

The Reaction of *N*-Imidoysulfimides with Carbon Disulfide

Hiroshi YOSHIDA, Tsuyoshi OGATA, and Saburo INOKAWA

Department of Synthetic Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432

(Received April 15, 1977)

The reaction of *S,S*-diphenyl- and *S,S*-dimethyl-*N*-imidoysulfimides (**1** and **2**) with carbon disulfide was studied. **1** yielded nitrile, isothiocyanate, diphenyl sulfide, and sulfur, whereas **2** gave *N*-thiocarbonyl-*S,S*-dimethylsulfimide together with isothiocyanate. Kinetic studies indicate that the reaction proceeds *via* a [2+2]cycloaddition mechanism, as is shown by the small effects of the solvents and the substituent on the rate.

A number of recent works¹⁾ on sulfimides have shown their importance in organic synthesis. Some interesting reactions of *N*-imidoysulfimides²⁾ and *N*-thiocarbonylsulfimides³⁾ have also been reported.

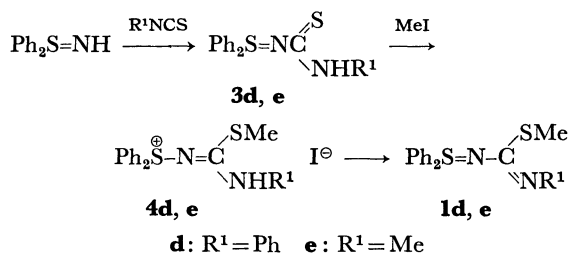
In continuation of our previous studies to explore the physical and chemical properties of *P*- and *S*-ylides and imides,³⁾ we have found an interesting reaction of the *S,S*-diphenyl- and *S,S*-dimethyl-*N*-imidoysulfimides **1** and **2** with carbon disulfide.

Results and Discussion

Preparation. The *N*-imidoysulfimides, **1a—c** and **2a—f** (Table 1), were prepared by the reaction of benzimidoyl chlorides with free *S,S*-diphenylsulfimide Ph₂S=NH or *N*-haloamidines with dimethyl sulfide,



modifying the reported methods.^{2a)} The *N*-[(methylthio)carbonimidoyl]sulfimides, **1d** and **e** were prepared by the reaction of the *N*-thiocarbamoylsulfimides, **3d** and **e** with methyl iodide, followed by treatment with a base.



The physical properties of **1** and **2** are collected in Table 1.

The Reaction of 1 and 2 with Carbon Disulfide. The **1b**, **2b**, and **c** sulfimides were shown to be stable up to 150 °C.^{2a)} On the other hand, the **1** and **2** sulfimides showed high reactivities with carbon disulfide even at room temperature. The products in the reaction of *S,S*-diphenylsulfimides **1a—e** with carbon disulfide were confirmed to be isothiocyanates, nitriles, diphenyl sulfide, and sulfur by comparing their IR and GLC with those of authentic samples.

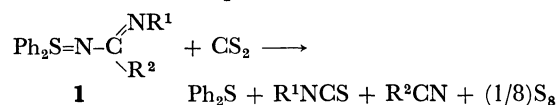


TABLE 2. PRODUCTS OF THE REACTION OF **1** OR **2** WITH CARBON DISULFIDE

	Condition ^{a)} (Time, day)	Products (%)
1a	1	R ¹ NCS(92), R ² CN(90), Ph ₂ S(96), S ₈
1b	1	R ¹ NCS(90), R ² CN(93), Ph ₂ S(95), S ₈
1c	1	R ¹ NCS(94), R ² CN(92), Ph ₂ S(96), S ₈
1d	2	R ¹ NCS(87), R ² CN(81), Ph ₂ S(96), S ₈
1e	1	R ¹ NCS(80), R ² CN(82), Ph ₂ S(97), S ₈
2a	2	5a (93), R ¹ NCS
2b	2	5a (96), R ¹ NCS
2c	2	5a (91), R ¹ NCS
2d	2	5d (94), R ¹ NCS
2e	2	5e (91), R ¹ NCS
2f	2	5f (93), R ¹ NCS

a) **1** or **2** (1 mmol) with carbon disulfide(10 mmol) in chloroform (20 ml) at room temperature.

