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Sulfilimine. XVII. Syntheses and Reactions of *N*-Carbamoylsulfilimines

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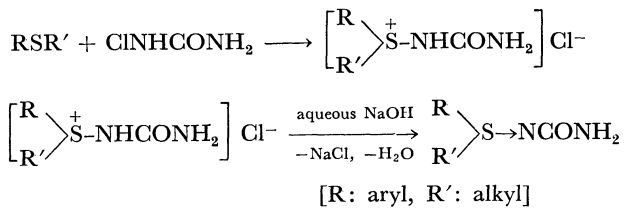
The physical and chemical properties of several new sulfilimines, *N*-carbamoylsulfilimines, and their syntheses were studied. The sulfilimines were prepared by the action of *N*-chlorourea on appropriate sulfides in acetonitrile, and their IR and NMR spectra were obtained. Thermolysis, hydrolysis and reactions with thiophenol and sodium nitrite were carried out and the results were discussed.

Sulfilimines with the general structural formula R′RS→NR″ were first prepared by Nicolet and Willard[1] in 1921. Recently, Whitfield *et al.*[2] reported the syntheses of a new class of sulfilimines, dimethyl and diethyl *N*-ethoxycarbonylsulfilimines from the corresponding sulfides and *N*-chloroethyl carbamate.

We have found that *N*-chlorourea[3] also reacts with sulfides giving the corresponding sulfilimines, *N*-carbamoylsulfilimines. Their syntheses and reactions are reported.

Results and Discussion

Syntheses and Spectroscopic Data. Syntheses of *N*-carbamoylsulfilimines are shown in Scheme 1.



[R: aryl, R′: alkyl]

Scheme 1.

1) B. H. Nicolet and J. Willard, *Science*, **53**, 217 (1921).
2) G. F. Whitfield, H. S. Beilan, D. Saika, and D. Swern, *Tetrahedron Lett.*, **1970**, 3534.
3) R. A. Wiesboeck, *J. Org. Chem.*, **30**, 3161 (1965).

Alkyl aryl sulfides were treated with *N*-chlorourea in acetonitrile to afford the corresponding *N*-carbamoyliminosulfonium chlorides. They were treated directly with an aqueous alkaline solution without being isolated. *N*-carbamoylsulfilimines were obtained as white solids in 40—70% yield, after the aqueous alkaline solution had been extracted with chloroform. No diaryl sulfilimines were obtained under the same conditions. The sulfilimines were recrystallized from chloroform, acetone-alcohol or benzene-alcohol. The products and their yields are shown in Table 1.

Table 1. Products and yields

$\left[\begin{matrix}R\\R'\end{matrix}\!\!>\!S\rightarrow NCONH_2\right]$

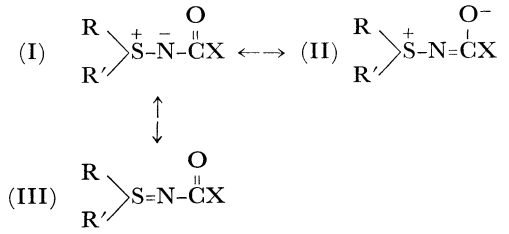
R	R′	Mp, °C	Yield, %
Ph	Me	175—6	64
p-MeC_6H_4	Me	168—9	55
p-ClC_6H_4	Me	150—1	42
p-$MeOC_6H_4$	Me	160—1	42
Ph	Et	173—4	68
Ph	*n*-Pr	122—3	50
p-MeC_6H_4	*n*-Pr	119—20	59
Ph	*i*-Pr	122—3	67
Ph	*n*-Bu	101—2	66

Kucsman *et al.*[4] and Whitfield *et al.*[2] reported that the C=O and S=N IR absorption bands of *N*-dihaloacetyl- or *N*-ethoxycarbonylsulfilimine appear at 1620—1640 cm^{-1} (C–O), and 810—820 cm^{-1}(S–N), respectively. They proposed that the structure of the compound can best be represented by betaine form (II). However, the strong C=O stretching absorption band of *N*-carbamoylsulfilimines appears at 1640—1685 cm^{-1} and is similar to that of urea, but the S–N band is at 960—1040 cm^{-1}. Thus, the major contributing form of the *N*-carbamoylsulfilimines is not always form (II) but either form (I) or (II) depending on the kind of sulfilimine.

