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Catalytic Decomposition of Stable Sulfur Ylids[1]

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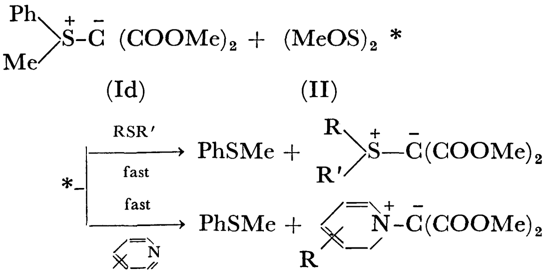
In the presence of dimethoxy disulfide, such stable sulfur ylids as $Me_2S^+{-}C^-(COOMe)_2$, $Me_2S^+{-}C^-(CN)_2$, and $Me_2S^+{-}C^-HCOPh$ were found to decompose at 35 °C, forming methyl sulfide and an olefin or a cyclopropane. Thiocyanogen and trifluoromethyl disulfide were found to possess similar catalytic activity. The scope and mechanism of these reactions are discussed.

Sulfur ylids possessing two electron-withdrawing substituents on the negatively-charged carbon atom are thermally stable, and their nucleophilicity is much less than that of mono-substituted sulfur ylids. Recently, we have reported that methylphenylsulfonium bis(methoxycarbonyl)methylid (Id) undergoes transylidation with alkyl sulfides and pyridines at 35 °C when dimethoxy disulfide (II) is present.[2]



It has been found that, when an alkyl sulfide or a pyridine is absent and II is present, Id slowly decomposes, yielding methyl phenyl sulfide and methyl ethylenetetracarboxylate almost quantitatively.

$$[\mathrm{Id}] + [\mathrm{II}] \xrightarrow{\text{slow}} \mathrm{PhSMe} + (\mathrm{MeOOC})_2\mathrm{C}{=}\mathrm{C}(\mathrm{COOMe})_2$$

The decompositions of ylids under acidic conditions[3] or at higher temperatures[4] have been reported, but the decomposition of thermally stable ylids under such mild conditions have never been reported yet. In order to clarify the mechanism of this reaction, the effects of catalysts and ylid substituents on the decomposition have now been studied; the results will be described in this paper.

Results and Discussion

In the absence of dimethoxy disulfide [II], the ylids [I] listed in Table 1 are stable for a long time at 35 °C and show no change. However, when equimolar amounts of I and II are mixed in, the decomposition of I takes place slowly.

Ic is a mono-substituted ylid; it decomposes much faster than di-substituted ylides, producing methyl sulfide and *trans*-1,2,3-tribenzoylcyclopropane. Disubstituted ylids (Ia, Ib, and Id) decompose slowly and give the corresponding sulfide and olefin. Two ylids containing acetyl groups (Ie: $Me_2S^+{—}C^-(COOMe)(COMe)$, If: $Me_2S^+{—}C^-(COMe)_2$) do not decompose under the same conditions.

Thiocyanogen $(SC{\equiv}N)_2$ and bistrifluoromethyl disulfide showed catalytic activity similar to that of II. The common feature in these sulfides is that the electron density on the –S–S– group is much lowered by the electron-withdrawing substituents:

$$\overset{\delta-}{\mathrm{MeO}}\leftarrow\overset{\delta+}{\mathrm{S}}—\overset{\delta+}{\mathrm{S}}\rightarrow\overset{\delta-}{\mathrm{OMe}} \qquad \overset{\delta-}{\mathrm{N}}{\equiv}\mathrm{C}\leftarrow\overset{\delta+}{\mathrm{S}}—\overset{\delta+}{\mathrm{S}}\rightarrow\mathrm{C}{\equiv}\overset{\delta-}{\mathrm{N}}$$

$$\overset{\delta-}{\mathrm{F_3C}}\leftarrow\overset{\delta+}{\mathrm{S}}—\overset{\delta+}{\mathrm{S}}\rightarrow\overset{\delta-}{\mathrm{CF_3}}$$

Trost reported that, when an ylid was heated with copper(II) sulfate, it quantitatively decomposed.[5] In order to explain this reaction, he proposed that the copper(II)-ylid complex is formed.

