such stable sulfonium ylides.[6,7]

This paper deals with the details of the reaction and some properties of the ylides thus prepared.

$$N_2CR_2 \xrightarrow{h\nu} :CR_2 \xrightarrow{R'SR'} R_2'\overset{+}{S}-\bar{C}R_2$$

Several studies on the chemical behavior of triplet carbenes have documented that the most marked difference in the chemical nature between singlet and triplet carbenes is found in the stereochemistry of addition to olefins.[8-15]

Jones and coworkers have shown that direct photolysis of diazomalonate generates singlet biscarbomethoxycarbene, which adds to olefins in a stereospecific manner, while photosensitized decomposition generates the corresponding triplet carbene, which reacts with olefins to give nonstereospecific addition products.[16,17]

Now, it is not unreasonable to suppose that carbenes in the two different spin states may react in different ways with molecules containing heteroatoms; *i.e.*, the singlet carbene might react with such a molecule to afford ylide, whereas the triplet might not. From this viewpoint, the photosensitized reactions of diazomalonate in alkyl sulfides were also investigated.

Results and Discussions

Formation of Sulfonium and Sulfoxonium Ylides in the Reactions of Dimethyl Diazomalonate in Sulfides and Sulfoxides.—Photolysis of dimethyl diazomalonate in various alkyl and aryl sulfides was carried out in Pyrex tubes with a high pressure mercury lamp. The crystalline major products of the reactions were stable sulfonium ylides. Thus, the reaction of dimethyl diazomalonate with dimethyl sulfide gave in 88% yield dimethylsulfonium biscarbomethoxymethylide (**1**), ν_{CO} 1625 and 1675 cm^{-1}, δ ($CDCl_3$) 3.71 (s, -COOMe) and 2.89 (s, $-SCH_3$). The proton shift of the SCH_3 and the carbonyl shift are analogous to those observed in other sulfonium ylides[18] and suggest that the ylide **1** is strongly resonance stabilized by partici-

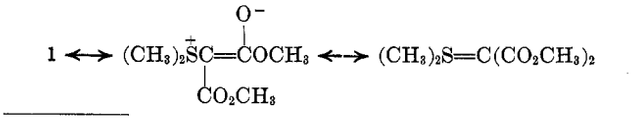

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TABLE I

THE FORMATION OF SULFONIUM YLIDES[a]

$$N_2C(COR)_2 + R^1SR^2 \longrightarrow R^1R^2\overset{+}{S}-\overset{-}{C}(COR)_2$$

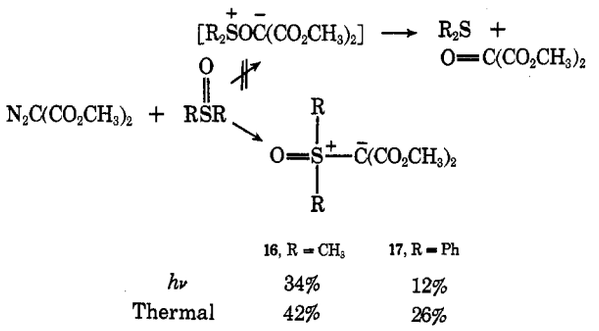
Ylide	R	R^1	R^2	Mp, °C	Ir (C=O), cm^{-1}	Nmr, ppm[b]	Photolysis,[c] %	Thermal reaction,[d]
1	OCH_3	CH_3	CH_3	169–170	1625, 1675	2.89 ($-SCH_3$)	88	75
2	OCH_3	C_2H_5	C_2H_5	150–151	1620, 1655	2.95, 1.30 ($-CH_2-$, $-CH_3$)	57	71
3	OCH_3	*i*-C_3H_7	*i*-C_3H_7	121–122	1625, 1685	4.14, 1.40 [$-CH-$, $-C(CH_3)_2$]	20	
4	OCH_3	CH_3	C_2H_5	144–145	1625, 1677	2.84 ($-SCH_3$)	40	48
5	OCH_3	CH_3	*n*-C_4H_9	121–123	1620, 1675	2.86 ($-SCH_3$)	56	50
6	OCH_3	CH_3	*tert*-C_4H_9	86–87	1620, 1640, 1672	2.90 ($-SCH_3$)	40	
7	OCH_3	C_2H_5	*n*-C_4H_9	93–94	1620, 1670	2.95 ($-SCH_2-$)	45	
8	OCH_3	CH_3	C_6H_5	126–127	1640, 1680	3.25 ($-SCH_3$)	40	83
9	OCH_3	CH_3	$CH_2C_6H_5$	157–159	1620, 1678, 1675	2.77 ($-SCH_3$)	39	56
10	OCH_3	C_6H_5	C_6H_5	127–128	1650, 1675	7.53 ($-SC_6H_5$)	12	85
11	OC_2H_5	CH_3	CH_3	134–135	1635, 1670	2.88 ($-SCH_3$)	87	
12	OC_2H_5	CH_3	*n*-C_4H_9	63–64	1620, 1672	2.87 ($-SCH_3$)	50	
13	OC_2H_5	CH_3	$CH_2C_6H_5$	128–129	1618, 1670	2.76 ($-SCH_3$)	15	
14	CH_3	CH_3	CH_3	166–167	1565, 1595	3.00 ($-SCH_3$)	52	
15	OCH_3	C_2H_5	$CH_2CO_2CH_3$	118–119	1620, 1673, 1745	3.10, 1.31[e] ($-SCH_2-$, $-CH_3$)	53	

