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S-ACYL S-ACYLOXYSULPHONIUM IONS: A NEW PUMMERER-TYPE REARRANGEMENT-FRAGMENTATION REACTION

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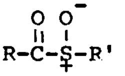
S-acylthiol S-oxides of general formula  $R-\overset{O}{\overset{\|}{C}}-\overset{O^-}{\overset{|}{\underset{+}{S}}}-R'$ are a new class of organic compounds, first postulated as possible intermediates in thiol ester oxidations with either NBS or iodosobenzene[1] and later on isolated by Barton and co . who obtained some stable representatives of this group of compounds by oxidation of thiocarbonates O,S-diesters with m-chloroperbenzoic acid[2]. We wish now to report on the results of our work on the chemistry of these novel compounds.

When a 5 - 10% solution of primary and secondary S-alkyl thiol esters in 1,2-dichloroethane is submitted to the action of ozonized oxygen (ca. 0,05 mmole ozone/min) at room temperature, it can be shown that a highly reactive S-acylthiol S-oxide (α-keto sulphoxide) is formed[3]. After 18 hrs. the initial thiol ester is totally consumed and after work-up, the corresponding carboxylic acid anhydrides and dialkyl disulphides are isolated in high yields (table I). We now believe that these results can be conveniently explained through the formation of an intermediate S-acyl S-acyloxisulphonium ion, resulting from the attack of the sulphoxide O-atom on the thiolcarbonyl group of the thiol ester, which further decomposes to the products, according to the following scheme:

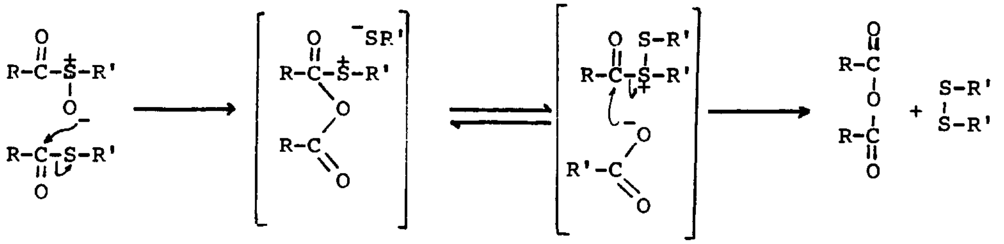


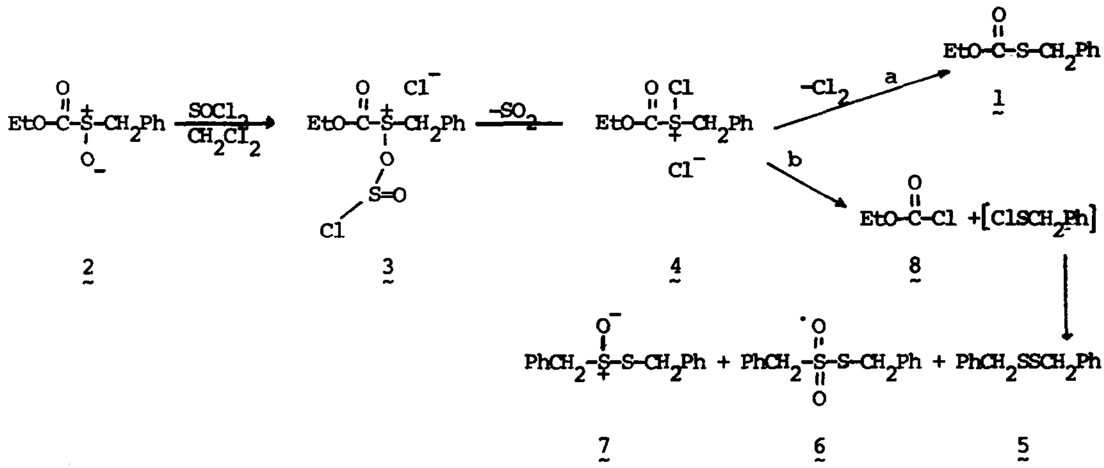
Table I[4]

Thiolester $R-\overset{O}{\overset{\|}{C}}-S-R'$		Product yields (%)	
R	R'	$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ 1)	R'-S-S-R'
cyclo-C_6H_{11}	n-C_3H_7	85	84
	iso-C_3H_7	97	86
	n-C_4H_9	94	84
	sec-C_4H_9	91	84
	n-C_6H_{13}	82	82
	cyclo-C_6H_{11}-CH_2-	90	85

