Formation of Sulfur Ylids by Catalytic Action of Dialkoxy Disulfides[1]

Haruo Matsuyama, Hiroshi Minato, and Michio Kobayashi
Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya, Tokyo

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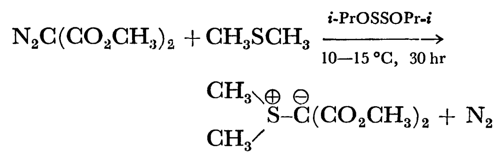
In the presence of a catalytic amount of a dialkoxy disulfide, dimethyl diazomalonate spontaneously reacted with a dialkyl sulfide in the absence of light at room temperature, and the corresponding sulfonium ylid was formed. The kinetics and products of this reaction were investigated, and its mechanism was discussed.

Very little has been published on the chemistry of dialkoxy disulfides, which can be prepared from sulfur monochloride and alcohols. In our laboratories various reactions of these interesting compounds have been studied, and the mechanisms of their reactions with Lewis acids have been described in a recent publication.²⁾

In an attempt to study the reaction between diisopropoxy disulfide and bis(methoxycarbonyl)carbene, the disulfide was mixed with dimethyl diazomalonate in dimethyl sulfide at room temperature. Surprisingly, an ylid was formed in the absence of light at room temperature.

The formation of an ylid from dimethyl diazomalonate and dimethyl sulfide was reported by Ando *et al.*³⁾ They stated that the diazomalonate decomposed and yielded the corresponding carbene only when the diazo compound was irradiated with a UV light or heated near 110 °C in the presence of a copper catalyst.

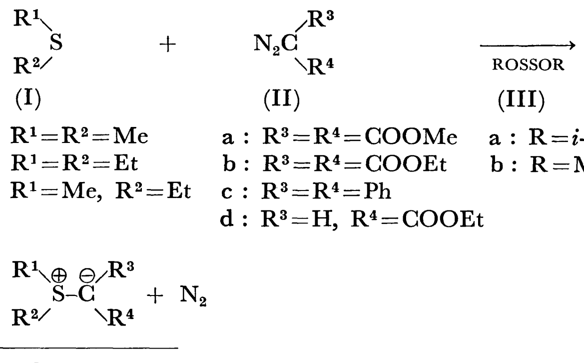


$$N_2C(CO_2CH_3)_2 + CH_3SCH_3 \xrightarrow[10\text{—}15\,^\circ\mathrm{C},\ 30\,\mathrm{hr}]{i\text{-PrOSSOPr-}i} (CH_3)_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(CO_2CH_3)_2 + N_2$$

The formation of sulfur ylids by catalytic action of dialkoxy disulfides was studied, and the results are described in this paper.

Results and Discussion

When dimethyl diazomalonate (IIa) was dissolved in a dialkyl sulfide (I) in the presence of a catalytic amount of diisopropoxy disulfide (IIIa) at room temperature, nitrogen gas was evolved and the corresponding ylid was formed in a good yield. Table 1 summarized the results of the reactions with several sulfides.



$$R^1R^2S + N_2CR^3R^4 \xrightarrow{\mathrm{ROSSOR}} R^1R^2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}R^3R^4 + N_2$$

(I)
a : $R^1=R^2=Me$
b : $R^1=R^2=Et$
c : $R^1=Me$, $R^2=Et$

(II)
a : $R^3=R^4=COOMe$
b : $R^3=R^4=COOEt$
c : $R^3=R^4=Ph$
d : $R^3=H$, $R^4=COOEt$

(III)
a : $R=i$-Pr
b : $R=Me$

Table 1. Formation of ylids from dimethyl diazomalonate and sulfides in the presence of diisopropoxy disulfide[a]

R^1-S-R^2	Temp. (°C)	Ylid (%)	N_2 (%)
$R^1=R^2=Me$	17	80	96
	20	75	90
	20[b]	67	100
$R^1=R^2=Et$	17	78	90
	20	67	84
	20[b]	76	92
$R^1=Me$, $R^2=Et$	20	72	75
$R^1=R^2=Me$	($h\nu$)[c]	88	
	($CuSO_4$, 110 °C)[c]	75	

a) A mixture consists of a sulfide 30 mmol, $N_2C(CO_2Me)_2$ 5 mmol, and *i*-PrOSSOPr-*i* 1 mmol.
b) Dark reaction (covered with aluminum foil).
c) Reference 3); in the absence of diisopropoxy disulfide.