[a] Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds listed in the table: Ed. [b] Nmr signal of CO_2CH_3 generally appears in the range of 3.69 and 3.75 ppm, and $CO_2CH_2CH_3$ appears at 4.17 (q, OCH_2-) and 1.29 (t, $-CH_3$). [c] High pressure mercury lamp (3660 Å). [d] Copper sulfate catalyzed thermal reaction at 90°. [e] Nmr signals also appear at 3.66 (s, 3 H), 3.78 (s, 6 H), 3.95 (d, 1 H, J = 16.0 Hz), 4.68 ppm (d, 1 H, J = 16.0 Hz).

pation of sulfur d orbitals and two carbonyl groups. Similar types of reactions in a variety of monosulfides were applied to give sulfonium ylide in high yield (Table I). However, the yields of the ylides were not satisfactory in the reaction with aryl and high branched sulfides.

Thermal decomposition of diazomalonate in sulfides in the presence of copper sulfate or copper metal powder also gave the corresponding stable sulfonium ylides in high yields even in aryl sulfides.

Reactions of diazomalonate in sulfoxides were also studied. Irradiation of a solution of diazomalonate in sulfoxide carried out in a Pyrex vessel with a high pressure mercury lamp. The corresponding sulfoxonium biscarbomethoxymethylides, **16** and **17**, from dimethyl and diphenyl sulfoxides were obtained as pure colorless solids. Copper sulfate catalyzed thermal decomposition of diazomalonate also gave sulfoxonium ylides in better yields than did the photolysis. More sulfoxonium ylides from the thermal reaction of various diazo compounds with dimethyl sulfoxide were also reported recently.[19] Moreover, methyl oxomal-



	16, R = CH_3	17, R = Ph
hν	34%	12%
Thermal	42%	26%

onate could not be detected from the reaction mixture, and this suggests that the diazo compound interacts with the sulfur, not with oxygen.

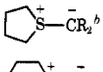
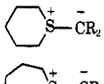
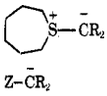
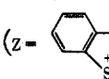
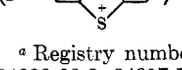
(19) F. Dost and J. G. Gosseleck, *Tetrahedron Lett.*, 509 (1970).

The formation of sulfonium and sulfoxonium ylides, together with data already reported,[16] clearly demonstrates that the direct irradiation of diazomalonate in solution probably produces biscarbomethoxycarbene in the singlet state. Thus, the electrophilic singlet carbene attacks the nonbonding electron pairs on sulfur giving ylide. This is direct evidence for the involvement of ylides in the reaction of carbenes with compounds containing heteroatoms.

In the reaction of dimethyl diazomalonate with saturated cyclic sulfides, the corresponding sulfonium ylides were also obtained as stable colorless solids. Irradiation of dimethyl diazomalonate in pentamethylene sulfide gave 41% sulfonium ylide (Table II), but

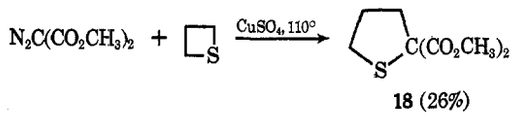
TABLE II

FORMATION OF CYCLIC SULFONIUM YLIDES IN THE REACTION OF DIAZOMALONATE WITH CYCLIC SULFIDES

Ylide[a]	Mp, °C	Ir (C=O), cm^{-1}	Photolysis, %	Thermal reaction, %
	*c*	1615, 1670	75[d]	23
	104–105	1620, 1675	41	90
	73–75	1610, 1670	11	61
	173–175	1655, 1675		68
				

[a] Registry numbers are, respectively, 34281-98-6, 34281-99-7, 34282-00-3, 34297-79-5. [b] R = CO_2CH_3. [c] Oily product and it is difficult to recrystallize. [d] Yield of crude product.

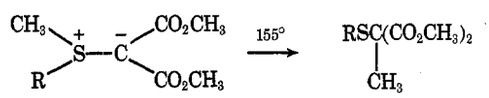
in thietane it did not give any sulfonium ylide because of the polymerization of thietane. On the other hand, copper-catalyzed thermal reaction of diazomalonate in thietane gave the insertion product of the carbene into



18 (26%)

the carbon–sulfur bond. This ring expansion product is probably formed through the facile rearrangement of the intermediate sulfonium ylide.

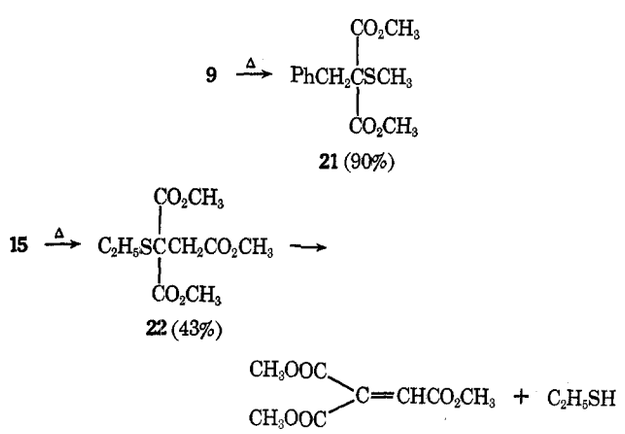
Pyrolysis of Sulfonium Ylides.—One of the many interesting properties of sulfonium ylides is their susceptibility to thermal cleavage of the dipolar sulfur–carbon bond to give the products of Stevens rearrangement or Hofmann-like elimination. When **1** was heated in sealed tubes at temperatures above 155° for >20 hr, the product in which the biscarbomethoxymethylene group was inserted into a methyl–sulfur bond was obtained.[20]



