The Preparation and Reactions of α-Thiocarbonyl Dimethyloxosulfonium Ylides

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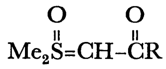
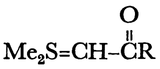
α-Thiocarbonyl dimethyloxosulfonium ylides IIIa—e were prepared in moderate yields. The ester-stabilized ylides, IIIa—c, were mixtures of *E* and *Z* isomers, and IIIe was *Z*. The methylation of III with methyl iodide gave *S*-methylated products, IV, in quantitative yields. The thermal decomposition of IVa and IVe gave I(R=Me) and V respectively in good yields. The treatment of IIIb—e with carbon disulfide afforded 1,2-dithiole-3-thiones VIIIb—e in moderate yields.

The physical and chemical properties of carbonyl-stabilized sulfur ylides, such as I and II, have been widely studied in recent years.



$Me_2\overset{O}{\overset{\|}{S}}{=}CH{-}\overset{O}{\overset{\|}{C}}R$

I



$Me_2S{=}CH{-}\overset{O}{\overset{\|}{C}}R$

II

In the course of our studies of α-thiocarbonyl-stabilized[1] *P*- and *S*-ylides and imines, we have found interesting results on α-thiocarbonyl-stabilized dimethyloxosulfonium ylides, III. Here we will report our experimental observations of the structure and reactions of III. Some α-thiocarbonyl-stabilized sulfonium ylides are isolated as unstable compounds.[2]

Results and Discussion

Preparation of Ylides, III. A number of carbonyl-stabilized ylides, I, have previously been prepared from dimethyloxosulfonium methylide with such acylating reagents as acid chloride, acid anhydride, and alkyl carboxylate.[3] However, the reaction of dimethyloxosulfonium methylide with such thionoesters as dimethyl trithiocarbonate or methyl dithiobenzoate gives olefinic products.[4] We also could not isolate any ylide from the reaction of dimethyloxosulfonium methylide with alkyl xanthates. However, the action of the methylide with thioacylating reagents, such as xanthic anhydride, tetramethylthiuram monosulfide, and thiobenzoyl chloride, afforded α-thiocarbonyl dimethyloxosulfonium methylides, IIIa—e, in moderate yields (Table 1). The use of good leaving groups may give the expected products.

$$Me_2\overset{O}{\overset{\|}{S}}{=}CH_2 + R\overset{S}{\overset{\|}{C}}X \longrightarrow Me_2\overset{O}{\overset{\|}{S}}{=}CH{-}\overset{S}{\overset{\|}{C}}R + Me_3\overset{O}{\overset{\|}{S}}{}^{\oplus}\,X^{\ominus}$$

IIIa—e

	a	b	c	d	e
R:	MeO	EtO	*i*-PrO	Me_2N	Ph

$X{=}RCS_2$ or Cl

Structure and Methylation of IIIa—e. Evidence for the resonance interaction of ylide carbanion with a thiocarbonyl group can be obtained by an examination of the infrared spectra of thioacyl ylides, III. The S=O and C=S streching frequencies of III occurred at 1020—1030 and 1160—1190 cm^{-1} respectively, as is shown in Table 1. Considering the C=S stretching frequencies of the model compounds (*O*-ethyl thioacetate (1250—1260 cm^{-1}),[5] diaryl thioketone (≈1220 cm^{-1}),[6] dialkyl thioketones (≈1260 cm^{-1}),[7] *N*,*N*-dimethylthioacetamide(1122 cm^{-1})[8]], the shift of 50—100 cm^{-1} for IIIa—c,e may be attributed to the increased single-bond character to the delocalization of the carbanion electrons through the thiocarbonyl groups (*i.e.*, betain forms). A shift to the higher frequency for IIId may diminish the