In order to compare the disulfide-catalyzed decomposition with the Cu(II)-catalyzed decomposition, Ia and Ib were heated under the conditions used by Trost. In the presence of Cu(II), Ia decomposed and formed the corresponding sulfide and olefin, but Ib did not decompose appreciably. Id slowly decomposed

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[1] Organic Sulfur Compounds. Part XLIII.

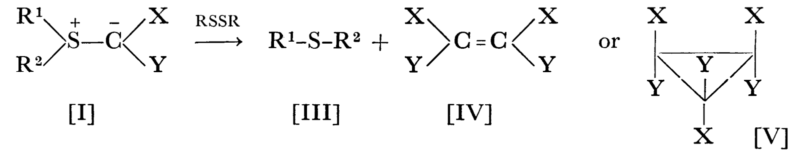
[2] H. Matsuyama, H. Minato, and M. Kobayashi, This Bulletin, **46**, 2845 (1973).

[3] T. Yagihara and S. Oae, *Int. J. Sulfur Chem.*, **A**, **1**, 159 (1971).

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

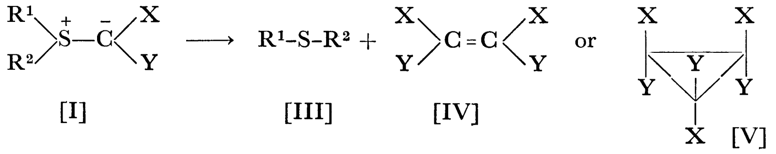
[5] B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967).

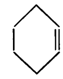
TABLE 1. DECOMPOSITION OF STABLE SULFUR YLIDS IN THE PRESENCE OF A CATALYTIC DISULFIDE IN $CDCl_3$ AT 35°C



	I				Catalyst	Time (hr)	Products (mol%)			
	R^1	R^2	X	Y			Recovered I	III	IV	V
Ia	Me	Me	COOMe	COOMe	$(MeOS)_2$	21	—	93	88	—
Ib	Me	Me	CN	CN	$(MeOS)_2$	4	36	64	46	—
					$(N\equiv CS)_2$	27	8	83	57	—
					$(F_3CS)_2$	67	36	60	50	—
Ic	Me	Me	H	COPh	$(MeOS)_2$	1	—	95	—	90
Id	Ph	Me	COOMe	COOMe	$(MeOS)_2$	24	—	98	92	—

TABLE 2. THERMAL AND Cu(II)-CATALYZED DECOMPOSITION OF SULFUR YLIDS[a)]



Ylid	Solvent	Catalyst[b)]	Temp. (°C)	Time (hr)	Products (mol%)			
					Recovered I	III	IV	V
Ia	$CHCl_3$	$CuSO_4$	62	48	30	60	60	—
Ib	$CHCl_3$	$CuSO_4$	62	48	92	—	—	—
Ic	$CHCl_3$	—[c)]	62	144	100		No Reaction	
		$CuSO_4$[c)]	83	24	—	90	—	90
Id	CH_3NO_2	—	86	48	80	18	18	—
	—	—[d)]	155	>20		Rearrangement		

a) When a solvent was used, [I] was about 0.5 M. b) Molar ratio, $CuSO_4$: I, was about 2. c) Ref. 5; benzoylnorcarane was found in 4.9% yield. d) Ref. 4; the Stevens-type product, $PhSC(CH_3)(COOCH_3)_2$, was found in 10% yield.

TABLE 3. RATES OF DECOMPOSITION OF Ia IN THE PRESENCE OF II IN $CDCl_3$ AT 35°C

$Me_2S^+—C^-(COOMe)_2 + (MeOS)_2 \rightarrow$
[Ia] [II]
$Me_2S + (MeOOC)_2C{=}C(COOMe)_2$

Concentration (mol/l)		[II]/[Ia]	First-order Rate Constant[a)] 10^5k_1 (s^{-1})
[Ia]	[II]		
0.46	0.45	1.0	0.7
0.46	0.91	2.0	1.8
0.46	1.82	4.0	8.3
0.46	2.73	6.0	19.0

a) Calculated from $-d[Ia]/dt = k[Ia]$.

even in the absence of $CuSO_4$. The results are shown in Table 2.