19, R = CH_3 (16%)
20, R = Ph (10%)

This example represents a Stevens-type rearrangement, involving the migration of a methyl group from a sulfonium center to an adjacent carbanionic carbon. Similar results were obtained in the thermal decomposition of other sulfonium ylides by heating in sealed tubes above 180°. These observations strongly support the proposal that the insertion of carboalkoxycarbene into the carbon–oxygen and carbon–nitrogen bonds in the reaction of ethers and amines with carboalkoxycarbene actually takes place through the rearrangement of oxygen and nitrogen ylides.[1,2,17] Recently on the basis of observations of chemically induced dynamic nuclear polarization (CIDNP) in the nmr spectrum of the product, the intervention of radical pair intermediates in the Stevens rearrangement has been suggested.[21–24]

The ylides **9** and **15** were converted into the rearranged products **21** and **22** by heating at 160°. The later ylide also gave the ethylenetricarboxylate, which may be formed by thermal elimination of mercaptan from **22**, since prolonged heating gave a larger amount



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(22) A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 1237 (1969).
(23) R. W. Jemison and D. J. Morries, *Chem. Commun.*, 1226 (1969).
(24) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *ibid.*, 576 (1970).

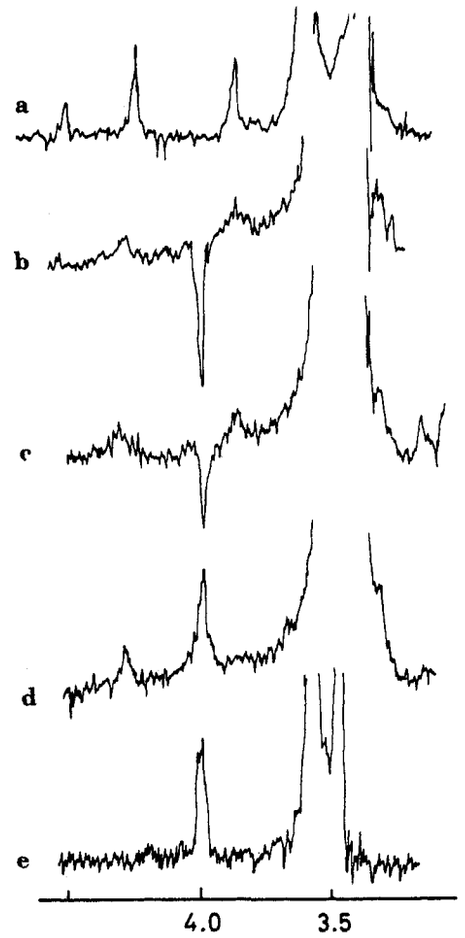
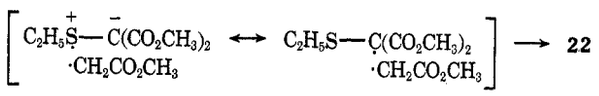
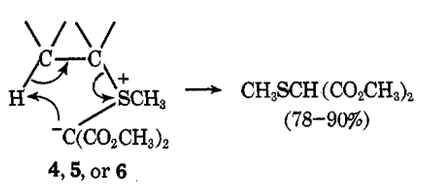


Figure 1.—CIDNP effect observed for β-methylene protons of the product **22** forming in thermolysis of **15**. Spectrum was taken at 60 MHz (δ, parts per million) with TMS as a lock signal: a, **15** (0 min); b, **15** (4.5 min); c, **15** (7.0 min); d, **15** (18.0 min); e, **22**.

of the ethylenic product. We have examined the formation of **22** in the rearrangement of **15** in diphenyl ether using nmr spectroscopy, scanning the region of the developing β-methylene singlet of the product **22** (Figure 1). Within 20 sec after inserting the sample into the probe heated at 160°, a CIDNP effect could be observed for ~9 min. These results are consistent with a mechanism involving homolytic cleavage from **15** yielding a radical pair intermediate, which collapses to **22**.



Thermal decomposition of **4**, **5**, and **6** at 180° gave dimethyl methylthiomalonate in 90, 84, and 78%



4, **5**, or **6**

yields, respectively, together with olefins. The eliminative decomposition of sulfonium ylides probably a cis elimination through a five-membered cyclic transition state. These observations give support to the

proposed ylide mechanism in the reaction of carboalkoxycarbene with ethers and amines bearing β hydrogens, which give similar elimination products.[1,2]

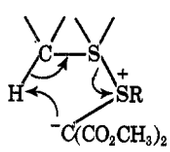
Pyrolysis of cyclic sulfonium ylides in Pyrex tubes was carried out at temperatures above 235° for 10 hr, but no decomposition or reaction products could be detected by gas chromatography. However, the sulfonium ylide from dibenzothiophene was pyrolyzed to give dibenzothiophene and dimethyl malonate.

