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SULFUR-NITROGEN YLIDS (IMINOSULFURANES): THE PREPARATION AND PROPERTIES OF N-ETHOXYCARBONYLIMINODIALKYLSULFURANES

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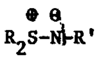
The study of iminosulfuranes (or sulfilimines) has received little attention during the past 50 years. Since the first reported preparation of an iminosulfurane, N-tosyliminodiethylsulfurane (Ia) by Mann and Pope[1] in 1922, most published work on iminosulfuranes[2,3] has been devoted to compounds of this general structural type. Notable exceptions to this include three papers on the preparation of N-acyliminodialkyl- and N-acyliminodibenzylsulfuranes[4,5,6] (Ib), and the preparation of iminodialkylsulfuranes, (Ic) by Appel and coworkers.[7] Little is known about the chemistry and spectroscopic characteristics of iminosulfuranes, and the structures of iminosulfuranes Ib and Ic have not been rigorously established.



$$R_2\overset{\oplus}{S}\text{-}\overset{\ominus}{N}\text{-}R' \quad (I)$$

Ia. R=Et; $R'=p\text{-}H_3C\cdot C_6H_4SO_2\text{-}$

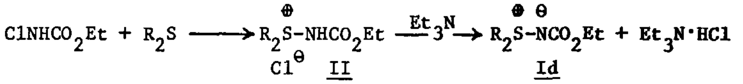
Ib. R=Me, Et, $PhCH_2$; R'=CO-alkyl, CO-Ph

Ic. R=Me, Et; R'=H

Id. R=alkyl; $R'=CO_2Et$

We report here the preparation of a new class of iminosulfuranes: N-ethoxycarbonyliminodialkylsulfuranes (Id: R=Me, Et; $R'=CO_2Et$). I.r., n.m.r., and mass spectrometry have been used to substantiate the structures.

The synthesis of N-ethoxycarbonyliminodialkylsulfuranes is shown in Scheme I.



$$ClNHCO_2Et + R_2S \longrightarrow \underset{Cl^{\ominus}\ \ II}{R_2\overset{\oplus}{S}\text{-}NHCO_2Et} \xrightarrow{Et_3N} \underset{Id}{R_2\overset{\oplus}{S}\text{-}\overset{\ominus}{N}CO_2Et} + Et_3N\cdot HCl$$

Scheme I. R=Me, Et

Treatment of dimethyl sulfide with ethyl N-chlorocarbamate[8] (1.2:1 molar ratio) in chloroform at 0-5° gave N-ethoxycarbonyliminodimethylsulfonium chloride (II, R=Me) in 50-60% yield. The sulfonium salt is a white crystalline solid, mp 121° (d) (recrystallized from 1:4 methanol/ether). The reaction of diethyl sulfide and ethyl N-chlorocarbamate (1.2:1 molar ratio) in carbon tetrachloride at -15 to -20° afforded N-ethoxycarbonyliminodiethylsulfonium chloride, (II, R=Et) in 50% yield. This salt is also a white solid, mp 98-99° (d) (recrystallized from 1:5 chloroform/carbon tetrachloride). In the purification of these sulfonium salts, temperatures in excess of 25° must be avoided in the recrystallization, and prolonged drying *in vacuo* was necessary before the mp stabilized.

Treatment of the dimethyl salt (II, R=Me) with triethylamine (1:1.2 molar ratio) in chloroform gave N-ethoxycarbonyliminodimethylsulfurane (Id, R=Me), a pale-yellow liquid, in 80-90% yield. In a similar manner, reaction of the diethyl salt, (II, R=Et) with triethylamine in dichloromethane afforded N-ethoxycarbonyliminodiethylsulfurane (Id, R=Et; 80-90% yield, bp 135-140°/0.05 mm). The distilled ylid is a colorless liquid. Short-path distillation is feasible only if the temperature is kept below 150° since Id (R=Et) decomposes at 150°.