The methyl protons of the NMR spectra of the methyl phenyl *N*-carbamoylsulfilimine appear as a singlet at δ 2.97 ppm, and the chemical shift appears about 0.3 ppm and 0.1 ppm downfield from those of the corresponding sulfoxide and dimethyl *N*-ethoxycarbonylsulfilimine,[2] respectively. Thus, the S(IV) atom in the methyl phenyl *N*-carbamoylsulfilimine is considered to have a more positive charge than that of the corresponding sulfoxide or dimethyl *N*-ethoxycarbonylsulfilimine, and the shift is analogous to that of the methyl protons of methyl phenyl *N*-*p*-tolylsulfonylsulfilimine.

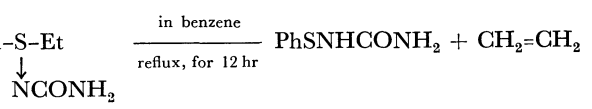
Thus the canonical form (I) appears to be the major contributor to the *N*-carbamoylsulfilimine structure.

Reactions. We have carried out extensive studies on the reactions of sulfilimines, particularly *N*-sulfonylsulfilimines.[5–10] In order to compare the chemical behaviors of *N*-carbamoylsulfilimine with those of the *N*-sulfonyl derivative, we treated the new sulfilimine under similar reaction conditions as those of the *N*-*p*-tolylsulfonyl derivative.



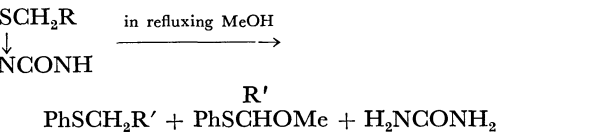
Scheme 2.

1) Thermolysis: *N*-*p*-Tolylsulfonylsulfilimines with β-proton have recently been found to give olefins in high yields.[6] When ethyl phenyl *N*-carbamoylsulfilimine was heated in benzene, sulfenamide and ethylene were similarly found to be obtained in good yields.



Scheme 3.

The mechanism of the reaction is not clear but the reaction is considered to proceed *via* an Ei mechanism involving a five membered cyclic transition state as in the case of *N*-*p*-tolylsulfonylsulfilimines.[6),10] When thermolysis was carried out in methanol solution, the sulfide, α-methoxy sulfide and urea were obtained as shown in Scheme 4.



		A	B	C
R′	H	75%	14%	~100%
	Me	73%	17%	~100%

Scheme 4.

The reaction with this type of sulfilimine is unique since the *N*-*p*-tolylsulfonyl derivatives do not react under the same conditions. An analogous reaction was observed when alkoxysulfonium salt[11] or *N*-*p*-tolylsulfonylsulfilimine[12] was treated with a base such as alkoxide or hydroxide in alcohol solution. As in the case of the sulfonium salt or *N*-*p*-tolylsulfonylsul-

4) A. Kucsman, I. Kapovits, and F. Ruff, *Tetrahedron*, **22**, 1843 (1966).

5) K. Tsujihara, N. Furukawa, and S. Oae, This Bulletin, **43**, 2153 (1970).

6) S. Oae, K. Tsujihara, and N. Furukawa, *Tetrahedron Lett.*, **1970**, 2663.

7) K. Tsujihara, T. Aida, N. Furukawa, and S. Oae, *ibid.*, **1970**, 3415.