Reactions of Dimethyl Diazomalonate in Alkyl Disulfides.—In the photolysis of dimethyl diazomalonate in disulfides, the expected sulfonium ylides were not isolable, in contrast to the case of the reactions in alkylmonosulfides. The photolysis of diazomalonate in dimethyl disulfide afforded the principal product, dimethyl methylthiomalonate (**23**) in 43.6% yield and the minor product, thioketal **24**, in 2.2% yield. Similar products were obtained in diethyl disulfide. The structures of these products were determined by comparison of ir and nmr spectra with those of authentic samples. The main products **23** and **25**

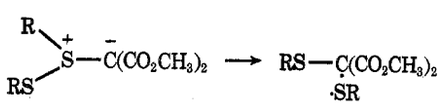
$$N_2C(CO_2CH_3)_2 + RSSR \xrightarrow{h\nu} RSCH(CO_2CH_3)_2 + (RS)_2C(CO_2CH_3)_2$$

23, R = CH_3 (44%) **24**, R = CH_3 (2.2%)
25, R = C_2H_5 (41%) (trace)

correspond to the β-elimination products from the corresponding sulfonium ylides. These can be postulated to form through ylide formation from the carbene and the disulfides, followed by α- or β-hydrogen abstraction concerted with heterolysis of S–S$^+$ bonds (mechanism I). The minor S–S bond insertion product can be re-



(I)



(II)

garded as a Stevens-type rearrangement product from an intermediate sulfonium ylide. The formation and recombination of a radical pair seems to be a higher plausible process because of the weakness of the S–S bond. However, supporting experimental evidence is not given (mechanism II).

In the reaction with di-*tert*-butyl disulfide, biscarbomethoxy-carbene gave three products only in small yields, although the reactions of di-*tert*-butyl disulfide with dichlorocarbene have been reported[25] to give selectively *tert*-butyldichloromethyl disulfide through the elimination of isobutylene from the intermediate sulfonium ylide.

$$N_2C(CO_2CH_3)_2 + (CH_3)_3CSSC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3CSCH(CO_2CH_3)_2 + (CH_3)_3CSSCH(CO_2CH_3)_2 + [(CH_3)_3CS]_2C(CO_2CH_3)_2$$

26 (6.2%) **27** (3.3%) **28** (13.2%)

Reactivity of Dimethyl Sulfide toward Carbene.—The relative reactivity of the sulfur atom in dimethyl sulfide toward the carbene was estimated from product distributions in the photolysis of dimethyl diazomalonate in mixtures of cyclohexene and dimethyl sulfide. The results are shown in Table III. Control experiments

TABLE III
YIELD OF PRODUCTS FROM DIMETHYL DIAZOMALONATE IN CYCLOHEXENE AND DIMETHYL SULFIDE

Mole ratio of cyclohexene/sulfide	Products, % Ylide **1**	Products, % Adducts to cyclohexene[a]
1	61	15
2	49	25
5	36	41
∞	0	92

[a] 7,7-Dicarbomethoxynorcarane and dimethyl 2-cyclohexenylmalonate in the ratio of 2.1:1.

showed that the products are stable under the reaction conditions. The results indicate that biscarbomethoxycarbene reacts with dimethyl sulfide about six times as fast as with double bond of cyclohexene. In all cases, the sulfonium ylide was separated and weighed, and the reaction products from cyclohexene were determined by gas chromatography using an appropriate internal standard. The adducts to cyclohexene were found to be 7,7-dicarbomethoxynorcarane and dimethyl 2-cyclohexenylmalonate in the ratio of 2.1:1. Table IV shows the yields of the reaction products

TABLE IV
YIELD OF PRODUCTS OF DIMETHYL DIAZOMALONATE IN EQUIMOLAR REACTANTS

Pair of reactants with dimethyl sulfide	Products, % Ylide, **1**	Products, % Adducts to the other
Cyclohexene	61	15[a]
2-Methyl-2-butene	49	8.5[b]
cis-4-Methyl-2-pentene	60	5[b]
Cyclopentadiene	44	
Methanol	78	10
Ethyl ether	73	12[c]

[a] Mixtures of olefin adduct and C–H insertion product. [b] Olefin adduct only. [c] Ethylene elimination product and C–H insertion product.

from the photolysis of dimethyl diazomalonate in equimolar mixtures of dimethyl sulfide and other nucleophiles. These observations suggest that dimethyl sulfide can be used as a more effective and convenient acceptor of negatively substituted carbenes than olefins when the sulfonium ylides are stable under the reaction conditions, because of the high reactivity of dimethyl sulfide and the ease of isolation of the ylide products. Biscarbomethoxycarbene reacts with dimethyl sulfide six–eleven times as fast as with olefins.

Photosensitized Reactions of Dimethyl Diazomalonate in Alkyl Sulfides.—Contrary to the earlier expectation, photosensitized decomposition of diazomalonate in dimethyl sulfide was found to give a considerable amount of the ylide. Irradiation of dimethyl sulfide solutions of dimethyl diazomalonate in the presence of benzophenone as a sensitizer was carried out with the high pressure mercury lamp and found to produce sulfonium ylide in 60–65% yields. The absolute yield of the sulfonium ylide **1** was estimated by relative sizes of the integrated nmr signal of the $-S^+CH_3$ (2.68 ppm in Ph_2CO and $CHCl_3$ solution)

(25) S. Searles, Jr., and R. E. Wann, *Tetrahedron Lett.*, 2899 (1965).

$$N_2C(CO_2CH_3)_2 + RSR + Ph_2CO \xrightarrow{h\nu} R_2\overset{+}{S}-\overset{-}{C}(CO_2CH_3)_2$$
1, R = CH_3 (60–65%)
2, R = C_2H_5 (40–43%)

of the ylide in the solution with respect to that of the CH_2 signal (4.50 ppm in Ph_2CO and $CHCl_3$ solution) from known amounts of dibenzyl ether added as an internal standard. In the photosensitized reaction of diazomalonate in di-*tert*-butyl sulfide, *tert*-butylthiomalonate, the elimination product of the corresponding sulfonium ylide, was obtained in 21% yield.

