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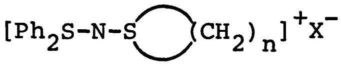
A POSSIBLE SULFURANE: N-DIPHENYLSULFILIMINYL SULFONIUM SALT



$[Ph_2S\text{-}N\text{-}S(CH_2)_n]^+X^-$

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Sulfiliminyl sulfonium salts($III_{a,b}$) were prepared. NMR spectra indicate that III has a sulfurane structure.

Sulfurane has been considered to be a reactive intermediate or incipient activated complex in the nucleophilic substitution on a trivalent sulfur atom.$^{1)}$ Recently, a few sulfuranes were actually isolated and their structures were determined by X-ray crystallography,$^{2)}$ while some have been identified as unstable intermediates by nmr spectroscopy.$^{3)}$ In the course of the study of free sulfilimines, we found that N-halo(Cl,Br)diphenylsulfilimine(I) reacts readily with sulfides to afford the corresponding sulfiliminyl sulfonium salt(II).$^{4)}$

$$\underset{\text{(I) X=Cl,Br,I}}{Ph_2SNX} \quad + \quad R_2S \longrightarrow \underset{\text{(II)}}{[Ph_2S\text{-}N\text{-}SR_2]^+X^-} \qquad \text{R:aryl, alkyl}$$

While a detailed structural analysis of II is now underway, we believe some of II have a kind of sulfurane structure.

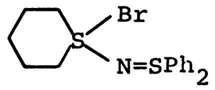
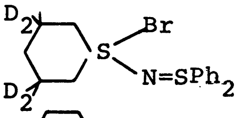
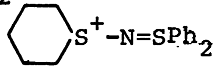
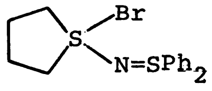
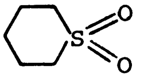
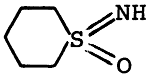
When six and five membered sulfides were allowed to react with I($X=Cl^-,Br^-$),III_a ($R,R=-(CH_2)_5-$) and III_b($R,R=-(CH_2)_4-$) were obtained in quantitative yields.$^{5)}$ The nmr spectra of III_a and III_b change dramatically with solvents and counter anions (X^-). The ring protons in III_a have multiplet absorption centered at δ(ppm) 3.90, 3.05 and 1.90 respectively with 2:2:6 ratio in $CDCl_3$. This indicates that the α-protons of the thiane ring are magnetically nonequivalent. Meanwhile, those of the corresponding sulfone or sulfoximine are only of one kind and of triplet chemical shifts for the α-protons. Furthermore, III_a deuterated at β-positions have AB type quartets centered at δ(ppm) 3.90 and 3.12 and a singlet at 1.73(γ-H).

The nmr pattern of III_a($X=NO_3^-$) in $CDCl_3$ is also quite similar to that of III_a ($X=Cl^-$, Br^-). However, when the nmr spectrum of III_a with $X=ClO_4^-$ or BF_4^- or the solvent is changed from $CDCl_3$ to D_2O or DMSO, the ring protons of III_a do not show 2:2:6 pattern but the spectrum gives multiplets at δ(ppm) 2.90, 1.50 ($X=Br^-$ in D_2O), 3.22, 1.73($X=BF_4^-$ in $CDCl_3$) in 4:6 ratio, suggesting that III_a with $X=ClO_4^-$ or BF_4^- and even III_a with $X=Cl^-$, Br^- and NO_3^- in such polar solvents as D_2O and DMSO are assumed having a structure similar to those of other trivalent sulfur compounds as sulfoxide or sulfilimine.

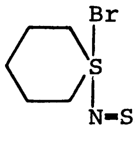
These nmr behavior of III can be explained nicely by assuming that III($X=Cl^-$, Br^-, NO_3^-) have a sulfurane structure in such nonpolar solvent as $CDCl_3$ but in polar solvent such as D_2O or d_6-DMSO, a strong solvation of the counter anion separates X anion from the central S(III) atom thus destroying the sulfurane structure.

Apparently, counter anions such as ClO_4^- and BF_4^- are not as nucleophilic as but bulkier than Cl^- or Br^- and hence the sulfurane structure cannot be maintained with these ligands. The nmr pattern of III_a($X=Br^-$) in $CDCl_3$ did not change even though the temperature was varied from room temperature to 120°C and above 120°C III_a decomposed to afford diphenyl sulfide and thiane. This indicates that III_a($X=Br^-$) has a moderately tight structure in $CDCl_3$. Johnson et al. suggested earlier that the chemical shifts of the α-protons attached to the sulfur atom of sulfurane appeared at a field lower than that of sulfonium salt or sulfoxide.$^{3)}$ The α-protons of III_a($X=Br^-$) in $CDCl_3$ resonate at lowest field among other sulfur analogs as shown in Table. All these nmr data suggest that III_a($X=Cl^-$, Br^-) in $CDCl_3$ is assumed to have a sulfurane-like structure as shown below and III_a($X=Cl^-$, Br^-) dissociates in such polar media as D_2O and DMSO to afford sulfonium ion while III_a ($X=ClO_4^-$ or BF_4^-) is a normal sulfonium salt even in $CDCl_3$.

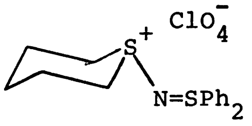
Table Chemical Shifts of α,β and γ Protons of Thiane Derivatives

Compounds		α	β	γ
		3.90(m)2H, 3.05(m)2H	1.90(m)6H	
" "a)		2.90(m)4H	1.50(m)6H	
		3.90(d)2H, 3.12(d)2H	1.73(s)2H	
	BF_4^-	3.22(m)4H	1.73(m)6H	
" "	ClO_4^-	3.30(m)4H	1.80(m)6H	
		4.00(m)2H, 3.15(m)2H	2.40(m)4H	
		3.02(t)4H	2.10(m)4H	1.70(m)2H
		3.10(t)4H	2.10(m)4H	1.70(m)2H

All chemical shifts were measured in $CDCl_3$ at 35°C by using TMS as an internal standard. a) measured in D_2O



Sulfurane



Sulfonium Salt

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5) III_a(mp 163-164°C ir 920cm^{-1}), III_b(mp 135-136°C ir 930cm^{-1})

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