In the absence of III, no reaction was observed between I and II. No reaction was observed between II and III either. Reaction took place only when the three components are present. III is simply a catalyst and remains unchanged. The diazo compounds decompose smoothly at room temperature without irradiation of UV light. Visible light cannot be the cause for the reaction, since the decomposition proceeded equally well when the reaction flask was completely covered and shielded from light.

When the rates of evolution of nitrogen from a mixture of I, IIa and IIIa were determined, they were of first order in IIa at least until about 50% decomposition. The half life of IIa at 20 °C was about 4 hr, and the first order rate constant k_1 was 3.84×10^{-5} sec.$^{-1}$

Table 2. Comparison of the sulfides possessing catalytic activity on the reaction between dimethyl diazomalonate and dimethyl sulfide[a]

Catalytic sulfides[b]	Temp. (°C)	10^5k_1 (sec^{-1})	$\tau_{1/2}$ (hr)	Ylid (%)	N_2 (%)
MeOSSOMe	20	4.5	4.7	71	81
EtOSSOEt	20	8.1	2.6	68	96
i-PrOSSOPr-*i*	20	5.1	4.0	75	90
EtOSOEt	20	6.4	5.0	66	93
NC-SS-CN	25		*ca.* 3 days	50	

a) A mixture consists of Me_2S 30 mmol, $N_2C(CO_2Me)_2$ 5 mmol, and a catalytic sulfide, 1 mmol.
b) Found to be inactive: MeSSMe, $Et_2NSSNEt_2$, BzSSBz, ClSSCl.

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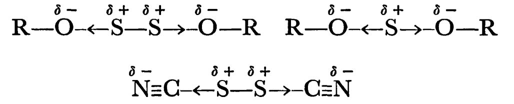
1) Organic Sulfur Compounds. Part XL.
2) M. Kobayashi, H. Minato, and K. Shimada, *Int. J. Sulfur Chem.*, **A**, **1**, 105 (1971).

In an attempt to determine what is responsible for the catalytic activity of III, other compounds possessing similar catalytic activity were sought for. As Table 2 shows, dialkyl sulfoxylates, ROSOR, and thiocyanogen, NC–SS–CN, were found to be effective, whereas dimethyl disulfide, diethylamino disulfide, benzoyl disulfide and sulfur monochloride were inactive.

Since the electronegativity of sulfur is 2.5 and that of oxygen is 3.5,[4] the electron density on the sulfur atoms of III must be smaller due to the presence of the electron-withdrawing oxygen atoms. The electron density on the sulfur atoms of dialkyl sulfoxylates and thiocyanogen must be small due to the presence of the electron-withdrawing alkoxy and cyano groups.



$$R—\overset{\delta-}{O}\leftarrow\overset{\delta+}{S}—\overset{\delta+}{S}\rightarrow\overset{\delta-}{O}—R \quad R—\overset{\delta-}{O}\leftarrow\overset{\delta+}{S}\rightarrow\overset{\delta-}{O}—R$$

$$\overset{\delta-}{N}\equiv C\leftarrow\overset{\delta+}{S}—\overset{\delta+}{S}\rightarrow C\equiv\overset{\delta-}{N}$$

Therefore, the divalent sulfur atom containing a small positive charge due to electron-withdrawing substituents is probably responsible for the catalytic formation of ylids from I and II.