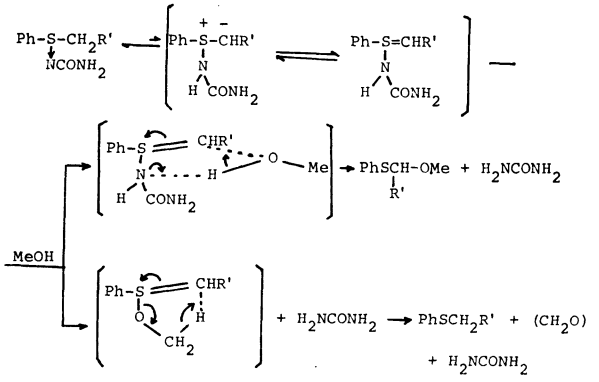
8) A. Nakanishi and S. Oae, *Chem. and Ind.*, **1971**, 960.

9) S. Oae, T. Aida, K. Tsujihara, and N. Furukawa, *Tetrahedron Lett.*, **1971**, 1145.

10) K. Tsujihara, K. Harada, N. Furukawa, and S. Oae, *Tetrahedron*, **27**, 6101 (1971).

11) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 682 (1969).

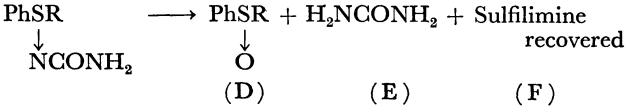
12) H. Kobayashi, N. Furukawa, T. Aida, K. Tsujihara, and S. Oae, *Tetrahedron Lett.*, **1971**, 3109.



Scheme 5.

filimine, the reaction seems to proceed through the initial proton transfer from C atom to N atom to form an intermediate which upon addition of methanol affords the α-alkoxy sulfide and the sulfide.

2) Hydrolysis: Treatment of methyl phenyl *N*-carbamoylsulfilimine with 5% aqueous alkaline solution, water or 5% aqueous hydrogen chloride solution at 55°C for 8 hr gave phenyl methyl sulfoxide.

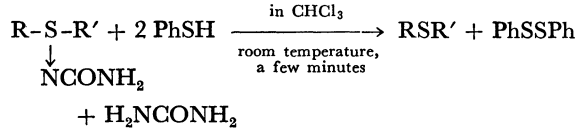


R	Reaction conditions	D	E	F
Me	5% KOH-H_2O	98%	not detd.	0%
	H_2O	99%	not detd.	0%
	5% HCl-H_2O	56%	not detd.	37%
Et	5% KOH-H_2O	98%	not detd.	0%

Scheme 6.

Thus, methyl phenyl *N*-carbamoylsulfilimine easily hydrolyzes in water as well as in aqueous alkaline solution. However, it hydrolyzed slowly in aqueous hydrogen chloride solution since the attack of hydroxide anion on the S(IV) atom is considered to lead to the hydrolysis product. A similar treatment of ethyl phenyl *N*-carbamoylsulfilimine with 5% aqueous alkaline solution at 60°C for 6 hr gave ethyl phenyl sulfoxide.

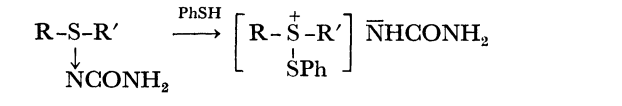
3) Reaction with Thiophenol: When the *N*-carbamoylsulfilimine was treated with thiophenol, it was easily reduced at room temperature within a few minutes to the corresponding sulfide (Scheme 7). Besides the sulfide, both urea and diphenyl disulfide were obtained quantitatively. For the reduction of one equivalent mole of sulfilimine two equivalent moles of thiophenol were required stoichiometrically.



[R, R′: Ph, Me; Ph, Et; *p*-MeC_6H_4, Me]

Scheme 7.

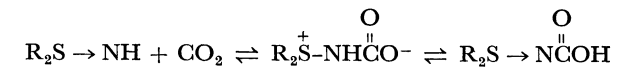
This reaction is analogous to that of sulfoxide or *N*-*p*-tolylsulfonylsulfilimine with thiophenol or *O,O*-dialkyl dithiophosphoric acid.[8] Thus the mechanism is considered to involve the initial nucleophilic attack by thiophenolate ion on S(IV) atom forming the sulfonium salt as an intermediate.



