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FORMATION OF S,S-DIPHENYL-S-METHOXYTHIAZYNE $Ph_2S(OMe)(\equiv N)$ IN THE ALKALINE HYDROLYSIS OF S,S-DIPHENYL-N-HALOSULFILIMINES.

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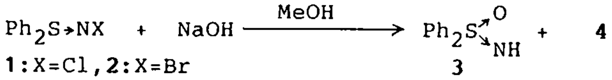
SUMMARY : The structure of a compound formed during the alkaline hydrolysis of S,S-diphenyl-N-halosulfilimines to the corresponding sulfoximine in methanol was assigned to $PhS(OMe)(\equiv N)Ph$, S,S-diphenyl-S-methoxythiazyne, on the basis of spectroscopic analyses and chemical reactions.

The alkaline hydrolysis of S,S-diaryl-N-chlorosulfilimine in methanol has been the most convenient method to prepare diaryl sulfoximines.1-4) However, the yield of diphenyl sulfoximine (**3**) obtained from diphenyl-N-bromosulfilimine (**2**) is not high enough (70%) as in the N-chlorosulfilimine **1** ,1,2) and one other compound (**4**) is always detected in the reaction. In order to examine the other product, we tried again the reaction of **2** in various conditions.



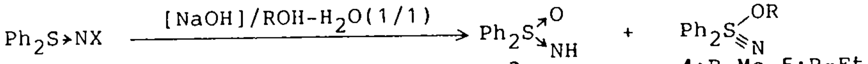
$$Ph_2S{\to}NX + NaOH \xrightarrow{MeOH} Ph_2S\overset{\nearrow O}{\underset{\searrow NH}{}} + \mathbf{4}$$

1:X=Cl,**2**:X=Br **3**

A methanol solution of **2** (50ml, 0.015M) mixed with aqueous sodium hydroxide solution (50ml, 0.2M) was allowed to react at 35°C for 1.5 hours. After the standard work up avoiding acidic conditions, ^{1}H-NMR of the organic material showed methoxyl signal at 3.7 ppm in addition to signals due to **3**. TLC on silica gel showed a spot of Rf 0.1-0.4 along with that of **3** (Rf 0.5) with chloroform. In spite of many efforts using column chromatography and liquid chromatography, the isolation of the unknown compound (**4**) was unsuccessful because of its facile conversion to **3** in the presence of silica gel or alumina. When the mixture of **3** and **4** was treated with dilute HCl or H_2SO_4, **4** was converted to **3** completely. Heating of the mixture without solvent or in methanol at 50°C gave **3** in 90-92% yield. Similarly, alkaline methanol at 35°C converted **4** to **3** in 60% yield (**3**:**4** = 28:72 to 71:28). From these observations, **4** was suggested to be an intermediate in the alkaline hydrolysis of **2** to **3**. Furthermore, reaction of **4** with thiophenol in methanol rapidly afforded **3** and thioanisole quantitatively indicating that **4** acted as an alkylating reagent for thiophenol. The structure of **4** was assigned as follows. In GC-Ms of the mixture of **3** and **4**, GC-peak separated from **3** (SE-52, 140°C, 25M) showed a parent peak at m/z 231 (high mass data Found:m/z 231.0750. Calcd for $C_{13}H_{13}NOS$:M,231.0713) and fragment peak at m/z 106 (high mass data Found:m/z 106.0666. Calcd for C_7H_8N:M,106.0654). The ^{1}H-NMR of the phenyl group of **4** showed the ortho protons at 7.80-8.05 ppm and the meta and the para protons at 7.35-7.60 ppm which are very similar to those of diphenyl sulfone (7.80-8.05 ppm, and 7.31-7.60 ppm) and **3** (7.95-8.15 ppm, and 7.37-7.60 ppm). The ^{13}C-NMR spectrum of **4** ($CDCl_3$ δ=144.4, 132.1, 129.0, 127.1, 48.2) is also very similar to that of **3** ($CDCl_3$ δ=143.5, 132.4, 129.0, 127.8), indicating that the structure of **4** is close to the sulfone. These observations suggest that the methoxyl group attaches on the sulfur atom rather than the nitrogen atom. The IR SN stretching band of **4** observed at 1340 cm^{-1} is higher than that of diphenyl sulfilimine (940 cm^{-1}) or sulfoximine **3** (965, 1097, 1225 cm^{-1}) indicating that the SN bond has a triple bond character. The ^{15}N-NMR signal of **4** at 126.43 ppm in $CDCl_3$ lies to the downfield of **3** (88.52 ppm) and diphenyl-N-tosylsulfilimine (99.50 ppm). The structure of this compound **4** is considered to be a new type of organic sulfur compound having an SN triple bond, S,S-diphenyl-S-methoxythiazyne. In fluorine chemistry, an example of this type of structure is involved in thiazyl trifluoride (F_3SN) in which SN triple bond is established,$^{5-7)}$ and the similar compound $Ph_2SF(\equiv N)$ was prepared and first named as thiazyne by Clifford et al.$^{8)}$

The alkaline hydrolysis of N-halosulfilimines affording the intermediate **4** under various conditions are shown in Table. The reaction of **2** in shorter time (20 min) at higher alkali concentration also gave **4** in similar yield. Meanwhile, the alkaline hydrolysis of chlorine derivative **1** also afforded **3** (50%) and **4** (43%). In addition, the reaction of **2** in ethanol in the similar conditions also gave the corresponding ethoxythiazyne **5** , though the yield was a little low. Further investigations for these interesting alkoxythiazynes are now underway in these laboratories.

Hydrolysis of N-Halosulfilimines (35°C).



$$Ph_2S\rightarrow NX \xrightarrow{[NaOH]/ROH-H_2O(1/1)} Ph_2S{\overset{\nearrow O}{\searrow NH}} + Ph_2S{\overset{\diagup OR}{\equiv N}}$$

1:X=Cl,2:X=Br　　　3　　　4:R=Me,5:R=Et

Conditions				Products and Yields (%)
X	[NaOH](M)	Time	Solvent	
Br,	0.1,	92 min,	$MeOH/H_2O$	**3** (34), **4** (60)
Br,	1.0,	20 min,	$MeOH/H_2O$	**3** (19), **4** (62)
Cl,	0.1,	17 min,	$MeOH/H_2O$	**3** (50), **4** (43)
Br,	0.1,	3.4 hr,	$EtOH/H_2O$	**3** (22), **5** (22), $Ph_2S\rightarrow NH\cdot H_2O$ (44)

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