The Thermal Decomposition of *N*-Thiocarbonyl Diphenylsulfimides

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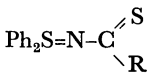
N-Thiocarbonyl diphenylsulfimides, Ia—i (R=Ph, *p*- and *m*-MeC_6H_4, *p*- and *m*-$MeOC_6H_4$, MeO, EtO, MeNH, and Me_2N), were prepared, and their thermal decomposition were studied. At 70 °C, Ia—h decomposed easily to give nitriles (or their derivatives), together with diphenyl sulfide and sulfur. Contrary to these results, the oxygen analog of Ia, g showed no decomposition even upon heating at 140 °C. The thermolysis of Ia—e in the presence of excess acetylenes(III) gave isothiazoles(IV) in moderate yields. Thiazirine(V) and nitrile sulfide(VI) may be supposed, on the basis of the kinetic experiments, to be possible intermediates for the thermal decomposition of Ib—e.

Recently a number of workers have reported on the preparation and reactions of free sulfimides[1-3] and their *N*-substituted derivatives, such as *N*-acetyl,[2,4,5] and *N*-tosyl.[3,6,7] In the course of our studies of the thiocarbonyl-stabilized *P*- and *S*-ylides and imides, we have found an interesting thermal decomposition of *N*-thiocarbonyl diphenylsulfimides(I):



I

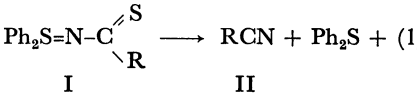
We wish to report here on the thermal decomposition of I in the presence and in the absence of acetylenes(III).

Results and Discussion

It has been reported that free diphenylsulfimide reacts with acylating reagents, such as acid chloride and acid anhydride, to give *N*-acylsulfimides.[1,2] Here we have found the reactions of free diphenylsulfimide with methyl dithiobenzoates and xanthates to give *N*-thiocarbonyl substituted sulfimide(I) in moderate yields. The results are shown in Table 1. The sulfimides, Ia—e, decomposed slowly, even at room temperature.

The thermal decomposition of some sulfimides which have α- or β-hydrogen has been studied.[4-6] The thermolysis of *N*-acetyl dialkylsulfimide having β-hydrogen gives olefin and *N*-(alkylthio)acetamide.[4,5] However, *N*-acetyl dimethylsulfimide gives dimethyl sulfide, bis-(methylthio)methane, *N,N'*-methylenebisacetamide, and *N,N',N''*-methylenetrisacetamide, which are formed by a mechanism involving a Pummerer-type rearrangement.[4,5]

N-Benzoyl and ethoxycarbonyl diphenylsulfimides (oxygen analogs of Ia and Ig) were highly stable, and did not decompose even under heating at 140 °C for 10 h. Contrary to these results, *N*-thiocarbonyl sulfimides(I) were thermally unstable, as is shown in Table 1. All the reaction products were identified by comparing their NMR and IR spectra with those of the authentic samples. Generally *N*-thiocarbonyl sulfimides(I) decomposed to give nitriles(II) (or their derivatives), together with diphenyl sulfide and sulfur. The thermolysis of If and Ig gave methyl and ethyl cyanates respectively as the initial products (NMR observation),



I II

but they easily rearranged to isocyanates and trimerized to tri(alkyl isocyanates). The instability of alkyl cyanates is well known.[8]

The thermolysis of Ia—e in the presence of excess acetylenes(III) gave isothiazoles(IV), together with nitrile(II), diphenyl sulfide, and sulfur. The structure of IV was confirmed by comparing the NMR and IR spectra with those of the authentically prepared samples and by elemental analyses (Table 2).