Various diazo compounds were examined as to their reactivity, and the results are summarized in Table 3. In mixtures with Ib and IIIa, dimethyl and diethyl diazomalonates decomposed smoothly at room temperature, yielding an ylid and nitrogen. Ethyl diazoacetate, diphenyldiazomethane and ethyl azidoformate decomposed very slowly (about 10% decomposition in 4 days). Three diazo compounds containing an acetyl group did not decompose at all.

Then, various dialkyl sulfides were examined as to their reactivity, and the results are summarized in Table 4. In mixtures with IIa and IIIa, methyl phenyl sulfide, ethyl phenyl sulfide and dimethyl sulfoxide did not react at all, and *n*-butyl methyl sulfide reacted very slowly (the yield of ylid was 66% after 10 days at 20°C). These findings suggest that an electron-rich sulfide is reactive, and the reaction is slow with a bulky alkyl group.

The pseudo first order rate constants determined from the rates of nitrogen evolution show that dimethyl sulfide and diethyl sulfide react with IIa quite rapidly, whereas ethyl methyl sulfide and tetrahydrothiophene react slowly. Thus, the electronic and steric effects in this reaction are rather complex, and not straightfoward.

When Ia, IIa and IIIb were mixed in an NMR tube, and the changes of the concentrations of the reactants were observed, it was found that the decrease of IIa corresponded to the formation of the ylid, whereas IIIb remained unchanged. The results are shown in Fig. 1. It is clear that III is not a reactant, but a catalyst. However, the increase in the concentration of III resulted in the increase in the rate of nitrogen evolution. An induction period of about 10 min was observed, during which nitrogen was not evolved.

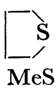
Table 3. Comparison of the reactivities of diazo compounds with diethyl sulfide in the presence of diisopropoxy disulfide at 20 °C[a]

Diazo compounds[b]	10^5k_1 (sec^{-1})	$\tau_{1/2}$ (hr)	Ylid (%)	N_2 (%)
$N_2C(COOMe)_2$	3.8	4.3	67	84
$N_2C(COOEt)_2$	0.7	27.5	45	57

a) A mixture consists of Et_2S 30 mmol, R_2CN_2 5 mmol, and *i*-PrOSSOPr-*i* 1 mmol.

b) No Reaction: $N_2C(COMe)_2$, $N_2C(COMe)(COOMe)$, $N_2C(COMe)(COOEt)$. Very slow decomposition (ca 10%/4 day): $N_2CHCOOEt$, N_2CPh_2, N_3CO_2Et.

Table 4. Comparison of the reactivities of sulfides with dimethyl diazomalonate in the presence of diisopropoxy disulfide[a]

Sulfides[b]	Temp. (°C)	10^5k_1 (sec^{-1})	Rel. React.	$\tau_{1/2}$ (hr)
MeSMe	17	4.0	5	5.2
EtSEt	17	3.2	4	5.9
	17	0.80	1	24
MeSEt	20	0.66	0.8	29

a) A mixture consists of a sulfide 30 mmol, $N_2C(COOMe)_2$ 5 mmol, and *i*-PrOSSOPr-*i*, 1 mmol.

b) No reaction: PhSMe, PhSEt, Dimethyl sulfoxide.
Slow reaction: *n*-BuSMe (ylid 66% in 10 days at 20 °C).

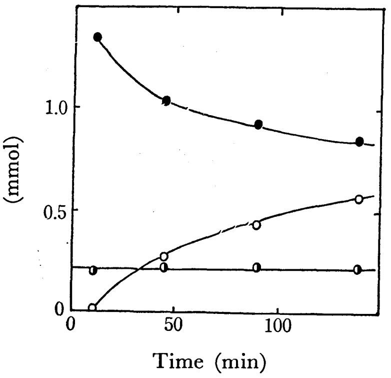


Fig. 1. Changes of amounts of the reactants and products in an NMR Tube at 35 °C.
(The initial mixture consists of Ia 2.42, IIa 1.35, IIIb 0.20, and CH_3NO_2 1.85 mmol)
●: $N_2C(CO_2Me)_2$, ○: $Me_2\overset{\oplus}{S}-\overset{\ominus}{C}(CO_2Me)_2$, ◐: MeOSSOMe

The experiments described so far used excess I as the solvent. When the mixture was diluted with such polar solvents as nitromethane and acetonitrile, the decomposition of IIa became slower. When *n*-hexane was used as the solvent, IIa did not decompose.