Table 1. Preparation of III's and their physical properties

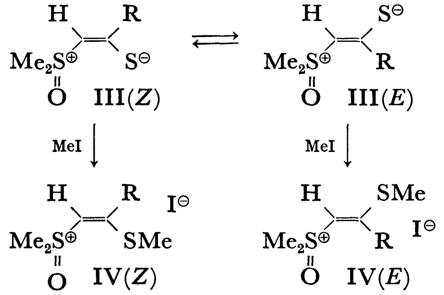
		IIIa		IIIb		IIIc		IIId	IIIe
Acylating reagent		$(MeOCS)_2S$		$(EtOCS)_2S$		$(i\text{-}PrOCS)_2S$		$(Me_2NCS)_2S$	PhCSCl
Yield (%)		35		60		60		38	30
Mp (°C)		67.5—70.5		76.5—78.5		120.5—122		124—125	140
IR (KBr) cm^{-1}	$\nu_{S=O}$	1030		1025		1025		1015	1020
	$\nu_{C=S}$	1125		1145		1135		1165	1180
NMR ($CDCl_3$)	Conf.	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*Z*
	(%)	33	67	30	70	28	72	100	100
	CH	5.21	4.90	5.20	4.88	5.16	4.80	4.18	6.04
	$SOMe_2$	3.35	3.63	3.38	3.68	3.32	3.68	3.72	4.12
	R	3.98	3.87	4.59q	4.41q		5.57sept	3.24	7.7—8.3m
	(*J*(Hz))			1.44t (7.0)	1.32t (7.0)	1.41d (6.5)	1.27d (6.5)		
Found (%) (Calcd)	C	36.01 (36.12)		39.79 (39.97)		43.38 (43.27)		40.25 (40.19)	56.33 (56.57)
	H	6.15 (6.06)		6.80 (6.71)		7.40 (7.26)		7.16 (7.31)	5.54 (5.70)
	N							7.59 (7.81)	

Table 2. Physical properties of IV

		IVa		IVb		IVc		IVd	IVe
Mp (°C)		114—5		108—9		96—8		126—8	104—6
Conf.		*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*Z*
(%)		42	58	39	61	26	74	100	100
NMR δ	CH	6.62	6.13	6.64	6.24	6.68	6.28	5.86	7.15
	$SOMe_2$	4.08	4.03	4.12	4.08	4.04	3.99	3.98	4.39
	SMe	2.47	2.77	2.49	2.78	2.40	2.75	2.50	2.23
	R	4.18	4.15	4.48q	4.51q		5.03sept	3.35	7.4—7.9m
	(J(Hz))			1.48t (7.0)	1.50t (7.0)	1.54d (6.5)	1.48d (6.5)		

double-bond character of the thioamide resonance form, $\overset{\ominus}{S}\!>\!C{=}\overset{\oplus}{N}Me_2$. This observation accords with the appearance of only one peak for two *N*-methyl groups in the NMR spectrum of IIId.[9]

The structure of the III ylide was confirmed on the basis of NMR spectroscopic studies and methylation reaction. These ylides, IIIa—e, reacted easily with methyl iodide to give only *S*-methylation products, IVa—e, in good yields. IIIa—c were mixtures of *E* and *Z* isomers, while IIId,e were composed of only *Z* isomers.



The NMR spectra of the carbonyl-stabilized sulfur ylides, I and II, have been widely studied in recent years. Much of this interest has involved the observation of geometrical isomers in these compounds.[4] Ester-stabilized ylides, I(R=alkyl-O)[10] and II(R=alkyl-O),[11] are known to be mixtures of *E* and *Z* isomers at lower temperatures.

The NMR spectra of ester-stabilized ylides, IIIa—c, at 34.5 °C showed peaks of two groups corresponding to the *E* and *Z* isomers. The stereochemistry of IIIa—c was assigned on the assumption that the methine proton *cis* to the thiolate sulfur may appear at a higher field than the methine proton *trans* to the thiolate sulfur as a result of the anisotropic shielding by the thiolate sulfur.[12] The results are shown in Table 1. The *E* isomers are much more favored than the *Z* isomers in $CDCl_3$. The methylation reactions of IIIa—c with methyl iodide to give IVa—c also support the structure determination of IIIa—c. The stereochemistry of the methylation products, IVa—c, was assigned on the basis of the chemical shifts of the vinyl protons using the values of Pascuel, Meier, and Simon.[13] Table 2 indicates that the *Z*/*E* ratio for IVc agrees well with that for IIIc. The marked deviation of the *Z*/*E* value for IVa, b from that of IIIa, b is caused by the partial decomposition of IVa, b during the methylation reaction, since IVa, b decomposes much faster than does IVc (the thermal decomposition of IVa—c will be described later). As a result, IIIa—c and IVa—c exist mainly in *E* forms.