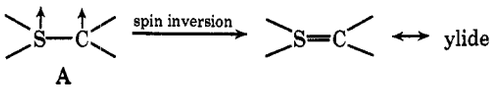
In alkyl disulfides, the photolysis of diazomalonate in the presence of benzophenone gave the same products obtained in the direct photolysis. These

$$N_2C(CO_2CH_3)_2 + RSSR + Ph_2CO \xrightarrow{h\nu} RSCH(CO_2CH_3)_2 + (RS)_2C(CO_2CH_3)_2$$

R = CH_3	32%	14%
R = C_2H_5	61%	Trace
R = $C(CH_3)_3$	5%	Trace

findings suggest that the photosensitized reaction of the diazomalonate can produce the sulfonium ylide in the dialkyl disulfides.

One might explain the unexpected ylide formation in the photosensitized decomposition of dimethyl diazomalonate in alkyl sulfides and disulfides by a process in which a triplet carbene attacks the sulfur atom producing the intermediate represented by formular A. Spin inversion of A leads to ylide formation.



A

Structure A requires the expansion of the valence shell on the sulfur atom to accomodate nine electrons. Such an attack on a sulfur atom by a triplet carbene has not been previously proposed. However, similar examples of such a shell expanded sulfur has been proposed on the basis of studies of the decomposition of *tert*-butyl *o*-(methylthio)perbenzoate[26] and of the copolymerization of vinyl sulfide.[27]

However, the additional information concerning the behavior of triplet carbene in dimethyl sulfide solution is available. The sensitized decomposition of dimethyl diazomalonate[28] in mixtures of dimethyl sulfide and *cis*-4-methyl-2-pentene gave cis- and trans-disubstituted cyclopropanes and the dimethylsulfonium biscarbomethoxymethylide (1) in yields shown in

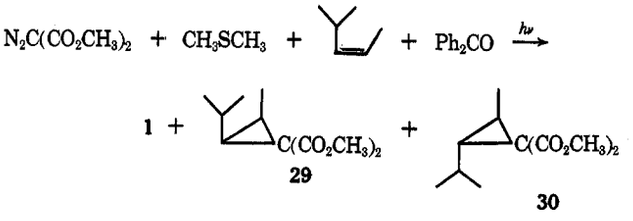


Table V. It is noteworthy that, as the concentration of dimethyl sulfide increases, the ratio of the cis adduct to the trans isomer increases. This fact indicates that, in the reaction system diluted with dimethyl sulfide, the species attacking olefin reacts in a more stereospecific fashion than the triplet carbene derived by the photosensitized decomposition of the diazomalonate in olefin alone.

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TABLE V

PHOTOSENSITIZED DECOMPOSITION OF DIAZOMALONATE IN *cis*-4-METHYL-2-PENTENE AND DIMETHYL SULFIDE[a]

Molar ratio of olefin/sulfide	Products, %[b] 29	30
0.23	24.2	75.8
0.33	22.5	77.5
0.66	19.5	80.5
1.0	16.8	83.2
Olefin only	12.3	87.7

[a] Appropriate control experiments were performed. Under the reaction conditions there is insignificant isomerization of the solvent and the products are neither isomerized nor destroyed. [b] Sulfonium ylide 1 was also obtained in 40–65% yields and the yields of olefin adducts increase with olefin concentrations.

One may postulate a transition of carbene from triplet to singlet brought about by the presence of dimethyl sulfide. The singlet carbene thus formed will react with sulfide giving the sulfonium ylide, as well as with olefin in a stereospecific manner. However, there are a number of alternative explanations of these facts, and the question of even the gross mechanism is therefore still open.

Although detailed mechanism of participation of sulfide in the transition are not yet clear, the transition seems to require the presence of sulfide, since, when the reactants (olefin and diazomalonate) were diluted with other invert solvent such as Freon 113, no change in stereochemistry of addition was observed.

Sensitized reaction of diazomalonate in diethyl ether, which gave no product presumed to form from ylide precursor, showed that ethers are incapable of assisting the transition of the triplet to the singlet.

It is interesting to note that, as shown in Table VI,

TABLE VI

PHOTOSENSITIZED DECOMPOSITION OF DIAZOMALONATE IN *cis*-4-METHYL-2-PENTENE AND DI-*tert*-BUTYL SULFIDE

Molar ratio of olefin/sulfide	Products, % Cis adduct 29	Trans adduct 30
0.09	9.5	90.5
0.34	9.5	90.5
1.0	10.5	89.5

no change in stereochemistry of addition was observed when photolysis was carried out in the presence of di-*tert*-butyl sulfide, which does not afford the corresponding ylide even in the reaction with singlet carbene.[7] The triplet and singlet carbenes would hardly interact with a sulfur atom of di-*tert*-butyl sulfide because of steric hindrance caused by bulky *tert*-butyl groups.