[R, R′; Ph, Me; Ph, Et; *p*-MeC_6H_4, Me]

Scheme 8.

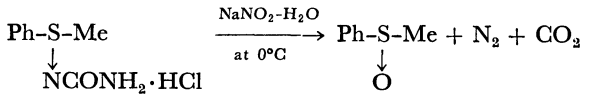
4) Reaction with Sodium Nitrite: It was reported by Appel and Buechner[13] that treatment of dialkyl sulfilimine with carbon dioxide gives the compound $R_2SNH \cdot CO_2$.



[R: Me, Et]

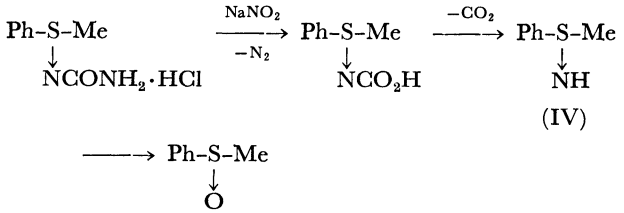
Scheme 9.

We therefore carried out the diazo-decomposition of *N*-carbamoylsulfilimine in the hope of obtaining the alkyl aryl sulfilimine. However, treatment of *N*-carbamoylsulfilimine hydrochloride with sodium nitrite at 0°C in water led to the evolution of N_2 and CO_2 gases, and the product obtained was found to be only the sulfoxide, no free sulfilimine derivative being obtained.



Scheme 10.

Although free sulfilimine (IV) was not actually isolated, its formation as an intermediate during the diazo-decomposition of *N*-carbamoylsulfilimine might be expected, since decarboxylation was observed as by Appel *et al.* The mechanism is considered as shown in Scheme 11.



Scheme 11.

Experimental

Materials. All the solvents, *i.e.*, benzene, methanol and chloroform were purified by standard procedures.[14] The others used were of chemical grade. Aqueous hydrogen chloride, sodium nitrite and sodium hydroxide were of special

13) R. Appel and W. Buechner, *Chem. Ber.*, **95**, 849 (1962).
14) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvents", Interscience Publishers, New York (1955).

grade. Thiophenol, sulfide, sulfoxide and disulfide were prepared by the usual procedures.

N-Chlorourea.[3] A suspension of 0.25 mol (15 g) of pulverized urea in 100 ml of acetonitrile was cooled to 0°C and chlorinated with Cl_2 gas with rapid stirring. Moisture was excluded by means of dry nitrogen gas.

Introduction of Cl_2 gas was stopped as soon as 0.1 mole (7.1 g) of chlorine was absorbed. The resulting clear, colorless solution was stirred for 30 min.

Synthesis of N-*carbamoylsulfilimine.* A solution of about

TABLE 2. IR SPECTRA OF *N*-CARBAMOYLSULFILIMINE[a]

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!S\rightarrow NCONH_2$$

R	R′	NH (cm^{-1})	C=O (cm^{-1})	S-N (cm^{-1})	Anal, %, Found (Calcd) C	H	N
Ph	Me	3340, 3170	1655	968	52.80(52.72)	5.44(5.54)	15.20(15.35)
p-MeC_6H_4	Me	3320, 3170	1640	960	54.53(55.08)	6.14(6.16)	14.43(14.26)
p-ClC_6H_4	Me	3350, 3180	1658	980	43.65(44.35)	4.21(4.20)	12.86(12.96)
p-$MeOC_6H_4$	Me	3350, 3180	1660	975	50.61(50.92)	5.75(5.70)	13.50(13.19)
Ph	Et	3340, 3180	1650	1028	55.42(55.07)	6.11(6.16)	13.93(14.26)
Ph	*n*-Pr	3360, 3190	1662	1021	56.61(57.11)	6.86(6.70)	13.44(13.31)
Ph	*i*-Pr	3350, 3200	1649	1039	57.17(57.11)	6.67(6.70)	13.47(13.31)
Me	*n*-Pr	3320, 3180	1680	1038	59.00(58.89)	7.02(7.18)	12.21(12.48)
Ph	*n*-Bu	3320, 3190	1685	1035	59.04(58.89)	7.24(7.18)	12.51(12.48)
Ph, Me>S→NTs[5]				930			
Ph, Me>S→NCOCHCl$_2$[4]			1638, 1625	821, 808			
Me, Me>S→NCO$_2$Et[2]			1620				

a) All IR spectra were taken as KBr disks with a 215 Hitachi grating infrared spectrophotometer.