TABLE 1. PREPARATION AND PHYSICAL PROPERTIES OF **1** AND **2**

	R ¹	R ²	Yield(%)	Mp(°C)	NMR(δ in CDCl ₃) ^{a)}	C	Found(Calcd) (%) H	N
1a	<i>p</i> -Tol	Ph	76	140—141	2.113(CH ₃ C ₆ H ₄)	79.38(79.15)	5.73(5.62)	7.02(7.10)
1b	Ph	Ph	59	142—143 ^{b)}		78.76(78.91)	5.09(5.30)	7.44(7.36)
1c	Ph	<i>p</i> -Tol	73	150—151	2.25(CH ₃ C ₆ H ₄)	79.03(79.15)	5.44(5.62)	7.36(7.10)
1d	Ph	SMe	89	119—120	2.64(SMe)	68.23(68.54)	5.30(5.18)	7.75(7.99)
1e	Me	SMe	93	82—83	2.61(SMe), 2.96(NMe)	62.09(62.46)	5.37(5.59)	9.88(9.71)
2a	<i>p</i> -Tol	Ph	43	180—182	2.17(CH ₃ C ₆ H ₄), 2.73(Me ₂ S)	71.24(71.07)	6.52(6.71)	10.11(10.36)
2b	Ph	Ph	41	167—169 ^{c)}	2.70(Me ₂ S)	70.05(70.28)	6.41(6.29)	10.80(10.93)
2c	<i>p</i> -ClC ₆ H ₄	Ph	36	185—187 ^{d)}	2.71(Me ₂ S)	61.83(61.95)	5.03(5.20)	9.76(9.63)
2d	Ph	<i>p</i> -Tol	48	155—156	2.16(CH ₃ C ₆ H ₄), 2.65(Me ₂ S)	70.91(71.07)	6.53(6.71)	10.15(10.36)
2e	Ph	<i>p</i> -ClC ₆ H ₄	31	162—164	2.67(Me ₂ S)	61.77(61.95)	5.06(5.20)	9.52(9.63)
2f	Ph	<i>m</i> -Tol	47	169—171	2.20(CH ₃ C ₆ H ₄), 2.69(Me ₂ S)	71.20(71.07)	6.53(6.71)	10.15(10.36)

a) The phenyl-ring protons appeared at 6.5—8 as multiplets. b) Lit,^{2a)} mp 141—143 °C. c) Lit,^{2a)} mp 167—169 °C.

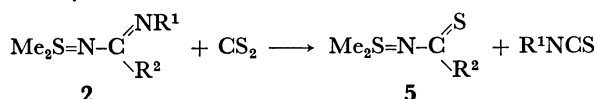
d) Lit,^{2a)} mp 180—182 °C.

TABLE 3. PHYSICAL PROPERTIES OF **5**

5	R ²	Mp(°C)	M ⁺	NMR(δ in CDCl ₃) ^{a)}	C	Found (Calcd)(%)	H	N
5a	Ph	106—107	197	2.89(Me ₂ S)	54.53(54.78)	5.69(5.62)	6.93(7.10)	
5d	<i>p</i> -Tol	107—108	211	2.36(CH ₃ C ₆ H ₄), 2.93(Me ₂ S)	56.67(56.83)	6.32(6.20)	6.53(6.62)	
5e	<i>p</i> -ClC ₆ H ₄	156—158	231	2.82(Me ₂ S)	46.71(46.64)	4.51(4.35)	6.17(6.04)	
5f	<i>m</i> -Tol	95—96	211	2.34(CH ₃ C ₆ H ₄), 2.83(Me ₂ S)	56.58(56.83)	6.12(6.20)	6.48(6.62)	

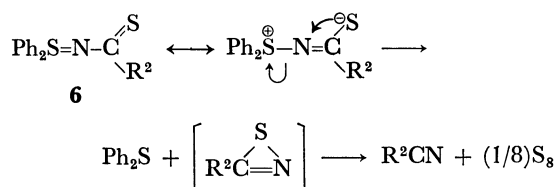
a) The phenyl-ring protons appeared at δ 7—8 as multiplets.

S,S-Dimethylsulfimides **2a—f** also reacted easily with carbon disulfide at room temperature yielding the *N*-thiocarbonyl-*S,S*-dimethylsulfimides together with the isothiocyanates.