Experimental Section

General.—Ir spectra were determined on a Japan Spectroscopic Co., Ltd, DS-21 instrument in chloroform, carbon tetrachloride, or neat. The nmr spectra were recorded on a Varian A-60D spectrometer using solutions in carbon tetrachloride or deuteriochloroform with internal tetramethylsilane (TMS) as standard. Chemical shifts are reported in parts per million (ppm) downfield from TMS, with the parentheses designating the multiplicity of the signals: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. The number immediately following the parentheses

indicates the number of protons causing the signal. Samples of dimethyl diazomalonate 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 low intensities at 3126–2132 Å. The photolyses were carried to the disappearance of diazo band in ir spectra. The solutions were analyzed on an Ohkura glpc with a calibrated 5 ft × 1/4 in. stainless steel column of 10% DC-710 and Carbowax 20M on C-22 firebrick. Peak areas were obtained by multiplying the height of the peak times the width at half-height. Absolute yields were then obtained relative to the area of the known amounts internal peak.

Materials.—The reagents [dimethyl, diethyl, and di-*tert*-butyl sulfides, dimethyl, diethyl, and di-*tert*-butyl disulfides, tetrahydrothiophene, and *cis*-4-methyl-2-pentene (contained <1% trans isomer)] were obtained commercially and purified by distillation before use. Methyl ethyl sulfide,[29] methyl *n*-butyl sulfide,[29] methyl *tert*-butyl sulfide,[29] methyl benzyl sulfide,[29] ethyl *n*-butyl sulfide,[30] methyl phenyl sulfide,[31] diphenyl sulfide,[32] thietane,[33] and cyclic sulfides[34] were prepared by known procedure as referenced. Dimethyl diazomalonate was prepared as follows. A solution of dimethyl malonate (26.4 g, 0.2 mol) and tosyl azide (39.4 g, 0.2 mol) in diethyl ether (200 ml) at 0° was treated with dry diethyl amine (20 ml, 0.2 mol).[35] The mixture was stirred for 1 hr at 0° and for a further 1 hr at room temperature. When solid was deposited, the mixture was treated with petroleum ether (bp <60°) and the solid was filtered off. Removal of solvent from the filtrate and distillation of the residue gave dimethyl diazomalonate, 50% yield, bp 60–61° (2 mm) [lit.[36] bp 63° (1 mm)], $\nu_{N=N}$ 2140 cm^{-1}, uv absorption maximum at 352 nm (ϵ 22).

Reactions of Dimethyl Diazomalonate in Alkyl and Aryl Sulfides. Formation of Stable Sulfonium Ylides.—Most of the dialkyl- and diarylsulfonium biscarbomethoxymethylides were prepared by the photolysis of dimethyl diazomalonate in the corresponding dialkyl and diaryl sulfides. For example, compound **1** was prepared in 88% yield by the photolysis of 0.52 g (3.3 mmol) of diazomalonate in 3 ml of dimethyl sulfide. **1** was obtained as pure white solid by decantating the unreacted dimethyl sulfide and washing the remaining solid with petroleum ether (bp 30–60°). The product easily dissolved in water and chloroform, but not in carbon tetrachloride or acetone. The dialkyl- and diarylsulfonium biscarbomethoxymethylides were often prepared with copper and copper salt catalyzed thermal decomposition of diazomalonate in the corresponding sulfides. For example, the stable diphenylsulfonium biscarbomethoxymethylide (**10**) was obtained when a solution of 1.02 g (6.6 mmol) of diazomalonate in 5 ml of diphenyl sulfide was heated at 90° for 5 hr in the presence of anhydrous cupric sulfate (20 mg). Chloroform was added and the undissolved materials were separated from the reaction mixture. After the chloroform was distilled off, the solid was recrystallized from ethanol to give the ylide in 85% yield. The nmr and ir spectra and other physical properties are recorded in Tables I and II.

Reactions of Dimethyl Diazomalonate in Sulfoxides.—Photolysis of 0.52 g (3.3 mmol) of diazomalonate in 3 ml of dimethyl sulfoxide, according to the procedure above, gave dimethylsulfoxonium biscarbomethoxymethylide (**16**) in 34% yield, which showed ir 1640 cm^{-1}; nmr ($CDCl_3$) 3.54 (s, 6 H) and 3.72 ppm (s, 6 H); mp 157–158°. *Anal.* Calcd for $C_7H_{12}O_6S$: C, 40.38; H, 5.77. Found: C, 40.80; H, 5.88. Cupric sulfate catalyzed thermal decomposition of diazomalonate in dimethyl sulfoxide, according to the procedure above, also gave the sulfoxonium methylide **16** in 42% yield. Photolysis of the diazomalonate in 2 ml of diphenyl sulfoxide was carried out in the same manner described above to give **17** in 12% yield, in contrast to the 26% yield in thermal reaction. **17** showed ir (CCl_4) 1680 cm^{-1}; nmr ($CDCl_3$) 3.40 (s, 6 H) and 7.77 ppm (m, 10 H); mp 196–197°. *Anal.* Calcd for $C_{17}H_{16}O_6S$: C, 61.44; H, 4.81. Found: C, 61.21; H, 4.78.

Reactions of Dimethyl Diazomalonate in Thietane.—Photolysis of diazomalonate in thietane was carried out with the high pressure mercury lamp. During the photolysis, white thin film was deposited on the glass wall of reaction tubes. After 40-hr irradiation, the ir band of the reaction mixture showed no decomposition of diazo compound. The white thin film on the glass wall was found to be the polymeric material from thietane. Thermal decomposition of diazomalonate in thietane was carried out in the presence of cupric sulfate at 110°. From the analysis by gas chromatography, one product (**18**) was isolated. **18** showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) 2.20 (m, 4 H), 3.15 (m, 2 H), 3.73 ppm (s, 6 H). *Anal.* Calcd for $C_8H_{12}O_4S$: C, 47.06; H, 5.92. Found: C, 47.33; H, 6.20.