Table 1. Preparation and thermal decomposition of I

	R	Acylating reagent	Yield (%)	Mp (°C)	NMR (δ in $CDCl_3$) R[a]	Thermal decomposition at 70°C: Solvent	Time (min)	Product[b] (Yield %)
Ia	Ph	RCS_2Me	38	109—112		PhH	5	RCN(95)
Ib	*p*-MeC_6H_4	RCS_2Me	58	107	2.38(Me)	PhH	5	RCN(93)
Ic	*m*-MeC_6H_4	RCS_2Me	45	90—91	2.34(Me)	PhH	5	RCN(96)
Id	*p*-$MeOC_6H_4$	RCS_2Me	45	117—119	3.80(MeO)	PhH	5	RCN(97)
Ie	*m*-$MeOC_6H_4$	RCS_2Me	49	68—70	3.74(MeO)	PhH	5	RCN(95)
If	MeO	RCS_2Me	37	87—88	4.02(Me)	PhH	15	$(MeNCO)_3$(67), MeNCO(27)
Ig	EtO	RCS_2Me	34	78—79	1.37(t, Me, J=7) 4.45(q, CH_2)	PhH	15	$(EtNCO)_3$(45), EtNCO(37)
Ih	MeNH	MeNCS	44	130—131	3.03 (d,Me, J=5) 6.35(d, H)	$CHCl_3$	200	$(MeNHCN)_3$(75)
Ii	Me_2N	RCSCl	42	156—157	3.35(Me_2N)	$CHCl_3$	900	Recovery

a) Phenyl ring protons were observed at 6.7—8.5 as multiplets. b) Diphenyl sulfide and sulfur were obtained in quantitative yields.

Table 2. Physical properties of isothiazoles IV

	IV Ar	IV R′	Mp (°C)[a]	MS (M^+)	Anal % Found (Calcd) C	H	N	NMR (δ in $CDCl_3$)
IVa	Ph	CO_2Me[b]	73(A)	277	55.87 (56.32)	3.92 (4.00)	4.87 (5.05)	3.82 (s, MeO), 3.84 (s, MeO), 7.1—7.7 (m, Ar)
	Ph	COPh	149—150(B)	369	75.11 (74.79)	4.05 (4.09)	3.72 (3.79)	7.2—8.5 (m, Ar)
IVb	*p*-MeC_6H_4	CO_2Me[c]	91—92(A)	291	57.48 (57.73)	4.58 (4.50)	4.62 (4.82)	2.33 (s, Me), 3.83 (s, MeO), 3.84 (s,MeO), 6.9—7.5 (m, Ar)
	p-MeC_6H_4	COPh	142—143(B)	383	75.19 (75.18)	4.21 (4.47)	3.67 (3.65)	2.20 (s, Me), 6.9—8.0 (m, Ar)
IVc	*p*-$MeOC_6H_4$	CO_2Me	88—90(A)	307	54.65 (54.72)	3.93 (4.26)	4.03 (4.56)	3.63 (s, MeOPh), 3.73 (s, 2MeOCO) 6.7—7.5 (m, Ar)
	p-$MeOC_6H_4$	COPh	166—168(B)	399	72.30 (72.17)	4.13 (4.29)	3.49 (3.51)	3.57 (s, MeO), 6.7—7.8 (m, Ar)

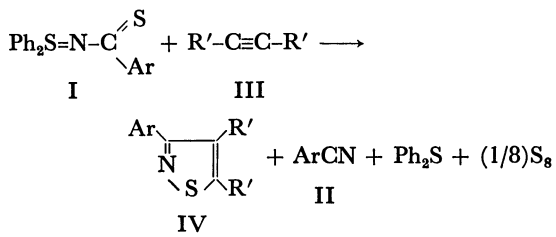
a) Recrestallization solvents: A petroleum ether; B benzene–petroleum ether. b) Lit,[9,10] mp 72—73°C. c) Lit,[9] mp 90—91 °C.

Table 3. Effect of the concentration of III ($R'=CO_2Me$) on the product composition (IIb: IVb) for the thermal decomposition of Ib benzene at 50 °C

Ib mol/l	III($R'=CO_2Me$) mol/l	Ib/III	IVb($R'=CO_2Me$): IIb
0.130	0.106	0.815	25:75
0.100	0.132	1.32	25:75
0.130	0.201	1.55	27:73
0.144	0.482	3.34	28:72

Table 4. The effect of the substituents of I and III on the product composition (II: IV) for the decomposition of Ib—e in benzene
I: 0.05—0.30 mol/l, III: 0.13—0.7 mol/l.