When Tables 1 and 2 are compared, it is clear that the disulfide-catalyzed decomposition proceeds much faster under milder conditions than the Cu(II)-catalyzed decomposition.

Then, the effect of the concentration of IIa on the rate of the decomposition of Ia was examined; the results are shown in Table 3. The first-order rate constants for the decomposition of Ia were greater when the concentration of IIa was greater.

The results of the investigations of the disulfide-catalyzed transylidation and decomposition of ylids can be summarized as follows:

1) Disulfides containing electron-withdrawing substituents catalyze both the transylidation and decomposition.

2) The rates of both reactions increase with the concentration of catalytic disulfide.

3) The catalytic disulfide does not decompose during the reaction.

4) The order of reactivity for transylidation[2)] is:

$$R_2S^+—C^-(COOMe)_2 > R_2S^+—C^-(COOMe)(COMe) \gg R_2S^+—C^-(COMe)_2$$

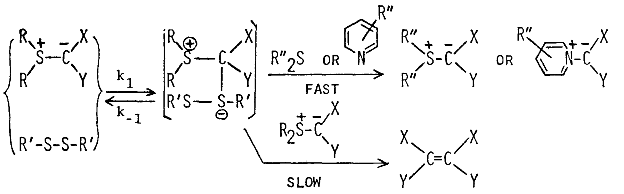
and that for decomposition is:

$$R_2S^+—C^-HCOPh > R_2S^+—C^-(COOMe)_2 \approx R_2S^+—C^-(CN)_2 \gg R_2S^+—C^-(COOMe)(COMe)$$

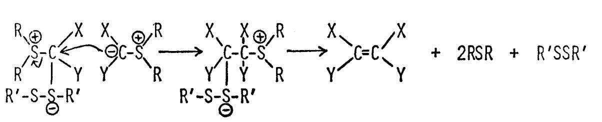
and $R_2S^+—C^-(COMe)_2$

These orders are similar to the order of the nucleophilicity of the negatively-charged carbon atom of ylids.

The transylidation and ylid decomposition may be expressed by the following scheme, involving a disulfide-ylid adduct:



When an alkyl sulfide or pyridine is present, their nucleophilic attack on the adduct takes place rapidly, and the corresponding new ylid is formed. When such a powerful nucleophile is absent, the ylid itself functions as a nucleophile, the nucleophilic attack of the negatively-charged carbon atom of the ylid on the adduct results in the C–C bond formation, and the corresponding olefin is obtained. This process may be represented as follows:



As Table 1 shows, Ic decomposed very rapidly. This is reasonable, because the mono-substituted ylid with great nucleophilicity must form the adduct readily; furthermore, the nucleophilic attack of Ic on the adduct must be faster than that of di-substituted ylids. Since Ic is known to undergo a Michael addition with dibenzoylethylene,[5] the olefin formed by the decomposition-dimerization of Ic reacts with another molecule of Ic faster than the adduct, and *trans*-1,2,3-tribenzoylcyclopropane is the final product.

The nucleophilicity of Ia and Ib is much smaller, and the olefins formed do not receive any further nucleophiclic attack of ylids. Two ylids, Ie and If, which did not decompose under the reaction conditions, underwent transylidation extremely slowly. The nucleophilicity of these ylids is very small, the adduct is formed to a very small extent, and both the transylidation and ylid decomposition take place very slowly.