The structure of **5** was confirmed on the basis of their NMR, MS, and elemental analyses. These results are shown in Tables 2 and 3.

In a previous paper³⁾ we have shown that the thermal decomposition of *N*-thiocarbonyl-*S,S*-diphenylsulfimides **6**, proceeds *via*



the nucleophilic attack of thiocarbonyl sulfur at the nitrogen atom, yielding thiazirine and diphenyl sulfide. On the other hand, **5** were stable under heating at 50 °C for a long time. We believe **6** to be the initial products of the reaction of **1** with carbon disulfide. The marked

TABLE 4. SECOND-ORDER RATE CONSTANTS(k_2) FOR THE REACTION OF **1** OR **2** WITH CARBON DISULFIDE

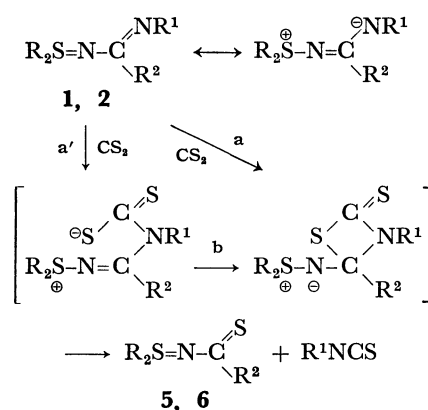
	Temp(°C)	Solvent	$k_2 \times 10^5$ l/mol s	E_a Cal/mol	ΔS e.u.
1a	50	CDCl ₃	4.52		
	50	PhCN	44.5		
2a	45	CDCl ₃	2.36	15.0	-32.9
	50	CDCl ₃	3.48		
	55	CDCl ₃	4.81		
	45	PhNO ₂	37.3		
	50	PhNO ₂	55.8	12.2	-36.2
	55	PhNO ₂	75.1		
	50	CH ₂ Cl ₂	9.03		
	50	PhCN	34.2		
2b	50	CDCl ₃	2.18		
	50	PhNO ₂	36.3		
2c	50	CDCl ₃	1.21		
	50	PhNO ₂	23.2		
2d	50	CDCl ₃	2.73		
	50	PhNO ₂	40.3		
2e	50	CDCl ₃	1.34		
	50	PhNO ₂	22.2		
2f	50	CDCl ₃	2.47		
	50	PhNO ₂	38.7		

TABLE 5. HAMMETT'S CONSTANTS FOR THE REACTION OF **2** WITH CARBON DISULFIDE AT 50°C

Solvent	CDCl ₃	PhNO ₂
ρ_{R^1} , R ² =Ph	-1.15	-0.94
ρ_{R^2} , R ¹ =Ph	-0.86	-0.80

difference in thermal stability between **5** and **6** may be attributed to the electron-attracting power of the groups on the sulfide sulfur. The phenyl groups of **6** may facilitate the nucleophilic attack of the thiocarbonyl sulfur on the nitrogen in the transition state.

The *N*-imidoysulfimides **1** and **2** reacted easily with carbon disulfide under mild conditions. Meanwhile, the action of hydrogen sulfide on amidines represents a useful route to thioamides.⁴⁾ In an old article,⁵⁾ it was reported that *N,N'*-diphenylbenzamidine reacts with carbon disulfide under drastic conditions (130—140 °C) to yield thiobenzanilide and phenyl isothiocyanate. We have performed kinetic experiments in order to find a reasonable mechanism for the reaction of **1** and **2** with carbon disulfide. The reaction gave good second-order rate constants (k_2), which were first-order with **1** or **2** and carbon disulfide respectively, when the reaction was followed by NMR spectroscopy. The results are listed in Tables 4 and 5, which indicate small effects of solvents and substituents on rate and negative entropies for the reaction. These observations indicate that the mechanism for the formation of 1,3-thiazetidine-2-thione *via* a rate-determining electrophilic attack on iminonitrogen, followed by ring closure (Routes a' and b), can be ruled out. The reaction of **1** or **2** with carbon disulfide seems to be a typical [2+2]cycloaddition reaction.⁶⁾ The mechanism we suggest is shown in Scheme 1, which involves the initial formation of 1,3-



Scheme 1.

thiazetidine-2-thione *via* cycloaddition (Route a), followed by a rapid ring cleavage to yield **5** or **6** and isothiocyanate.