Temp (°C)	III R′	Ib IIb:IVb	Ic IIc:IVc	Id IId:IVd	Ie IIe:IVe
50	COPh	54:46	48:52	51:49	48:52
	CO_2Me	73:27	70:30	72:28	66:34
	Ph	100:0	100:0	100:0	100:0
35	COPh	54:46			



Tables 3 and 4 show the effects of the concentrations and the substituents of I and III on the product compositions, II: IV, as determined by means of the NMR spectrum. The total yields(II+IV) were quantitative, and the II: IV ratios were independent of the concentration of III.

On ultraviolet irradiation in the presence of acetylenedicarboxylate, 4-aryl-1,3,2-oxathiazoline 5-oxides give isothiazole derivatives, together with nitrile and sulfur.[9] Thiazirine and nitrile sulfide are supposed to be intermediates for this photolysis. It has also been reported that benzonitrile sulfide is a possible intermediate for the thermolysis of 5-phenyl-1,3,4-oxathiazol-2-one in the presence of dimethyl acetylenedicarboxylate to give an isothiazole derivative.[10] We similarly supposed that nitrile sulfide was a probable intermediate for the thermolysis of Ia—e.

We have performed kinetic experiments to find a possible mechanism for the thermal decomposition of I. The decomposition of I gave a good first-order rate constant(k_1), as followed by NMR spectroscopy, and k_1 was independent of the concentration of I(0.08—0.25 mol/l). The results are summarized in Table 5. The effects of solvents and substituents ($\rho=+0.22$ to Hammett's σ in benzene at 50 °C) are very small, and positive activation entropies are observed.

Table 5. First-order rate constants for the thermal decomposition of Ib—f

I	Temp (°C)	Solvent	$k_1\times10^4$ s^{-1} [a]	
Ib	50.0	PhH	3.43	E_a=24.8kcal/mol
	43.0	PhH	1.47	ΔS=13.2eu
	34.5	PhH	0.377	
	50.0	PhCN	3.07	
	50.0	$PhNO_2$	2.90	
	50.0	*o*-$C_6H_4Cl_2$	3.84	
Ic	50.0	PhH	3.76	
Id	50.0	PhH	2.94	
	50.0	PhCN	2.63	
Ie	50.0	PhH	3.91	
If	60.2	PhH	5.55	E_a=29.3kcal/mol
	50.0	PhH	1.46	ΔS=13.5eu
	43.0	PhH	0.50	

a) Errors are within 5%.

When the reaction of Ib with III(R′=COPh) was carried out in a benzene solution, and followed by NMR spectroscopy, the product ratio, IIb/IVb (R′=COPh), was nearly constant while the reaction proceeded. Two representative kinetic runs are shown in Table 6, and the results are collected in Table 7. The results in the table indicate that k_{disapp}(I) is equal to k_{app}(II)+k_{app}(IV), that k_{app}(II) is constant in either the presence orabsence of III, and that, moreover, k_{app}(IV) is unaffected by the concentration of III, but highly de-

Table 6. Examples of the reaction of Ib with III (R=COPh) in benzene at 50 °C as followed by the NMR spectral changes of the methyl signals of Ib, IIb, and IVb (R′=COPh)

Example A. Initial concn: Ib 0.150; III(R′=COPh) 0.126 mol/l.

Time (min)	Composition (%) Ib	IIb	IVb	IIb/IVb	Disapp. Ib $k_1\times10^4$ s^{-1}
6	77.9	11.8	10.3	1.15	6.94
11	63.6	20.1	16.3	1.23	6.86
16	52.4	26.1	21.6	1.21	6.73
21	44.4	30.1	25.5	1.18	6.44
26	36.1	33.6	30.3	1.11	6.53
31	30.0	38.1	32.0	1.19	6.47
150	0.0	53.8	46.2	1.17	
		Aver.		1.18±0.03	6.73±0.21

k_{app}(IIb) $=3.64\pm0.11\times10^{-4}$ s^{-1}

k_{app}(IVb) $=3.09\pm0.10\times10^{-4}$ s^{-1}

Example B. Initial concn: Ib 0.123; III (R′=COPh) 0.260 mol/l.

