The Reaction of *N*-Imidoylsulfimides 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)

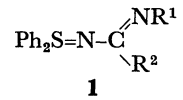
The reaction of *S,S*-diphenyl- and *S,S*-dimethyl-*N*-imidoylsulfimides (**1** and **2**) with carbon disulfide was studied. **1** yielded nitrile, isothiocyanate, diphenyl sulfide, and sulfur, whereas **2** gave *N*-thiocarbonyl-*S,S*-dimethylsulfimide together with isothiocyanate. Kinetic studies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

A number of recent works[1] on sulfimides have shown their importance in organic synthesis. Some interesting reactions of *N*-imidoyl-[2] and *N*-thiocarbonylsulfimides[3] have also been reported.

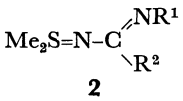
In continuation of our previous studies to explore the physical and chemical properties of *P*- and *S*-ylides and imides,[3] we have found an interesting reaction of the *S,S*-diphenyl- and *S,S*-dimethyl-*N*-imidoylsulfimides **1** and **2** with carbon disulfide.

Results and Discussion

Preparation. The *N*-imidoylsulfimides, **1a**—**c** and **2a**—**f** (Table 1), were prepared by the reaction of benzimidoyl chlorides with free *S,S*-diphenylsulfimide $Ph_2S{=}NH$ or *N*-haloamidines with dimethyl sulfide,

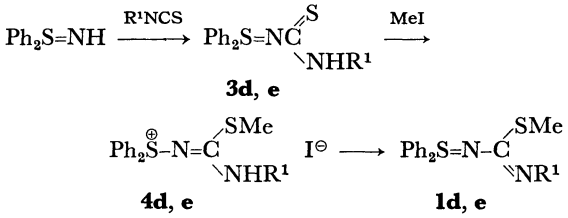


1



2

modifying the reported methods.[2a] The *N*-[(methythio)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.



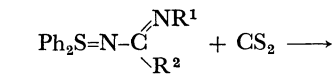
3d, e

4d, e **1d, e**

d: R^1=Ph **e**: R^1=Me

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.



1 $Ph_2S + R^1NCS + R^2CN + (1/8)S_8$

Table 2. Products of the reaction of **1** or **2** with carbon disulfide

	Condition[a] (Time, day)	Products (%)
1a	1	R^1NCS(92), R^2CN(90), Ph_2S(96), S_8
1b	1	R^1NCS(90), R^2CN(93), Ph_2S(95), S_8
1c	1	R^1NCS(94), R^2CN(92), Ph_2S(96), S_8
1d	2	R^1NCS(87), R^2CN(81), Ph_2S(96), S_8
1e	1	R^1NCS(80), R^2CN(82), Ph_2S(97), S_8
2a	2	**5a**(93), R^1NCS
2b	2	**5a**(96), R^1NCS
2c	2	**5a**(91), R^1NCS
2d	2	**5d**(94), R^1NCS
2e	2	**5e**(91), R^1NCS
2f	2	**5f**(93), R^1NCS

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]	Found(Calcd) (%) C	H	N
1a	*p*-Tol	Ph	76	140—141	2.113($CH_3C_6H_4$)	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	*p*-Tol	73	150—151	2.25($CH_3C_6H_4$)	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	*p*-Tol	Ph	43	180—182	2.17($CH_3C_6H_4$), 2.73(Me_2S)	71.24(71.07)	6.52(6.71)	10.11(10.36)
2b	Ph	Ph	41	167—169[c]	2.70(Me_2S)	70.05(70.28)	6.41(6.29)	10.80(10.93)
2c	*p*-ClC_6H_4	Ph	36	185—187[d]	2.71(Me_2S)	61.83(61.95)	5.03(5.20)	9.76(9.63)
2d	Ph	*p*-Tol	48	155—156	2.16($CH_3C_6H_4$), 2.65(Me_2S)	70.91(71.07)	6.53(6.71)	10.15(10.36)
2e	Ph	*p*-ClC_6H_4	31	162—164	2.67(Me_2S)	61.77(61.95)	5.06(5.20)	9.52(9.63)
2f	Ph	*m*-Tol	47	169—171	2.20($CH_3C_6H_4$), 2.69(Me_2S)	71.20(71.07)	6.53(6.71)	10.15(10.36)

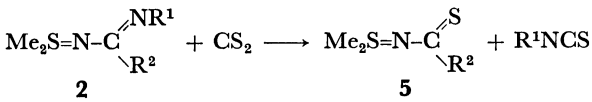
a) The phenyl-ring protons appeared at 6.5—8 as multiplets. b) Lit,[2a] mp 141—143 °C. c) Lit,[2a] mp 167—169 °C. d) Lit,[2a] mp180—182 °C.

Table 3. Physical properties of **5**

5	R^2	Mp(°C)	M^+	NMR(δ in $CDCl_3$)[a]	Found (Calcd)(%) C	H	N
5a	Ph	106—107	197	2.89($\underline{Me_2}S$)	54.53(54.78)	5.69(5.62)	6.93(7.10)
5d	*p*-Tol	107—108	211	2.36($C\underline{H_3}C_6H_4$), 2.93(Me_2S)	56.67(56.83)	6.32(6.20)	6.53(6.62)
5e	*p*-ClC_6H_4	156—158	231	2.82($\underline{Me_2}S$)	46.71(46.64)	4.51(4.35)	6.17(6.04)
5f	*m*-Tol	95—96	211	2.34($C\underline{H_3}C_6H_4$), 2.83(Me_2S)	56.58(56.83)	6.12(6.20)	6.48(6.62)

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

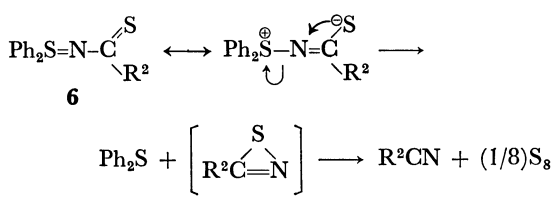
S,S-Dimethylsulfimides **2a—f** also reacted easily with carbon disulfide at room temperature yielding the *N*-thiocarbonyl-*S,S*-dimethylsulfimides together with the isothiocyanates.



2 **5**

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 paper[3] 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

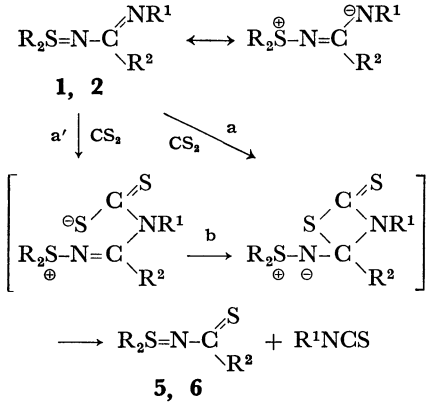
	Temp(°C)	Solvent	$k_2\times10^5$ l/mol s	E_a Cal/mol	ΔS e.u.
1a	50	$CDCl_3$	4.52		
	50	PhCN	44.5		
2a	45	$CDCl_3$	2.36		
	50	$CDCl_3$	3.48	15.0	−32.9
	55	$CDCl_3$	4.81		
	45	$PhNO_2$	37.3		
	50	$PhNO_2$	55.8	12.2	−36.2
	55	$PhNO_2$	75.1		
	50	CH_2Cl_2	9.03		
	50	PhCN	34.2		
2b	50	$CDCl_3$	2.18		
	50	$PhNO_2$	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*-imidoylsulfimides **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 is Scheme 1, which involves the initial formation of 1,3-



1, 2

5, 6

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.