Table 3. Solvent effects on the *Z*: *E* isomer ratios in IIIa-c at 34.5 °C

Solvent (ε)	IIIa *Z*:*E*	IIIb *Z*:*E*	IIIc *Z*:*E*
PhH (2.27)	16:84	15:85	16:84
$CDCl_3$ (4.7)	33:67	30:70	28:72
PhCl (5.61)	16:84	18:82	21:79
PhCN (25.2)	33:67	34:66	36:64
$PhNO_2$ (34.8)	28:72	32:68	38:62

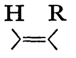
The *Z*/*E* isomer ratios for IIIa—c in a variety of solvents at 34.5 °C are summarized in Table 3.

The solvent effect on the isomer ratios for ester-stabilized *P*-ylides has been widely studied.[14] The population of the *E* isomer increases consistently with an increase in the solvent polarity and with the bulkiness of the alkoxyl group; also, the *Z*/*E* ratio is governed by the dipole interaction between $P^{\oplus}$ and $O^{\ominus}$, and by the solvation of the carbonyl group.

Unlike the ester-stabilized *P*-ylides, the oxosulfonium ylides, IIIa—c, show no solvent dependence (Table 3), and *E* isomers were favoured in all the solvent used. Some keto-stabilized *S*-ylides have been shown to be mixtures of *E* and *Z* isomers.[10] Simple *keto*-stabilized ylides, such as I (R=Me, Ph)[10] and II(R=Ph),[15] show no evidence of the restricted rotation on the NMR spectra; however, they are believed to be *Z* isomers, since the following reasons may favor the *Z* form: i) steric repulsion between the sulfonium and R groups, and ii) electrostatic attraction between the positive sulfur and the negative enolate oxygen. Moreover, the alkylation of *keto*-stabilized sulfur-ylides[15,16] with trialkyloxonium tetrafluoroborate gives a mixture of *E* and *Z* *O*-alkylation products. This result indicates that the alkylation reaction does not necessarily support the presence of rotational isomers.

The methylation of IIId, e with methyl iodide gave only one isomer in quantitative yields (Table 2). The isomer was supposed to be *Z* on the basis of the following two results.

Some reports[17] show the good correlation between the chemical shifts of olefinic protons situated at the *cis* position to R and Hammett's σ_p for R:



Similar treatments for IIIa—e and IVa—e (Figs. 1 and 2) gave straight lines for IIIa—c (*Z*), and IIId,e and for IVa—c (*Z*), and IVd,e respectively.

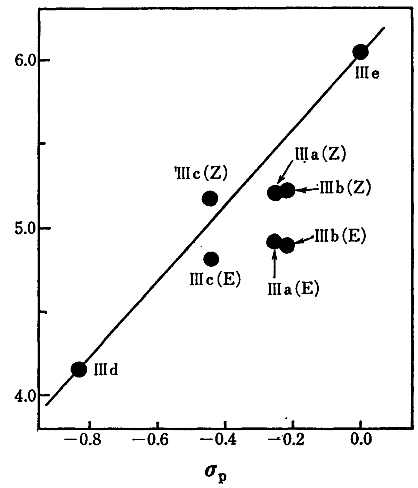


Fig. 1. Hammett's plot of δ_{CH} of ylides III.

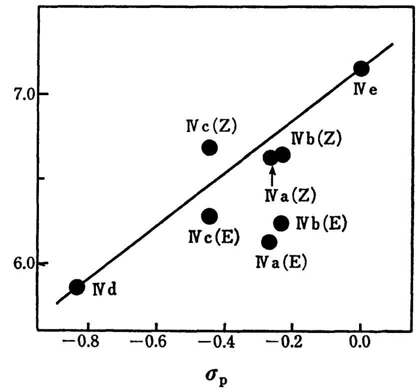
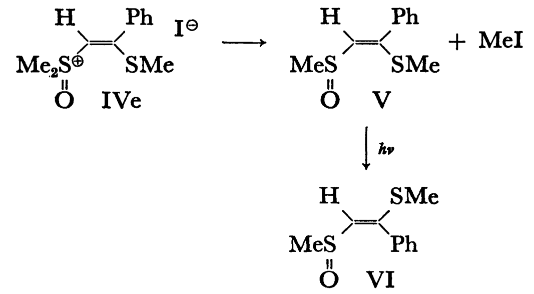


Fig. 2. Hammett's plot of δ_{CH} of oxosulfonium ions IV.