The rates of the decomposition of IIa in a mixture with Ib and IIIa were determined at various temperatures, and it was found that the rates were in the order of $k_{20°}>k_{17°}>k_{30°}$. It is clear that above a certain temperature this reaction becomes slower.

As for the mechanism of this reaction, the following two pathways seem possible. Scheme 1 involves the formation of a complex between II and III, and the complex is supposed to react with I.

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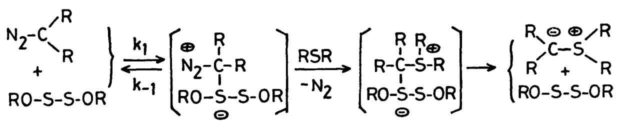
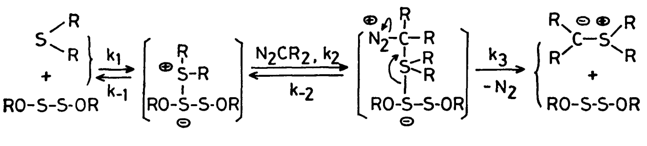
[3] W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, **1969**, 1979.

[4] L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca (1960), p. 88.



Scheme 1.

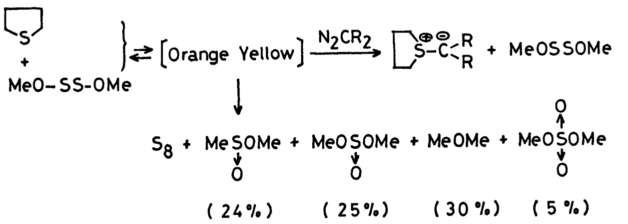


Scheme 2.

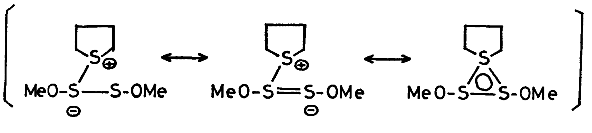
Scheme 2 involves the formation of a complex between I and III, and the complex is supposed to react with II.

Attempts were made in order to detect the presence of complexes in the mixtures of I, II, and III. The UV spectrum of a mixture of IIa and III did not show any sign of interaction between them. The UV spectra of the mixtures of Ia and III, or Ib and III showed no sign either.

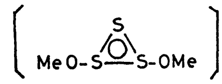
However, when tetrahydrothiophene was mixed with IIIb, the mixture turned orange yellow. If IIa was added to this colored mixture, the corresponding ylid was formed and IIIb was recovered unchanged. If IIa was not added and the mixture was allowed to stand at room temperature for more than ten minutes, sulfur precipitated, and the products of decomposition of IIIb were found.



The five products shown above are the compounds found as the products of the decomposition of IIIb when the latter was mixed with triethyloxonium tetrafluoroborate.[2] As the species present in the orange yellow mixture, the following structure seems probable.



In our previous paper dealing with the reaction between IIIb and $Et_3O^+BF_4^-$, evidence was presented indicating the presence of the following intermediate.



Scheme 2 is favored on the basis of the findings that IIIb and tetrahydrothiophene form the orange yellow complex which readily react with IIa, forming the ylid and nitrogen. Thus, the data described in this paper suggest that the reactions among I, II and III are represented by Scheme 2.

