

PREPARATION AND PROPERTIES OF DIPHENYL N-HALOSULFILIMINES

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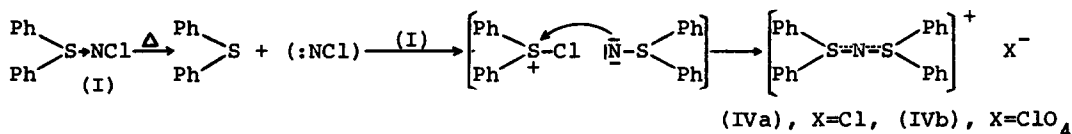
The chemistry of sulfilimine (iminosulfurane) has been explored mostly by means of N-acylderivatives.<sup>1)</sup> However, recently we found that most "free" sulfilimines (R<sub>2</sub>S<sup>NH</sup>R') (FS) can readily be prepared from the reaction of N-p-tosylsulfilimines with conc. H<sub>2</sub>SO<sub>4</sub>.<sup>2)</sup> This method may promise to the syntheses of other sulfilimine derivatives and actually a variety of diaryl N-acylsulfilimines were prepared from diphenyl(FS) and acylating agents.<sup>3)</sup> Furthermore, as an interesting approach for further study of sulfilimine, the synthesis of N-halogen substituted sulfilimines should be one of the most favored projects. Therefore, diphenyl(FS) was allowed to react with halogenating agents, and in fact we found that diphenyl N-halosulfilimines can readily be prepared as relatively stable compounds. In this communication, we report the synthesis and chemical properties of them.

Diphenyl N-Chlorosulfilimine (I)

The preparation method of (I) is as follows. Diphenyl (FS) (1g) and an equimolar amount of N-chlorosuccinimide were dissolved into 5ml of acetone at room temperature or an aqueous solution of H<sub>2</sub>SO<sub>4</sub> salt of (FS) was treated with aqueous solution of sodium hypochlorite. After 5min, the mixture was poured onto cold water and the oily substance formed was solidified immediately. The precipitates were filtered off, dried and recrystallized from benzene-hexane. (I) was obtained quantitatively, as pale yellow crystals m.p. 116-7°C (Dec.). I.R. 860 cm<sup>-1</sup> (ν<sub>S-N</sub>), Anal. Found C; 61.19, H; 3.92, N; 6.07. Calcd for C<sub>12</sub>H<sub>10</sub>SNCl, C; 61.14, H; 4.28, N; 5.94.

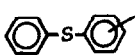
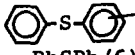
(I) is a relatively stable compound and it decomposed gradually at room temperature in the air for 20 days, affording diphenyl (FS) HCl salt in 75% yield. The pyrolysis of (I) was more facile than the corresponding (FS) and gave diphenyl sulfide as a major product. The decomposition of (I) took place more easily in solvents and the products and their yields were changed by changing the solvent used. The results are summarized in Table I. A characteristic feature of the decomposition of (I) is that it gave the compound (IVa) in substantial yield in every solvents. The structure of (IVa) was determined as follows.<sup>4)</sup> (IVa) has an I.R. absorption at  $930\text{ cm}^{-1}$  ( $\nu_{\text{S-N}}$ ) and N.M.R.  $\delta$  7.64-7.86 (4H), 7.33-7.64 (6H), but it did not give a constant m.p. Therefore, (IVa) was changed to its perchlorate salt (IVb) by adding sodium perchlorate in the aqueous solution of (IVa). (IVb) has m.p.  $172-2.5^{\circ}\text{C}$  and was recrystallized from chloroform-ether. I.R.  $900$  ( $\nu_{\text{S-N}}$ ),  $1095\text{ cm}^{-1}$  ( $\text{ClO}_4$ ), Anal. Found C; 58.77, H; 4.00, N; 2.68. Calcd for  $\text{C}_{24}\text{H}_{20}\text{NO}_4\text{S}_2\text{Cl}$ , C; 59.31, H; 4.15, N; 2.88.

The mechanism of the formation of (IVa) is considered to be the initial disproportionation of (I) to :NCl and diphenyl sulfide which is then chlorinated by (I) and then immediately substituted by the counter anion of (I) as shown below.



When the hydrolysis of (IVa) was carried out under alkaline condition, it yielded both diphenyl sulfoxide and diphenyl (FS) in quantitative yields supporting the structure (IVa). Meanwhile, decomposition of (I) in acetic acid gave a different kind of products as shown in Table I. Another interesting point of (I) is the reaction with nucleophiles. The product analysis seems to indicate that the attacking site depends upon the nucleophiles, namely either sulfur or nitrogen atom in the molecule. In the case of hydroxide anion sulfoximine was obtained quantitatively (S-attack) while cyanide anion gave N-cyanosulfilimine<sup>5)</sup> (N-attack). The reaction mechanism is not clear under the present experiments, however the result may suggest that the reaction of (I) with nucleophiles is to be a new approach for the syntheses of sulfilimine derivatives.

Table I. The Products and Yields for the Reaction of N-Halosulfilimines.