TABLE 3. NMR SPECTRA OF *N*-CARBAMOYLSULFILIMINE[a]

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!S\rightarrow NCONH_2$$

R	R′	Ar-H	$CH_3C_6H_4$	$CH_3OC_6H_4$	$=SCH_3$	$-NCONH_2$
Ph	Me	7.91(m)			2.97(s)	4.94(s)
p-MeC_6H_4	Me	7.82(q)	2.58(s)		2.95(s)	4.97(s)
p-ClC_6H_4	Me	8.03(q)			3.05(s)	4.97(s)
p-$MeOC_6H_4$	Me	7.56(q)		4.08(s)	2.98(s)	5.08(s)

R	R′	Ar-H	$CH_3C_6H_4$	$=S-CH_2$ or $=S-CH$	$=S-CH_2CH_2$ or $=S-CH_2(CH_2)_2$	$-CH_3$ or $=(CH_3)_2$	$-NCONH_2$
Ph	Et	7.77(m)		3.07(q)		2.27(t)	5.02(s)
Ph	*n*-Pr	7.95(m)		3.18(m)	1.86(m)	1.14(t)	5.44(s)
Me	*n*-Pr	7.66(q)	2.48(s)	3.10(m)	1.76(m)	1.10(t)	5.10(s)
Ph	*i*-Pr	7.73(m)		3.32(m)		1.27(d), 1.36(d)	5.08(s)
Ph	*n*-Bu	7.97(m)		3.15(m)	1.20—2.10(m)	1.10(t)	5.37(s)

	Ar-H	$=SCH_3$
Ph, Me>S→NTs	7.63(m)	2.83(s)
Me, Me>S→NCO$_2$Et[2]		2.73(s)
Ph, Me>S→O	7.52(m)	2.73(s)

a) The chemical shifts (ppm) were measured with a Hitachi Perkin-Elmer R-20 High Resolution NMR Spectrometer (60 MHz) using TMS as an internal standard (δ=0.00) in $CDCl_3$. The multiplicity of the signal is given by s=singlet, d=doublet, t=triplet, q=quartet and m=unresolved multiplet.

0.08 mol of sulfides in 50 ml of acetonitrile was dropped with stirring into the above mentioned *N*-chlorourea solution maintained at 15—20°C by external cooling. After the addition, the temperature was raised to 60—70°C for 1 hr. A 10% aqueous solution of sodium hydroxide was added dropwise for about 30 min until the solution became alkaline. *N*-Carbamoylsulfilimine was then extracted with chloroform from alkaline solution. The compound was recrystallized as white solid from chloroform, acetone-alcohol or benzene-alcohol. Yield, 40—70%. IR and NMR spectra of *N*-carbamoylsulfilimine are summarized in Tables 2 and 3.

Thermolysis of Ethyl Phenyl N-*Carbamoylsulfilimine in Benzene.* About 0.004 mol (0.88 g) of ethyl phenyl *N*-carbamoyl-sulfilimine was heated in refluxing benzene (10 ml) for 10 hr under nitrogen stream. Ethylene was produced in 60% yield by this reaction and was converted into 1,2-dibromoethylene. This was confimed by comparing its glc behavior with that of the authentic compound. Benzene was removed from the residue and *N*-phenylthiourea, mp 163°C, was isolated in 95% yield. IR spectra: (ν_{N-H} 3440, 3200, $\nu_{C=O}$ 1677), NMR spectra: (δ 7.43, 5-Ar-H (multiplet), δ 8.19, 1-H (singlet), δ 6.54, 2-H (singlet)). The NMR spectra were measured with TMS internal standards (δ=0.00) as a reference peak in DMSO-d_6.