Time (min)	Composition (%) Ib	IIb	IVb	IIb/IVb	Disapp. Ib $k_1\times10^4$ s^{-1}
8	70.4	16.5	13.1	1.26	7.31
13	59.2	22.4	18.4	1.22	6.72
23	42.7	31.7	25.6	1.24	6.17
29	34.2	35.6	30.3	1.17	6.17
37	25.3	40.4	34.3	1.18	6.19
150	0.0	54.5	45.5	1.20	
		Aver.		1.21±0.03	6.51±0.45

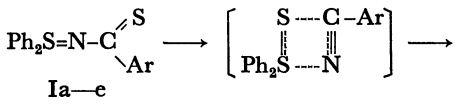
k_{app}(IIb) $=3.57\pm0.24\times10^{-4}$ s^{-1}

k_{app}(IVb) $=2.94\pm0.21\times10^{-4}$ s^{-1}

Table 7. Representative rate data for the decomposition of Ib, c in benzene at 50 °C

	III R′	Concn I mol/l	Concn III mol/l	Disapp. I $k_1\times10^4$ s^{-1}	App. II $k_1\times10^4$ s^{-1}	App. IV $k_1\times10^4$ s^{-1}
Ib	—	0.142		3.43	3.43	
	COPh	0.150	0.126	6.73	3.65	3.08
	COPh	0.123	0.260	6.51	3.57	2.94
	CO_2Me	0.133	0.116	4.72	3.47	1.25
	CO_2Me	0.133	0.244	5.06	3.61	1.44
	Ph	0.138	0.210	3.51	3.51	0.0
Ic	—	0.145		3.76	3.76	
	COPh	0.163	0.223	8.01	3.78	4.32

pendent on the electrophilic activity of III (R″: PhCO >MeOCO>Ph) as dipolarophiles with nitrile sulfides.

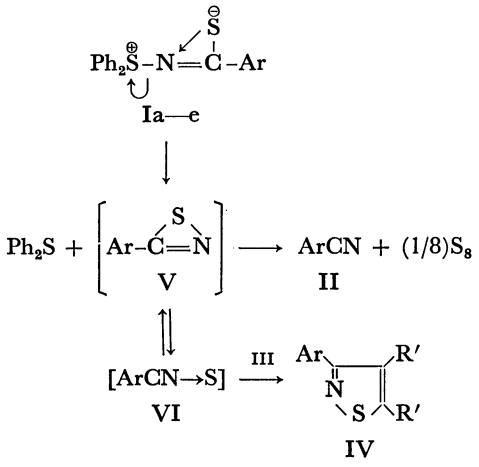


Ia—e

$$ArCN + Ph_2S{=}S \longrightarrow Ph_2S + (1/8)S_8$$

II

The explanation that II is formed by a simple four-membered cyclic transition state seems improbable,

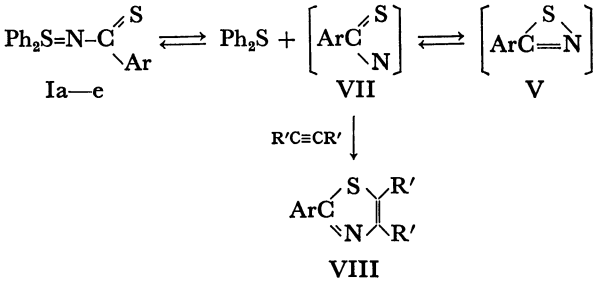


Scheme 1.

since the thermolysis of I showed positive activation entropies (Table 5) and I gave IV in the presence of III.

The mechanism we suggest is shown in Scheme 1: the initial formation of thiazirine(V), followed by two reaction paths. One is a rate-limiting cheletropic reaction of V to give II and sulfur, while the other is the ring opening of V to afford nitrile sulfide(VI), which then undergoes 1,3-dipolar cycloaddition to acetylene(III). A direct path from VI to yield II seems improbable, since rate for the appearance of II(k_{app} (II)) was unaffected by the III added (Table 7). Thus, we propose a rapid equilibrium between V and VI.