Another result is the decomposition of IVe. Compound IVe was stable in the crystalline state, but it decomposed entirely in a chloroform solution after 24 h at 34.5 °C to give vinyl sulfoxide(V) and methyl iodide in quantitative yields. Compound V(mp 68.5—70 °C) showed one *S*-methyl peak at δ 2.06, SOMe at 2.76, and an olefinic proton at 6.61 in the NMR spectrum. On UV irradiation V gave new peaks at 2.41 (SMe), 2.66 (SOMe), and 6.15 (olefinic proton). Fractional crystallization afforded VI with a mp of 138—140.5 °C, which again gave V on irradiation. The V: VI equilibrium ratio was 1 : 2. Using the values of Pascuel, Meier, and Simon[13] for the chemical shifts of the vinyl protons, the vinyl sulfoxides, V and VI, were confirmed to be the Z and *E* isomers respectively. Thus, we confirmed IIIe to be the *Z* isomer.



Compound IVd decomposed entirely at 40 °C for 3 days in chloroform to give a mixture of unidentifiable compounds (NMR and TLC). IVa, on the other hand, decomposed easily in $CDCl_3$ at 34.5 °C for 20 h to give a new carbonyl-stabilized ylide, I(R=SMe), and methyl iodide in quantitative yields. Although IVb,c also decomposed at 34.5 °C for 3 days to yield a mixture of I (R=SMe) and vinyl sulfoxides (NMR study), no effort was made to isolate them.

Reaction of III with Carbon Disulfide. A number of reactions of sulfur ylides with olefins and carbonyl compounds have been reported.[18] The reactions of IIIb with dimethyl fumarate or maleate failed, since the reagents were recovered after 48 h in THF at reflux. It has been reported that II(R=Ph)[2] reacts with carbon disulfide to give a 1,3-dithiane derivative in chloroform and a 1,2,4-trithiole derivative in ethanol.

The IIIb—e ylides reacted easily with carbon disulfide, even at room temperature, to give 1,2-dithiole-3-thione, VII, in moderate yields (Table 4). The products were confirmed to be VII, by comparison with known samples (VIId,e) and by analyses (VIIb,c) not 1,3-dithiole-2-thione. No crystalline compound was isolated from a reaction mixture of IIIa and carbon disulfide.

The reactivity of III decreased in this order; IIId> IIIb,c>IIIe. This is also the order of the pK_a values of

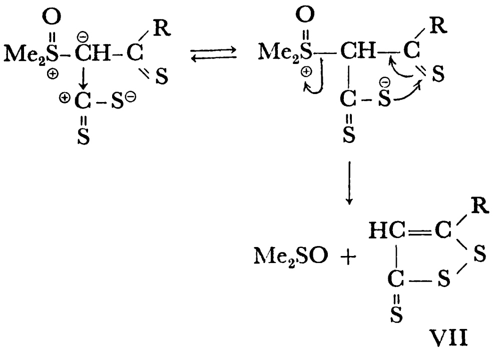


TABLE 4. YIELDS AND PHYSICAL PROPERTIES OF VII'S

		VIIb	VIIc	VIId	VIIe
Yield (%)		27	18	55	48
Mp (°C)		82—82.5	59.5—60.5	199—201	124.5—126.5
IR (KBr) cm^{-1}	$\nu_{C=S}$	1180	1190	1190	1180
NMR Solvent		$CDCl_3$	CCl_4	$CDCl_3$	$CDCl_3$
δ	CH	6.66	6.62	6.46	7.27
	R	4.27q	4.72sept	3.22	7.5—7.8m
	(*J*(Hz))	1.49t (7.1)	1.48d (6.5)		

a) Ref. 20. b) Ref. 21.

the conjugate acids of ylide carbanions.[19] Thus, the reaction of III with carbon disulfide may proceed as is shown below to give stable 6π compounds, VII.

