

SYNTHESIS OF STABLE SULFONIUM AND SULFOXONIUM YLIDES via THERMAL- AND PHOTO-
-DECOMPOSITION OF DIAZO-CARBONYL COMPOUNDS IN SULFIDES AND SULFOXIDES.

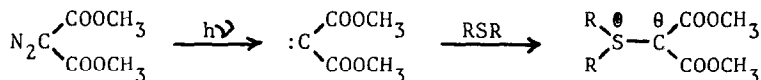
Wataru Ando, Tomio Yagihara, Shigeru Tozune,
Setuko Nakaido, and Toshihiko Migita

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

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Recent publications concerned with several different resonance-stabilized sulfonium ylides have covered their preparation and spectral properties, but relatively few of their chemical reactions have been described(1). Most recently we reported that photolysis of dimethyl diazomalonate in neat dimethyl sulfide gave the formation of dimethylsulfonium bis-carbomethoxymethylide(2).

We suggested the reaction involves the attack of the electrophilic single carbene formed by the photolysis of the diazo-compounds on a lone pair electron of the sulfur atom.



The work was extended to the studies on the photochemical and copper salt catalyzed thermal reactions of diazo-carbonyl compounds with various alkyl-, aryl-sulfides and sulfoxides, and we found that both reactions are quite useful for the synthesis of stable sulfonium and sulfoxonium ylides. In this paper we wish to describe the results.

Photolysis was carried out in Pyrex tubes with high pressure mercury lamp (3660 Å). In all cases the major products of the reactions were isolated in crystalline form, which was washed with petroleum ether(bp. 30-60°). These crystallines were proved to be stable sulfonium ylides by analytical and spectra data. The yields of the ylides and their physical properties are summarized in Table I.

Table I

The Formation of Sulfonium Ylides in the Reaction with Bis-carbonyl
Diazocompounds and Various Divalent Sulfides

Sulfide	Ylide	m.p. °C	n.m.r. (ppm)		Yield(%) ^(a,b)	
			(-SCH ₃)	(-COOCH ₃)	Photo.	Thermal
(CH ₃) ₂ S	(CH ₃) ₂ ^{⊙⊙} SCR ₂ ^(c)	169-170	2.89	3.71	88	75
(C ₂ H ₅) ₂ S	(C ₂ H ₅) ₂ ^{⊙⊙} SCR ₂	150	2.95, 1.30 [-CH ₂ -, -CH ₃]	3.76	57	71
(i-C ₃ H ₇) ₂ S	(i-C ₃ H ₇) ₂ ^{⊙⊙} SCR ₂	121	4.14, 1.40 [-CH-, -C(CH ₃) ₂]	3.69	20	--
CH ₃ SC ₂ H ₅	^{⊙⊙} CH ₃ -SCR ₂ C ₂ H ₅	144-145	2.84	3.70	40	48
CH ₃ S-n-C ₄ H ₉	^{⊙⊙} CH ₃ -SCR ₂ n-C ₄ H ₉	121-123	2.86	3.75	56	50
CH ₃ S-t-C ₄ H ₉	^{⊙⊙} CH ₃ -SCR ₂ t-C ₄ H ₉	86-87	2.90	3.69	40	--
CH ₃ SC ₆ H ₅	^{⊙⊙} CH ₃ -SCR ₂ C ₆ H ₅	126-127	3.25	3.78	40	83
CH ₃ SCH ₂ C ₆ H ₅	^{⊙⊙} CH ₃ -SCR ₂ C ₆ H ₅ CH ₂	157-159	2.77	3.68	39	56
(C ₆ H ₅) ₂ S	(C ₆ H ₅) ₂ ^{⊙⊙} SCR ₂	127-128	7.53 [-SC ₆ H ₅]	3.65	12	85
(CH ₃) ₂ S	(CH ₃) ₂ ^{⊙⊙} SCR ₂ ^(d)	134-135	2.88	4.17, 1.29 ^(d) [-CH ₂ -, -CH ₃]	87	--
(CH ₃) ₂ S	(CH ₃) ₂ ^{⊙⊙} SCR ₂ ^(e)	166-167	3.00	2.33 [-COCH ₃]	52	--