Experimental

Materials. Dimethyl sulfide, tetrahydrothiophene, dimethyl disulfide and dimethyl sulfoxide were of reagent grade and used without further purification. Other sulfides were prepared from the corresponding sodium mercaptides and alkyl halides.[5] Dimethoxy disulfide, diethoxy disulfide and diisopropoxy disulfide were synthesized by the method of Thompson.[6] Diethyl sulfoxylate was prepared from the reaction between diethoxy disulfide and sodium ethoxide by the method of Meusen.[7] Thiocyanogen[8] and benzoyl disulfide[9] were prepared by the methods described in the literature. Sulfur monochloride was freshly distilled, and used immediately. Diethylamino disulfide was synthesized by adding sulfur monochloride (0.1 mol) to a dichloromethane solution of diethylamine (0.4 mol) at 0 °C; bp 115 °C/6 mmHg. Dimethyl diazomalonate, diethyl diazomalonate, acetyldiazoacetone, methyl acetodiazoacetate and ethyl acetodiazoacetate were prepared by transdiazotization of corresponding carbonyl compounds with tosyl azide.[10] Ethyl diazoacetate,[11] diphenyldiazomethane (mp 31—32 °C; lit,[12] 29—33 °C) and ethyl azidoformate[13] were prepared according to the methods described in the literature.

Kinetics and Products. A 50 ml flask containing a mixture of 30 mmol of I, 5 mmol of II and 1 mmol of III was placed in a constant-temperature bath, and the amount of nitrogen evolved was determined by use of a gas buret. After the evolution of nitrogen ceased, a small amount of *n*-hexane was added to the mixture, and the ylid crystals formed were filtered and weighed. The melting points, IR and NMR spectra of the ylids obtained were identical with those reported in the literature.[14]

Reaction in an NMR Tube. A mixture of Ia (2.42 mmol), IIa (1.35 mmol) and IIIb (0.20 mmol) containing nitromethane (1.85 mmol) as the internal standard was placed in an NMR tube at 35 °C, and decreases of $(C\underline{H}_3)_2S$ (δ, 2.01 ppm) and $N_2C(CO_2C\underline{H}_3)_2$ (3.75 ppm) absorptions and increases of $(C\underline{H}_3)_2\overset{\oplus}{S}\text{–}\overset{\ominus}{C}(CO_2CH_3)_2$ (2.82 ppm) absorption were determined on the basis of the absorption of CH_3NO_2 (4.33 ppm).

Reaction between Dimethoxy Disulfide and Tetrahydrothiophene in an NMR Tube. When dimethoxy disulfide (3.2 mmol)

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[5] A. I. Vogel, *J. Chem. Soc.*, **1948**, 1822.

[6] Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich, and E. Pierron, *J. Org. Chem.*, **30**, 2692 (1965).

[7] A. Meusen, *Ber.*, **69**, 937 (1936).

[8] L. F. Fieser and M. Fieser, "Reagents for Organic Syntheses," Vol. 1, John Wiley, New York (1967), p. 1152.

[9] "Organic Syntheses," Coll. Vol. 3, p. 116.

[10] M. Rosenberg, P. Yates, J. Hendrickson, and W. Wolf, *Tetrahedron Lett.*, **1964**, 2285.

[11] "Organic Syntheses," Coll. Vol. 3, p. 392.

[12] "Organic Syntheses," Coll. Vol. 3, p. 351: J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

[13] R. S. Berry, D. Cornell, and W. Lwowski, *J. Amer. Chem. Soc.*, **85**, 1199 (1963).

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

and tetrahydrothiophene (3.0 mmol) were mixed at room temperature, the mixture turned orange yellow in a few minutes, and sulfur precipitated in about ten minutes. After 40 minutes, nitromethane was added as the internal standard, and the products were analyzed by means of their NMR absorptions. Reactants; $(CH_3OS)_2$, δ, 3.65 ppm, $(CH_2CH_2)_2S$, multiplets at 1.93 and 2.82 ppm: Products; $CH_3SO_2\underline{CH}_3$ (3.70 ppm, 0.48 mmol), $(CH_3O)_2SO$ (3.55 ppm, 0.50 mmol), $(CH_3O)_2SO_2$ (3.90 ppm, 0.10 mmol) and $(CH_3)_2O$ (3.20 ppm, 0.60 mmol).