Experimental

Preparation of III. Method A (in a mixture of DMSO and THF). Dimethyloxosulfonium methylide (0.15 mol) in DMSO (25 ml) was prepared from DMSO, NaH (0.15 mol), and trimethyloxosulfonium iodide (0.15 mol) according to the literature.[3] To a solution diluted with 70 ml of dry THF, we added methylxanthic anhydride (0.075 mol) in 15 ml of THF, portion by portion, for 15 min in an ice-water bath; stirring was then kept up for 2 h. The resulting mixture was quenched in ice water and extracted with 200 ml of chloroform. The chloroform extract was dried over magnesium sulfate and condenced *in vacuo* to give an oily product, which gave crystals (IIIa) from chloroform–petroleum ether. The yield and physical properties are shown in Table 1.

IIIb—e were prepared similarly.

Method B(in THF). Dimethyloxosulfonium methylide (0.15 mol) in THF (250 ml) was prepared from trimethyloxosulfonium chloride and NaH according to the literature.[3] To the solution we added tetramethylthiuram monosulfide (0.075 mol) in benzene (50 ml), portion by portion, at room temperature. The reaction mixture was stirred for 24 h, and then the precipitates were filtered off. The filtrate was condensed and chromatographed over silica gel with benzene–ethyl acetate (2: 1 v/v) to give IIId.

Reaction of III with Methyl Iodide. A solution of III in chloroform was treated with an excess of methyl iodide at room temperature for a few hours. The addition of benzene to the solution afforded IV in good yields (Table 2).

The decomposition of IV was run in $CDCl_3$ at 34.5 °C, the process being followed by NMR spectroscopy. IVa gave ylide I(R=SMe) and methyl iodide in quantitative yields after one day. I(R=SMe): Mp 109—110 °C (chloroform–ether). NMR (δ in $CDCl_3$): 2.30 (s, 3H, MeS), 3.42 (s, 6H, Me_2S), and 4.54 (s, 1H, C$\underline{H}$-CO). Found: C, 36.01; H, 5.92%. Calcd for $C_5H_{10}O_2S_2$: C, 36.12; H, 6.06%.

IVe gave V in about a 90% yield and methyl iodide in a quantitative yield. V: Mp 68.5—70 °C (ether). NMR (δ in $CDCl_3$): 2.06 (s, 3H, SMe), 2.76 (s, 3H, SOMe), and 6.61 (s, 1H, C$\underline{H}$=C). Found: C, 56.03; H, 5.97%. Calcd for $C_{10}H_{12}OS_2$: C, 56.57; H, 5.70%.

Photoisomerization was run in $CDCl_3$, with the NMR spectral change being followed. On irradiation with a high-pressure mercury lamp, V gave an equilibrium mixture of V and VI (1: 2) after 18—20 h. Subsequent condensation and the addition of a small amount of petroleum ether afforded VI. VI: Mp 138—140.5 °C. NMR (δ in $CDCl_3$): 2.41 (s, 3H, SMe), 2.66 (s, 3H, SOMe), and 6.15 (s, 1H, C$\underline{H}$=C). Found: C, 56.43; H, 5.57%. Calcd for $C_{10}H_{12}OS_2$: C, 56.57; H, 5.70%.

A similar irradiation of VI in $CDCl_3$ afforded again a mixture of V and VI (1: 2).

The Reaction of III with Carbon Disulfide. A solution of IIIb (1.0 g) and carbon disulfide (2.0 g) in chloroform (20 ml) was refluxed for 3 h in a stream of nitrogen. The resulting mixture was condensed and chlomatographed over silica gel with hexane–ethyl acetate (6: 1). VIIb was isolated and crystallized from benzene–ether. Yield, 0.27 g; Mp 82—82.5 °C. Ms: 178(M^+).

VIIc was similarly isolated. VIIc: Mp 59.5—60.5 °C. MS: 192 (M^+). Found: C, 37.56; H, 4.22%. Calcd for $C_6H_8OS_3$: C, 37.50; H, 4.17%.

VIId, e were isolated from a crude reaction mixture and confirmed by comparison with known samples.[20,21] The results are collected in Table 4.

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