Compounds	Reaction Conditions	Products and Yields (%)
	decomposition in the air r.t. 20 days	$\left[ \begin{array}{c} \text{PhSPh} \\   \\ \text{NH}_2 \end{array} \right]^+ \text{Cl}^-$ (VI) (75)
	pyrolysis neat 90°C 1.5 hr	PhSPh (52), HCl,  (trace)
	in benzene r.t. 24 hr	(IVa) (74), PhSPh (12), $\text{PhSPh} \begin{array}{c} \text{O} \\   \end{array}$ (20)
	in chloroform r.t. 24 hr	PhSPh (22), $\text{PhSPh} \begin{array}{c} \text{O} \\   \end{array}$ (49), $\text{NH}_4\text{Cl}$ (23) (IVa) (6), (VI) (4)
PhSPh ↓ NCl (I)	PhSPh in benzene r.t. 5 min	PhSPh, $\text{PhSPh} \begin{array}{c} \text{O} \\   \end{array}$ (30), (IVa) (65), (VI) (21)
	in acetic acid r.t. 2 days	PhSPh (4),  (6), $\text{NH}_4\text{Cl}$ (40) $\text{PhSO}_2\text{Ph}$ (50), $\text{PhSPh} \begin{array}{c} \text{O} \\   \end{array}$ (6), $\text{PhSPh} \begin{array}{c} \text{O} \\   \\ \text{NAC} \end{array}$ (9), (IVa) (15)
	NaOH in methanol 45°C, 12 hr	$\text{PhSPh} \begin{array}{c} \text{O} \\   \\ \text{NH} \end{array}$ (96)
	NaCN in methanol r.t. 12 hr	$\text{PhSPh} \begin{array}{c} \text{O} \\   \\ \text{NH} \end{array}$ (39), $\text{PhSPh} \begin{array}{c} \text{O} \\   \\ \text{NCN} \end{array}$ (VII) (4)
	NaCN in DMSO r.t. 12 hr	$\text{PhSPh} \begin{array}{c} \text{O} \\   \\ \text{NH} \end{array}$ (15), (VII) (50)
	in benzene r.t. 20 days	PhSPh (56), (V) (89)
PhSPh ↓ NBr (II)	in acetic acid r.t. 12 hr	(V) (quant.)
	NaOH in methanol	$\text{PhSPh} \begin{array}{c} \text{O} \\   \\ \text{NH} \end{array}$ (70)

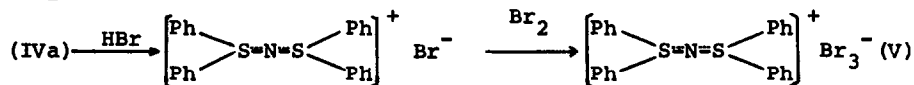
Diphenyl N-Bromosulfilimine (II)

(II) was prepared similarly as like (I) from N-bromosuccinimide in quantitative yield. The yellow crystals were recrystallized from benzene-hexane, m.p. 96-97°C (Dec.) I.R. 860  $\text{cm}^{-1}$  ( $\nu_{\text{S-N}}$ ), Anal. Found C; 51.87, H; 3.33, N; 5.02. Calcd. for  $\text{C}_{12}\text{H}_{10}\text{SNBr}$ , C; 51.44, H; 3.60, N; 5.00.

(II) is more stable than (I) and it can be stored for a month without decomposition even under exposing in the air and light. Unlike (I), decomposition of (II) in solvents gave an unknown compound (V), m.p. 184.5-5°C, which was

recrystallized from methanol. Especially in acetic acid, (II) gave (V) spontaneously when it was dissolved into the acid. The structure of (V) was estimated by the elemental and spectrum analyses as like as the compound (IV). I.R.  $935\text{ cm}^{-1}$  ( $\nu_{\text{S-N}}$ ), Anal. Found C; 45.04, H; 3.03, N; 2.11. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{S}_2\text{NBr}_3$ , C; 46.03, H; 3.22, N; 2.24.

Furthermore, when (IVa) was treated with HBr and then following with an excess of  $\text{Br}_2$  gave (V) quantitatively.



However the alternative possibility of the structure (V) namely whether a pentacoordinated structure or a sulfonium salt type can not be ruled out, thus, it is now underconsideration.

#### Diphenyl N-Iodosulfilimine (III)

An equimolar amount of diphenyl (FS), iodine and sodium hydroxide were dissolved into methanol at room temperature. After the reaction, the solution was poured onto ice water. The precipitates were filtered off, dried and recrystallized from benzene-hexane gave yellow crystals in quantitative yield, m.p.  $99-100^\circ\text{C}$  (Dec.). I.R.  $880\text{ cm}^{-1}$  ( $\nu_{\text{S-N}}$ ), Anal. C; 43.87, H; 2.89, N; 4.19. Calcd. for  $\text{C}_{12}\text{H}_{10}\text{SNI}$ , C; 44.05, H; 3.08, N; 4.28.

Further works on these and related compounds are now undergoing in these laboratories.

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