Experimental

Materials. The ylids (Ia, Ib,[6] Ic,[5] Id,[4] Ie, and If[7]), dimethoxy disulfide,[8] and thiocyanogen[9] were synthesized according to the procedures described in the literature. Bistrifluoromethyl disulfide was synthesized by the reaction between trichloromethanesulfenyl chloride and sodium fluoride in sulfolane.[10]

Decomposition of Ib in the presence of Thiocyanogen. A chloroform solution (50 ml) of Ib (1.15 g, 9.14 mmol) was mixed with thiocyanogen (3.0 g, 0.66 mmol; dissolved in CCl_4) in a 50-ml, egg-shaped flask at 35 °C. The disappearance of Ib (Me_2S^+—, δ, 2.80 ppm) and the formation of Me_2S (δ, 2.10 ppm) were followed by use of NMR spectroscopy. When the Me_2S^+— signal completely disappeared, the reaction mixture was concentrated with a rotatory evaporator. The residue was chromatographed (Wakogel Q-22, 200 mesh), and with a benzene-ether (1 : 1) mixture 0.66 g of tetracyanoethylene (5.2 mmol, 57%) was obtained. Sublimation gave 0.49 g (3.8 mmol, 42%), melting at 197—199 °C (lit,[11] 200 °C) and possessing the same infrared spectrum as that of an authentic sample.[12]

The Decomposition of Id in the Presence of II. A mixture of Id (0.85 g, 3.33 mmol), nitromethane (20 ml), and II (0.54 g, 4.32 mmol) in a 50-ml, egg-shaped flask was placed in a constant-temperature bath at 35 °C. The decrease in Id ($PhMeS^+$–, δ, 3.26 ppm) and the increase in PhSMe (δ, 2.50 ppm) were followed by NMR spectroscopy, using 1,1,2,2-tetrachloroethane as the internal standard. The chromatographic separation of the residue gave 0.40 g (3.08 mmol, 92%) of methyl ethylenetetracarboxylate. Its identity was established by a comparison of its infrared absorptions ($\nu_{C=O}$, 1740 cm^{-1}), mp (121—122 °C) and gas-chromatographic retention time (Carbowax 20 M, 10%, 2 m, 200 °C) with those of an authentic sample synthesized by the copper-catalyzed decomposition of methyl diazomalonate.

The Decomposition of Ic in the Presence of II. The reaction in a mixture of Ic (0.54 g, 3.0 mmol), nitromethane (20 ml), and II (0.63 g, 5.0 mmol) at 35 °C was followed by NMR spectroscopy, with 1,1,2,2-tetrachloroethane as the internal standard. After evaporation and chromatography, *trans*-1,2,3-tribenzoylcyclopropane was obtained; Yield, 0.32 g (0.27 mmol, 90%); mp 214—216 °C (lit,[13] 215 °C); IR ($\nu_{C=O}$ 1670 cm^{-1}); NMR, identical with that reported in the literature.[14]

The $CuSO_4$-Catalyzed Decomposition of Ia. A mixture of Ia (1.74 g, 9.04 mmol), chloroform (20 ml), and anhydrous $CuSO_4$ (3.42 g, 21.4 mmol) was refluxed for 48 hr. When the $CuSO_4$ was filtered and the solvent was evaporated, white solids remained. Their IR absorptions indicated the presence of methyl ethylenetetracarboxylate ($\nu_{C=O}$, 1740 cm^{-1}) and Ia ($\nu_{C=O}$, 1620—1660 cm^{-1}). The amount of Ia was determined by NMR, using nitromethane as the internal standard. Methyl ethylenetetracarboxylate was separated by column chromatography and determined by gas chromatography (5.42 mmol, 60%).

The Thermal Decomposition of Id in the Absence of a Catalyst. A mixture of Id (0.20 g, 0.77 mmol) and nitromethane (10 ml) in a 50-ml flask was heated at 86 °C for 48 hr. After the mixture had been concentrated, the amounts of methyl phenyl sulfide (0.14 mmol, 18%) and the remaining Id (0.62 mmol, 80%) were determined by NMR spectroscopy, using 1,1,2,2-tetrachloroethane as the internal standard.

The Determination of the Rate of Decomposition of Ia. A $CDCl_3$ solution of Ia (0.320 mmol) and a suitable amount of dimethoxy disulfide were mixed in an NMR tube. After nitromethane (0.79 mmol; δ, 4.33 ppm) had been added as the internal standard, more $CDCl_3$ was added with a microsyringe so that the total volume became 700 μl. The disappearance of Ia was followed by observing the decrease in Me_2S^+– (δ, 2.89 ppm).

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