Thermal Decomposition of Alkylsulfonium Biscarbomethoxymethylides.—The reaction described below exemplifies the general thermolysis of the sulfonium biscarbomethoxymethylides. Ylide **1** (0.32 g, 1.66 mmol) was sealed in 8 × 100 mm Pyrex tubes without degassing. The sample was heated at 200° for 20 hr in an oil bath. After complete decomposition of the ylide **1**, the reaction mixture was analyzed directly by gas chromatography. The structure of the product collected from the gas chromatography was determined by elemental analysis and the nmr and ir spectra. Ylide **1** gave **19**, dimethyl malonate, and dimethyl sulfide in 16, 15, and 10% yields, respectively. **19** showed ir (CCl_4) 1740 cm^{-1}; nmr (CCl_4) 1.62 (s, 3 H), 2.15 (s, 3 H), 3.75 ppm (s, 6 H). Ylide **8** gave **20** in 10% yield which showed ir (CCl_4) 1765 cm^{-1}; nmr (CCl_4) 1.54 (s, 3 H), 3.64 (s, 6 H), 7.32 ppm (m, 5 H). Ylide **9** gave **21** which showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) 2.12 (s, 3 H), 3.34 (s, 2 H), 3.74 (s, 6 H), 7.30 ppm (m, 5 H). Ylides **4**, **5**, and **6** gave dimethyl methylthiomalonate in 90, 84, and 78% yields, respectively. It was identified by the comparison of its physical properties with those of an authentic sample prepared by the irradiation of diazomalonate in methyl mercaptan: ir (CCl_4) 1750 cm^{-1}; nmr (CCl_4) 3.74 (s, 6 H), 3.91 (s, 1 H), 2.21 ppm (s, 3 H). *Anal.* Calcd for $C_6H_{10}O_4S$: C, 40.45; H, 5.62; S, 17.97. Found: C, 40.64; H, 5.67; S, 17.95.

Observation of CIDNP Effect on the Thermolysis of Ylide 15.—A solution of 10 mg of **15** and 0.5 ml of diphenyl ether in an nmr tube was sealed carefully. The nmr spectrum of this sulfonium ylide showed 1.31 (t, 3 H), 3.10 (q, 2 H), 3.66 (s, 3 H), 3.78 (s, 6 H), 3.95 (d, 1 H), 4.68 (d, 1 H). The sample tube was inserted into the probe heated at 160°, and one new nmr signal appeared as an emission line at 3.77 ppm after 20 sec. This new emission was observed for 9 min. The signal intensity decayed exponentially and the line width was approximately constant during the thermolysis. The final product from the thermolysis of ylide **15** was found to be **22**. **22** showed the following nmr spectrum in carbon tetrachloride: 1.24 (t, 3 H), 2.66 (q, 2 H), 3.72 (s, 3 H), 3.75 ppm [s + s, (6 + 2) H]. *Anal.* Calcd for $C_{10}H_{16}O_6S$: C, 45.45; H, 6.10. Found: C, 45.52; H, 5.98.

Reactions of Dimethyl Diazomalonate in Alkyl Disulfides.—The reaction described below is typical. Diazomalonate 0.35 g (2.2 mmol) was dissolved in 1.01 g (10.8 mmol) of dimethyl disulfide and then irradiated for 15 hr with a high pressure mercury lamp. The reaction products were analyzed directly by gas chromatography to give 44% **23** and 2.2% **24**. **23** was identified by comparison of its spectral data with that of an authentic sample. **24** showed nmr (CCl_4) 2.04 (s, 6 H), 3.78 ppm (s, 6 H). *Anal.* Calcd for $C_7H_{12}O_4S_2$: C, 37.50; H, 5.36. Found: C, 37.55; H, 5.09. The reaction of diazomalonate in diethyl disulfide gave 41% **25**, which showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) 1.27 (t, 3 H), 2.74 (q, 2 H), 3.78 (s, 6 H), 4.02 ppm (s, 1 H). *Anal.* Calcd for $C_7H_{12}O_4S$: C, 43.75; H, 6.29; S, 16.65. Found: C, 43.79; H, 6.34; S, 16.96.

The reaction of diazomalonate in di-*tert*-butyl disulfide gave three products, **26**, **27**, and **28**. **26** showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) 1.36 (s, 9 H), 3.76 (s, 6 H), 4.02 ppm (s, 1 H). *Anal.* Calcd for $C_9H_{16}O_4S$: C, 49.99; H, 7.27. Found: C, 50.23; H, 7.29. **27** showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4 1.31 (s, 9 H), 3.74 (s, 6 H), 4.14 ppm (s, 1 H). *Anal.* Calcd for $C_9H_{16}O_4S_2$: C, 42.86; H, 6.34. Found: C, 43.06; H, 6.8. **28** showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) 1.33 (s, 18 H), 3.77 ppm (s, 6 H). *Anal.* Calcd for $C_{13}H_{24}O_4S_2$: C, 52.50; H, 7.50. Found: C, 52.33; H, 7.75.