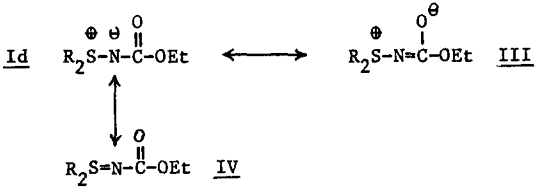
The spectral characteristics of the sulfonium salts (II) and the iminosulfuranes (Id) are summarized in Table I. The C=O stretching vibration of the sulfonium salts is at 1735-1740 cm^{-1}, while the iminosulfuranes have ν_{max} 1620-1630 cm^{-1}. This shift is analogous to that observed in converting carboxylic acids into carboxylate anions and suggests that the canonical form (III) is a major contributor to the iminosulfurane structure. The iminosulfuranes have λ_{max} 219 nm, ε_{max} 2200-2350 which indicates that the S-N bond possesses partial double bond character, i.e. it can be envisaged as a semi-polar bond with a small degree of π-bonding due to 2p-3d orbital overlap (canonical form IV).

Table I. Spectral Characteristics* of N-Ethoxycarbonyliminodialkylsulfonium Chlorides,(II), and N-Ethoxycarbonyliminodialkylsulfuranes, (Id).

		II (R=Me)	II (R=Et)	Id (R=Me)	Id (R=Et)
i.r. (cm^{-1}).	NH stretch	3465 (w)	3420 (w)	absent	absent
	C=O stretch	1740 (s)	1735 (s)	1620 (s)	1630 (s)
u.v.	λ_{max} (nm)	-	-	219	219.5
	ε_{max}	-	-	2200	2350
n.m.r.	(δ)	d_6-DMSO	d_6-DMSO	$CDCl_3$	$CDCl_3$
	$\underline{CH_3}CH_2O$	1.27t	1.24t	1.23t	1.24t
	$\underline{CH_3}CH_2\overset{\oplus}{S}-$	-	1.35t	-	1.35t
	$CH_3\underline{CH_2}\overset{\oplus}{S}-$	-	3.74q,3.78q	-	2.93q
	$CH_3\underline{CH_2}O-$	4.23q	4.22q	4.03q	4.06q
	-NH-	8.10s	7.25s	absent	absent
	$CH_3\overset{\oplus}{S}-$	3.37s	-	2.73s	-

* i.r. spectra were run as KBr discs (II) and liquid films (Id) using a Perkin-Elmer 225 Grating Infra-red spectrophotometer; u.v. spectra were performed with a Perkin-Elmer spectrophotometer, model 202, using EtOH as solvent (0.008% w/v); absorption did not follow the Beer-Lambert Law. N.m.r. spectra were obtained with a Varian A-60A spectrometer using TMS as internal standard (δ=0.00); s-singlet, t-triplet, q-quartet. The purity of all compounds was established by t.l.c. and microanalysis.

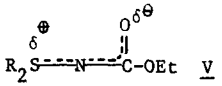
Comparison of the n.m.r. spectra of the sulfonium salts, (II) with those of the iminosulfuranes, (Id) revealed that the resonances of protons α to the positively charged sulfur atom are shifted upfield by 0.6-0.8 ppm in going from the salt to the ylid, suggesting that there is less deshielding by sulfur in the iminosulfuranes, i.e. it has a smaller positive charge. The overall structure can then be represented by V.



Id $R_2\overset{\oplus}{S}-\overset{\ominus}{N}-\overset{O}{\overset{\|}{C}}-OEt \longleftrightarrow R_2\overset{\oplus}{S}-N=\overset{O^{\ominus}}{\overset{|}{C}}-OEt$ III

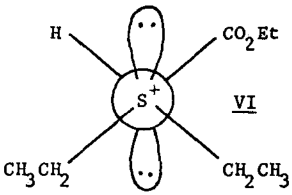
$\updownarrow$

$R_2S=N-\overset{O}{\overset{\|}{C}}-OEt$ IV

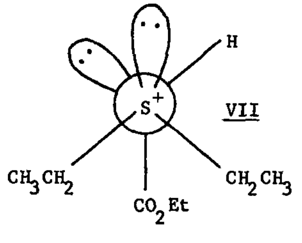


$R_2\overset{\delta\oplus}{S}\cdots N\cdots\overset{O^{\delta\ominus}}{\overset{\|}{C}}-OEt$ V