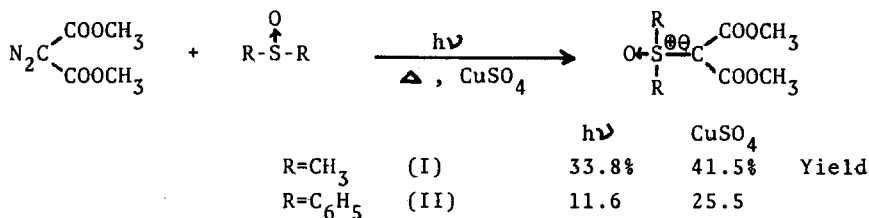
a. High pressure mercury lamp(3660 Å), b. Copper sulfate catalyzed thermal reaction. c. R=COOCH₃ d. R'=COOC₂H₅ e. R''=COCH₃

The table shows the photolysis of dimethyl diazomalonate in organic sulfides is a very good way for the synthesis of the corresponding sulfonium ylides.

However, the yields of ylides was not satisfactory in the reaction with highly branched sulfides and aryl or aralkyl sulfides. For example, the photolysis of dimethyl diazomalonate in di-t-butyl sulfide gave only trace amount of solid which was not isolated(3,4), while those in thioanisol, benzyl methyl sulfide and diphenyl sulfide, the yields of the corresponding stable sulfonium ylides were rather low. In all cases, however, there were no apparent carbon-hydrogen insertion products.

Meanwhile, we found the thermal decomposition of diazomalonate in sulfides in the presence of copper sulfate or copper metal powder also gave the corresponding stable sulfonium ylides(5). For example, the stable diphenylsulfonium bis-carbomethoxymethylide was obtained in the yield of 85% when a solution of dimethyl diazomalonate in diphenyl sulfide was heated at 90° for several hours in the presence of copper sulfate. The formations of other stable sulfonium ylides are also listed in Table I. It is interesting that the yields of arylsulfonium ylides under thermal conditions are higher than those under the photolytical conditions.

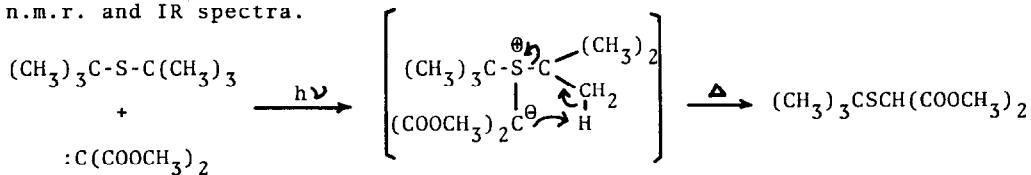
Reactions of dimethyl diazomalonate in sulfoxides were also studied. Irradiation of a solution of dimethyl diazomalonate in dimethyl sulfoxide was carried out in a Pyrex vessel with a high pressure mercury lamp(3660 Å). Dimethylsulfoxonium bis-carbomethoxymethylide(I) was obtained in a pure white solid by decantating unreacted dimethyl sulfoxide and washing the remaining solid with benzene in the yield of 33.8%, m.p. 157°, Anal. Calcd for $C_7H_{12}O_5S$: C, 40.38; H, 5.77; Found: C, 40.80; H, 5.88. This product showed two singlet n.m.r. signals at 3.64 ppm and 3.72 ppm in the equal intensity, and ir absorption maximum at 1640 cm^{-1} . Photolysis of dimethyl diazomalonate in diphenyl sulfoxide gave diphenylsulfoxonium bis-carbomethoxymethylide(II), m.p. 196-197°; n.m.r. signals at 3.40 and 7.77 ppm in the intensity ratio 3:5, ir absorption maximum at 1680 cm^{-1} ; Anal. Calcd for $C_{17}H_{16}O_5S$: C, 61.44; H, 4.81; Found: C, 61.21; H, 4.78.



Copper salt catalyzed thermal decomposition of dimethyl diazomalonate in dimethyl sulfoxide and diphenyl sulfoxide gave the corresponding sulfoxonium ylides in better yield than the photolytic conditions. Concerning the scope and limitation, further extensive studies are in progress.

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- (4) This unisolated sulfonium ylide may be thermally unstable and decompose under the conditions of gas chromatography. By analysis with vapor phase chromatography, several products were found in the reaction mixtures. Among them, dimethyl malonate and t-butylmercaptomalonate were identified based on their n.m.r. and IR spectra.



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