Experimental

Preparation of 1a—c. Free *S,S*-diphenylsulfimide was prepared according to the literature.⁷⁾ The general procedure for the preparation of **1a—c** is as follows: to a solution of *S,S*-diphenylsulfimide (2.01 g, 0.01 mol) in 50 ml of dry benzene we added a solution of imidoyl chloride (5 mmol) in 10 ml of dry benzene in one portion. After 30 min the liquid layer was condensed *in vacuo* to give a crystalline mass, which afforded needles, **1a—c**, from chloroform–hexane. The results are shown in Table 1.

Preparation of 1d and 1e. *N*-Thiocarbamoyl-*S,S*-diphenylsulfimides, **3d**, and **e** were prepared according to the literature.^{3,8)} To a solution of **3d** (0.01 mol) in chloroform we added methyl iodide (0.02 mol) in one portion. The resulting solution was kept standing at room temperature for 12 h. Then the solution was dried *in vacuo* to give a crystalline mass. We then added a solution of sodium ethoxide in ethanol [from sodium (0.015 mol) and ethanol (30 ml)] to the mass, portion by portion, under vigorous stirring. The mixture was stirred for 5 min and then poured into 100 ml of ice water. The product was extracted with chloroform, and crystallized from chloroform–hexane.

1e was prepared similarly; the results are shown in Table 1.

Preparation of 2a—f. **2** were prepared according to the literature.⁹⁾ The yields (based on amidines used) and physical properties are shown in Table 1.

The Reaction of 1a—e with Carbon Disulfide. A solution of **1a—e** (1 mmol) and carbon disulfide (10 mmol) in 20 ml of chloroform was kept standing for a day at room temperature. After the reaction, the mixture was dried *in vacuo* and separated into petroleum ether-soluble and insoluble parts. The former part was analyzed by GLC (silicone grease on celite) and found to be a mixture of diphenyl sulfide, isothiocyanate, and nitrile. The petroleum ether-insoluble part

was sulfur. The results are shown in Table 2.

The Reaction of 2a—f with Carbon Disulfide. A solution of **2a—f** (1 mmol) and carbon disulfide (10 mmol) in 20 ml of chloroform was kept standing at room temperature for 2 days. After drying the solvent *in vacuo*, the residue was separated into petroleum ether-soluble and insoluble parts. The former part was isothiocyanate, which was confirmed by comparing their IR and GLC with those of the known sample. The latter part was *N*-thiocarbonyl-*S,S*-dimethylsulfimide, **5**. The results are collected in Tables 2 and 3.

Kinetic Studies. A solution of **1** or **2** (0.05–0.3 mol/l) and carbon disulfide (0.4–0.8 mol/l) in chloroform-*d* (or other solvents) was sealed in an NMR sample tube; the rate was followed at suitable time intervals by analyzing the NMR signals of the methyl groups of **1a** or **2** and the products. The results are shown in Tables 4 and 5.

References

- 1) For example, Y. Tamura, H. Matsushima, M. Ikeda, and K. Sumoto, *Tetrahedron*, **32**, 431 (1976).
- 2) a) T. L. Gilchrist, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1964; b) T. L. Gilchrist, C. J. Moody, and C. W. Rees, *ibid.*, **1975**, 1969; c) T. L. Gilchrist, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, **1976**, 414.
- 3) H. Yoshida, H. Taketani, T. Ogata, and S. Inokawa, *Bull. Chem. Soc. Jpn.*, **49**, 3124 (1976).
- 4) W. Walter and J. Voss, "The Chemistry of Amides," ed by J. Zabicky, Interscience Publishers, London (1970), p. 383.
- 5) A. Bernthsen, *Justus Liebigs Ann. Chem.*, **192**, 1 (1878).
- 6) For example, R. C. Kerber, T. J. Ryan, and S. D. Hsu, *J. Org. Chem.*, **39**, 1215 (1974).
- 7) N. Furukawa, T. Omata, T. Yoshimura, T. Aida, and S. Oae, *Tetrahedron Lett.*, **1972**, 1619.
- 8) N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. Ind. (London)*, **1974**, 702.
- 9) T. Fuchigami and K. Odo, *Chem. Lett.*, **1974**, 247.