1) Together with some cyclohexanecarboxylic acid

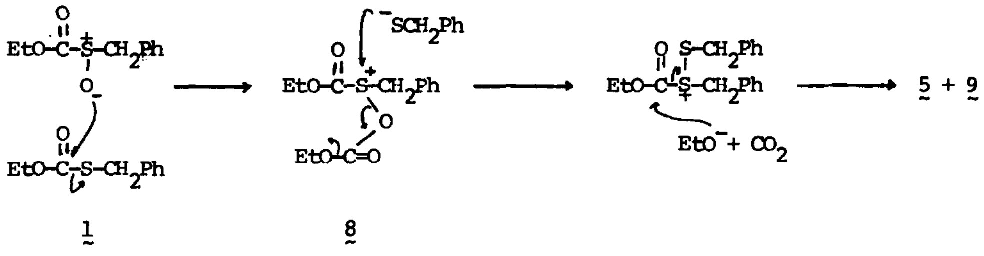
Though it is known that the sulphoxide O-atoms can act as nucleophiles in many reactions, previous attempts to prepare S-acyl S-alkoxysulphonium ions were rather unsuccessful[2]. We were, however, able to effect the acylation of S-oxides in order to confirm the above formulated mechanism.

We could find that ethoxycarbonyl benzyl sulphoxide 2 reacted rapidly with thionyl chloride in dichloromethane at -10°. The i.r. spectrum of the mixture ($\nu^{max.}$ /cm^{-1} (CH_2Cl_2) 1775, 1240, 1140) showed the formation of an intermediate 3 which rapidly decomposed, probably through a chlorosulphonium ion[6] 4 to yield dibenzyl disulphide 5 (18%), S-benzyl toluene- α-thiolsulphonate 6 (11%), dibenzyl disulphide S-oxide 7 (10%), ethyl chloroformate 8 (20%), and S-benzyl O-ethyl thiocarbonate 1 (32%). It is likely that those products arise from the attack of Cl^- at two different positions of 4: the thiol ester would arise from the attack on the chlorine atom while the other products would originate from the attack on th CO group:



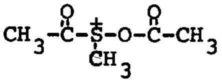
When the same reaction was performed in the presence of $AgBF_4$ at -15°, after filtration and evaporation of the solvent in vacuum at -3°, we obtained a pasty solid ($\nu^{max.}/cm^{-1}$ (CH_2Cl_2) 1775, 1240, 1140, 1060, 1025) which we believe to be the BF_4^- salt of 3. It rapidly decomposes at room temperature with liberation of SO_2, to yield 5, 6, and 8 but not 1. This strongly indicates the formation of 1 through path a, because it is not formed in the absence of Cl^-.

The reaction of 1 with 2 in dichloromethane at 40° took place very slowly as expected[5]. After 20 hrs. only 20% of the reaction had occurred with formation of 5 together with diethyl carbonate 9 and CO_2. We were not able to detect the formation of anhydride. In this case the course of the reaction could be formulated as follows:



In order to confirm this we carried out the reaction of 1 with ethyl chloroformate in dichloromethane at -10° in the presence of $AgBF_4$. After 16 hrs. the mixture was filtrated, the solvent evaporated in vacuum. The residue was dissolved in ethyl acetate : petroleum ether and kept at -20°. We obtained a white pasty solid ($\nu^{max.}/cm^{-1}$ (CH_2Cl_2) 1730, 1240, 1060, 1025) which rapidly decomposed at room temperature. We believe it to be the BF_4^- salt of 8. Performing the same reaction without isolation of the product, upon addition of equimolecular amount of $PhCH_2SNa$ under nitrogen atmoshpere, again we obtained diethyl carbonate 9 (30%) and dibenzyl disulphide 5 (65%). These results seem to confirm the mechanism outlined above. The formation of diethyl carbonate is likely to be due to the instability of the ethyl carbonic acid anion which decomposes to CO_2 and EtO^-, this being the nucleophile which actually attacks the CO group. When the same reaction was performed using e.g. benzoyl chloride as acylating agent, the mixed ethyl carbonic acid benzoic acid anhydride could be obtained.

When methyl thiolacetate was oxidized by ozone and the reaction run in a P.M.R. tube in CCl_4, the initially formed signal attributed to the S-methyl protons of the corresponding S-oxide (τ = 7,5) gradually disappeared and a new strong signal appeared at τ = 6,3 which could be attributed to the S-methyl protons of



$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{+}{S}}-O-\overset{O}{\overset{\|}{C}}-CH_3$ [6].

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6 - Higuinaldo José Chaves das Neves is indebted to Dr. Peter Samnes for facilities and help in the obtainment of P.M.R. spectra and to Prof. L.S. Godinho for advice.