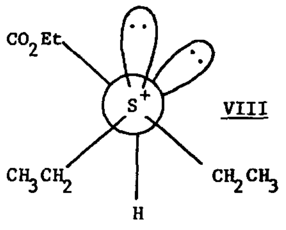
The n.m.r. spectrum of sulfonium salt II (R=Et) in d_6-DMSO at 37° reveals that the methylenes in the two ethyl groups attached to the sulfur atom are in dissimilar environments. This may be due to a conformational preference, in which the lone pairs on nitrogen and sulfur repel each other, thus placing the ethyl groups in different magnetic environments. The preferred conformation may be staggered (VI) or gauche (VII or VIII), any of which would give rise to non-identical ethyl groups:



VI



VII

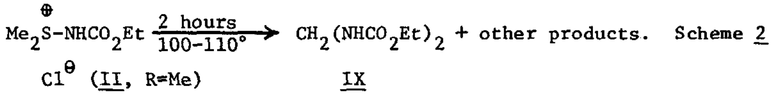


VIII

Rotational barriers attributable to lone-pair interactions have previously been observed in N-S,[9] N-O,[10] N-N,[11] and N-P[12] compounds.

Thermolysis of Sulfonium Salts (II) and Iminosulfuranes (Id).

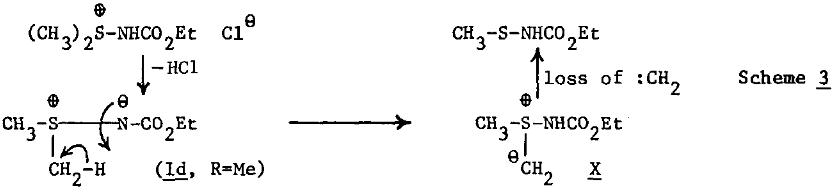
Thermolysis of sulfonium salt II, (R=Me) afforded three major components, one of which was 1,1-bis(N-ethoxycarbonylimino)methane, (IX) (Scheme 2).



$$\overset{\oplus}{Me_2S}\text{-}NHCO_2Et \xrightarrow[100\text{-}110°]{2\ hours} CH_2(NHCO_2Et)_2 + \text{other products.}\quad \text{Scheme 2}$$

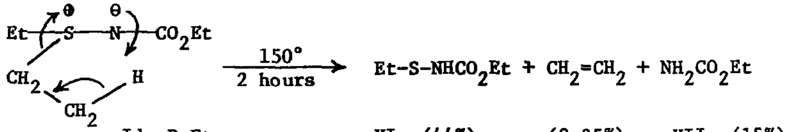
$Cl^{\ominus}$ (II, R=Me) IX

The mass spectrum of the sulfonium chloride (Scheme 3) revealed that the primary fragmentation was loss of HCl to give the iminosulfurane, (Id); subsequent formation of the sulfurane, (X) was followed by loss of methylene to yield ethyl N-methylthiocarbamate. Loss of methylene is an unusual process in mass spectrometry, and the ease with which it occurs in this case is strong evidence for the intermediacy of the sulfurane, (X). The mass spectrum of dimethylsulfonium 1-dodecylsulfonylmethylid has been rationalized on a similar basis.[13] It seems likely that the sulfurane, (X) is an intermediate also in the thermolysis of the sulfonium salt (scheme 2).



Scheme 3

Thermolysis of the iminosulfurane Id (R=Et) gave ethyl N-(ethylthio)carbamate, (XI), ethyl carbamate, (XII) and ethylene (Scheme 4, % yields in parentheses). The formation of XI involves a five-center transition state. In the mass spectrum of Id, (R=Et) loss of C_2H_4 from the molecular ion to give ethyl N-(ethylthio)carbamate was accompanied by a metastable peak, which indicated that electron-induced fragmentation gave rise to the same product as did thermal cleavage.



$\xrightarrow[\text{2 hours}]{150°}$ Et-S-NHCO$_2$Et + CH$_2$=CH$_2$ + NH$_2$CO$_2$Et

Scheme 4

Id, R=Et XI, (44%) (8-35%) XII, (15%)

A preliminary examination of the thermolysis of the sulfonium salt II (R=Et) showed that 1,1-bis(N-ethoxycarbonylimino)ethane is formed at ca. 20-70°, while at higher temperatures (>70°) the presence of structurally related carbamates is observed.

Further investigation of the thermolysis of the sulfonium salts, (II) and the dimethyliminosulfurane (Id, R=Me) is in progress. The preparation and reactions of iminodialkylsulfuranes, N-alkyl- and N-acyl-iminodialkylsulfuranes is also currently under examination.

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