Found: C, 49.20; H, 16.35: N, 16.42%. Calcd. for $PhSNHCONH_2$: C, 49.99; H, 16.68; N, 16.65%.

Thermolysis of Methyl Phenyl N-*Carbamoylsulfilimine in Methanol.* About 0.005 mol (0.88 g) of methyl phenyl *N*-carbamoyl-sulfilimine was heated in refluxing methanol (10 ml) for 10 hr. The products obtained were separated by column chromatography and identified by comparing their IR and NMR spectra with those of the authentic compounds. Yields of sulfide, α-methoxy sulfide and urea were 0.44 g (75%), 0.12 g (14%) and about 0.30 g (100%), respectively.

Thermolysis of Ethyl Phenyl N-*Carbamoylsulfilimine in Methanol.* About 0.004 mol (0.88 g) of ethyl phenyl *N*-carbamoyl-sulfilimine was heated in refluxing methanol (10 ml) for 6 hr as well as methyl *p*-tolyl *N*-carbamoylsulfilimine. The products were determined by comparing their IR and NMR spectra with those of the authentic compounds. Yields of sulfide, α-methoxy sulfide and urea were 0.43 g (73%), 0.13 g (17%) and about 0.30 g (100%), respectively.

Hydrolysis of Methyl Phenyl and Ethyl Phenyl N-*Carbamoylsulfilimine.* Methyl phenyl *N*-carbamoylsulfilimine 0.002 mol (0.363 g) was heated at 55°C for 8 hr in 5 ml of 5% aqueous potassium hydroxide solution, water or 5% aqueous hydrogen chloride solution. The reaction solution was then acidified with a 10% aqueous hydrogen chloride solution and reactants were extracted with chloroform. The solution was then made alkaline by a 10% aqueous sodium hydroxide solution and the reactants were again extracted with chloroform. The products were identified by comparing their IR, NMR spectra with those of the authentic samples. Yield of sulfoxide was 0.24 g (98%), 0.25 g (99%) and 0.14 g (56%), respectively. Yields of the sulfilimine recovered were 0%, 0% and 37%, respectively.

Ethyl phenyl *N*-carbamoylsulfilimine (0.002 mol) was hydrolyzed by the same method, to the corresponding sulfoxide (98% yield) at 60°C for 6 hr in 5 ml of 5% aqueous potassium hydroxide solution. The product was identified by comparing its IR, NMR spectra with those of the authentic compound.

Reaction of N-*Carbamoylsulfilimine with Thiophenol.* A 10% solution of thiophenol in chloroform was dropped with stirring into a solution of about 0.005 mol of *N*-carbamoylsulfilimines (methyl phenyl, methyl *p*-tolyl or ethyl phenyl *N*-carbamoylsulfilimine) in 10 ml of chloroform at room temperature. After the addition, the solution was maintained at room temperature for a few minutes. Thiophenol (0.01 mol) was required to complete the reaction. The products, sulfide, disulfide and urea were separated by column chromatography and were identified by comparing their IR, NMR spectra with those of the authentic compounds.

Reaction of Methyl Phenyl N-*Carbamoylsulfilimine with Sodium Nitrite.* Two drops of a 35% aqueous hydrogen chloride solution was added to a solution of about 0.002 mol (0.37 g) of methyl phenyl *N*-carbamoylsulfilimine in 3 ml of water. Into this was dropped a solution of about 0.003 mol (0.20 g) of sodium nitrite in 2 ml of water, the temperature being maintained at 0°C with an ice bath. The solution was stirred overnight at 0°C, and the products were then extracted with chloroform. Methyl phenyl sulfoxide was obtained in 28% yield (0.08 g) and identified by comparing its IR and and NMR spectra with those of the authentic compound. Methyl phenyl *N*-carbamoylsulfilimine was recovered in 63% yield.