Another possible mechanism or intermediate is the formation of thiocarbonyl nitrene(VII), followed by the formation of thiazirine(V):



Acyl nitrenes have proposed as intermediates in the Curtius rearrangement of carbonyl azides to isocyanates.[11] Some addition reactions of acyl nitrenes with sulfoxides, olefins, and acetylenes have been reported.[11] At present we have no positive evidence for the existence of the intermediate(VII). In the thermolysis of Ia—e, no isothiocyanate was observed. No addition product was isolated from the attempted reaction of Ib with dimethyl sulfoxide, cyclohexene, dimethyl fumarate, and maleate. Moreover, the result that the reaction of Ia—e with acetylenes gave isothiazoles, not thiazoles-(VIII), seems to show an intermediate(VII) having no possibility of existence or any significant lifetime.

Experimental

Preparation of Ia—i. Free diphenylsulfimide was prepared according to the literature.[3] A general procedure for the preparation of I is as follows: a mixture of diphenylsulfi-

mide (2.01 g (0.01 mol)) and methyl dithiobenzoate (2.02 g (0.012 mol)) in 50 ml of dry benzene was stirred for 3 h at room temperature. The resulting solution was treated with charcoal, and condensed *in vacuo* to give an oil, which gave needles Ia from benzene–hexane (without heat). Similarly, Ia—h were prepared in moderate yields.

Ii was prepared as follows: to a solution of diphenylsulfimide (2.01 g (0.01 mol)) and 0.9 g (0.012 mol) of pyridine in dry ether (30 ml), we slowly added 1.23 g (0.01 mol) of dimethylthiocarbamoyl chloride in ether (30 ml) at room temperature. After the mixture was stand for 4 h, the oily precipitate was separated and the resulting solution was dried *in vacuo* to give a crystalline mass, which afforded needles (Ii) from ethyl acetate–petroleum ether. The physical properties are shown in Table 1.

Thermal Decomposition of I. All the reactions were followed by NMR spectroscopy and TLC. The reaction products were identified by comparing their NMR and IR spectra with those of the authentic samples. The yields of the products were determined by VPC (IIa—e) or NMR (IIf—h), using mesityrene as the internal standard. The thermal decomposition of If, g in benzene was followed by NMR spectroscopy. The methyl signal of If, which appeared at δ 4.14, decreased in its intensity, giving new three peaks at 2.25 (MeNCO), 2.56 (MeOCN), and 3.08 [$(MeNCO)_3$]. Finally, the signals at 4.14 and 2.56 disappeared entirely. Similarly, on the thermolysis of Ig a methylene quartet (J=7 Hz) at 4.14 for Ig gave methylene quartets at 2.20(EtNCO), 3.31 (EtOCN), and 3.74 [$(EtNCO)_3$].

The yields of the products are collected in Table 1.

Thermal Decomposition of Ia—e in the Presence of Acetylene-(III). All the reactions were followed by means of the NMR spectral changes. The product compositions, II: IV were obtained by NMR spectroscopy. The isothiazoles were separated as follows: the resulting mixture was condensed *in vacuo*, and elemental sulfur was precipitated by the addition of petroleum ether. The subsequent condensation of the petroleum ether solution *in vacuo* (100 °C/1 Torr) afforded an oil which gave crystals upon the addition of a small amount of petroleum ether. The physical properties and analytical results of isothiazoles (IV) are collected in Tables 2 and 3.

Attempted Reactions of Ib with Olefins and DMSO. The reactions were followed by means of the NMR spectral changes. A solution of Ib (15 mg) and dimethyl fumarate or maleate or cyclohexene (30 mg) in benzene (0.4 ml) was heated in an oil bath at 70 °C for 15 min. The product was *p*-tolunitrile.

A solution of Ib (20 mg) in DMSO (0.5 ml) was heated at 70 °C for 20 min. Then the solution was quenched in 5 ml of water and extracted with 1 ml of chloroform. The extract was dried over sodium carbonate, and the product was found by NMR and VPC analyses to be a mixture of *p*-tolunitrile and diphenyl sulfide.

Kinetic Studies. A solution of I (0.05—0.25 mol/l) and III (0.0—0.45 mol/l) in dry benzene (or other solvents) was sealed in an NMR sample tube; the rate was followed at suitable time intervals by analyzing the NMR spectra of the methyl groups of I, II, and IV. The results are summarized Tables 5—7.

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