Photolysis of Dimethyl Diazomalonate in a Solution of Di-

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methyl Sulfide and Cyclohexene.—Photolysis of 1.02 g (6.6 mmol) of diazomalonate in a solution of 9.32 g (0.15 mol) of dimethyl sulfide and 12.01 g (0.15 mol) of cyclohexene was carried out with the high pressure mercury lamp described above. After the diazo band disappeared from the spectrum of the reaction mixture, a known amount of internal standard (biphenyl) was added to the reaction mixture. A white precipitate formed when the reaction was over.

The solid was filtered to give 0.75 g (61% yield) of sulfonium ylide **1** which was identified by comparison of spectra with those of an authentic sample. The reaction mixture was then analyzed directly by gas chromatography. Two major peaks appeared which were found to be the adducts of biscarbomethoxycarbene to cyclohexene. One of them was identified as the adduct of carbomethoxycarbene with the C=C bond of cyclohexene which showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) 1.15 (m, 2 H), 1.85 (m, 8 H), 3.66 (s, 3 H), 3.76 ppm s, 3 H). *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.79; H, 7.45. The other product was identified as the insertion product of biscarbomethoxycarbene into the allylic carbon–hydrogen bond, which showed ir (CCl_4) 860, 1025, 1740 cm^{-1}; nmr (CCl_4) 1.83 (m, 7 H), 3.15 (d, 1 H), 3.66 (s, 6 H), 5.88 ppm (m, 2 H). *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.03; H, 7.58.

Photosensitized Reactions of Dimethyl Diazomalonate in Dialkyl Sulfides and Disulfides.—Dimethyl diazomalonate (220 mg) was added to dimethyl sulfide (700 mg) solution with 880 mg of benzophenone. Irradiation of the sample in Pyrex tubes for 40 hr provided a white solid, which was washed with petroleum ether (bp 30–60°) and identified as sulfonium ylide **1** by comparison with an authentic sample. The overall yield of **1** was determined by nmr spectroscopy through addition of dibenzyl ether as an internal standard. The formation of benzopinacol was also observed, but it was neglibible before decomposition of diazomalonate. Irradiation of diazomalonate was also performed in diethyl and di-*tert*-butyl sulfides solution containing benzophenone: 220 mg of dimethyl diazomalonate was dissolved in 1 ml of diethyl or di-*tert*-butyl sulfides and 800 mg of benzophenone and irradiated for 40 hr in a Pyrex tube. Although no significant precipitation could be observed in the solution, the nmr analysis indicated the formation of **2**. On the other hand ethyl or *tert*-butylthiomalonate from the thermolysis of corresponding sulfonium ylides was isolated by preparative gas chromatograph. These were identified by comparison of their spectra with those of authentic samples. When 100 mg of dimethyl diazomalonate in a solution of 300 mg of dimethyl disulfide and 165 mg of benzophenone was irradiated for 40 hr in Pyrex tubes, no corresponding sulfonium ylide formation could be observed. However, the product analysis by gas chromatography indicated the formation of alkylthiomalonate. It was identified by comparison of its spectra with those of authentic samples.

Photosensitized Reaction of Dimethyl Diazomalonate in Dimethyl Sulfide and *cis*-4-Methyl-2-pentene. Competitive Reactions.—Dimethyl diazomalonate (1 mmol) and 4.5 mmol of benzophenone were dissolved in weighed quantities of dimethyl sulfide and *cis*-4-methyl-2-pentene. The solution was irradiated for 40–50 hr until the diazo band in ir spectrum disappeared. The analyses for sulfonium ylide were performed on Varian A-60D nmr spectrometer after the solid that appeared in the reaction mixture was dissolved with deuteriochloroform. The relative integral heights of ylide S^+CH_3 to internal standard CH_2 of dibenzyl ether were compared to obtain the yield of ylide formation. The reaction mixture was concentrated and analyzed by gas chromatograph. Two main products were isolated and shown to be *cis*- and *trans*-cyclopropane derivatives, **29** and **30**, by comparison of their spectra with those of authentic samples.[16]

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Synthesis and Antifungal Properties of Dithiocarboxylic Acid Derivatives. II.[1] Novel Preparation of 2-Alkylamino-1-cyclopentene-1-dithiocarboxylic Acids and Some of Their Derivatives

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2-Methylamino-1-cyclopentene-1-dithiocarboxylic acid (II) can be obtained in low yield from cyclopentanone with carbon disulfide and methylamine; no other 2-alkylamino analogs can be synthesized. The amino group of 2-amino-1-cyclopentene-1-dithiocarboxylic acid (I) and that of its methyl ester (VII) can be substituted by the alkylamino group by an amine exchange reaction, yielding the corresponding 2-alkylamino-1-cyclopentene-1-dithiocarboxylic acid (II) or its methyl ester (III–V, VIII–XII), respectively. The structures, including tautomeric forms of the synthesized compounds, were proved by ir and nmr spectroscopy.

In previous research it was found that 2-amino-1-cyclopentene-1-dithiocarboxylic acid (I) synthesized by Takeshima and coworkers[3] exerts a marked antifungal action against various fungi.[4] The steric arrangement of the functional groups in this compound permits the formation of six-membered chelates with metals, which fact may be responsible for the biological activity, too. Chelation plays an important role in the action of several antifungal compounds, among which are the dithiocarbamates.[5–7]

For studying the structure–activity relationship within this group we attempted to prepare the *N*-alkyl and *S*-alkyl derivatives of I. Some of these compounds have been synthesized by Mayer and coworkers[8] by treating *N*-alkyliminocyclopentanes with carbon disulfide. To avoid the tedious preparation of *N*-alkyl-

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