Tetrahedron Letters No. 25, pp 2171 - 2174, 1978.   0040-4039/78/0615-2171$02.00/0

Printed in Great Britain.

THE S→O ACYL SHIFT IN S-ACYLTHIOL S-OXIDES
MIXED SULPHONIC ACID CARBOXYLIC ACID ANHYDRIDES FROM THIOLESTERS

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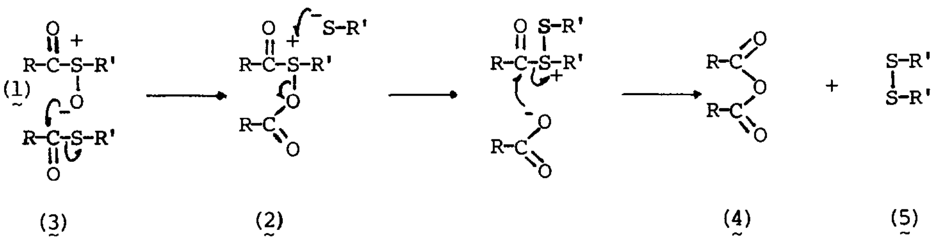
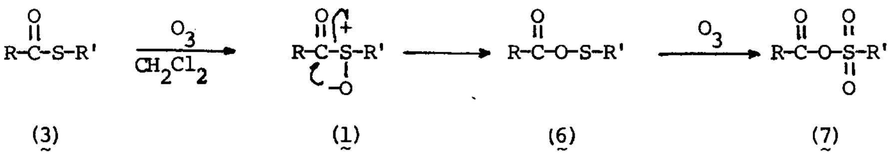
(Received in UK 17 April 1978; accepted for publication 27 April 1978)

In the course of our studies on the chemistry of the recently discovered S-Acylthiol S-oxides (1)[1-3], we have reported the ability of the sulphoxide O-atom to undergo acylation reactions to give unstable S-acyl S-acyloxysulphonium ions (2). These decompose affording the corresponding carboxylic acid anhydrides and disulphides (scheme I).



Scheme I

This reaction was found to take place spontaneously when (3) was submitted to the action of a stream of ozonized oxygen in CH_2Cl_2 at room temperature as described elsewhere[4]. We, however, found that if the nature of R or/and R' was such that the efficiency of the nucleophilic attack at the C=O group was diminished, the overall reaction took a different course. Under the conditions used, the mixed sulphonic acid carboxylic acid anhydrides (7) were obtained in good yields (table I). They probably arise from the further oxidation of an intermediate acyl sulphenate (6) originated by an S→O acyl shift of the acyl group of (1) (scheme II).



Scheme II

Furthermore, the initial thiolester was totally consumed after 3-4 hours.

The mixed sulphonic acid carboxylic acid anhydrides have been prepared by a number of not always

Table I - Mixed sulphonic acid carboxylic acid anhydrides obtained by oxidation of thiolesters[4]

Thiolester (3)		Yield % (7)
R	R'	
Ph	n-C_4H_9	55
Ph	sec-C_4H_9	86
Ph	ter-C_4H_9	50 a)
$PhCH_2$	n-C_4H_9	60 a)
$PhCH_2$	sec-C_4H_9	70 a)
$PhCH_2$	ter-C_4H_9	80
ter-C_4H_9	n-C_4H_9	50
cyclo-C_6H_{11}	ter-C_4H_9	70

a) Benzoic acid was also formed

satisfactory methods. They have recently been object of some attention. These compounds are powerful acylating agents, able to effect the cleavage of ethers to form esters[5]. Their properties make them very interesting reagents though it has not been possible to obtain them in a pure form owing to their exceeding susceptibility to hydrolysis and to their extensive decomposition on destilation[6]. They dismutate by heating, affording the corresponding carboxylic acid anhydrides and sulphonic acid anhydrides. Thus, the oxidation of thiolesters by ozone, seems to be a very interesting method for their preparation.

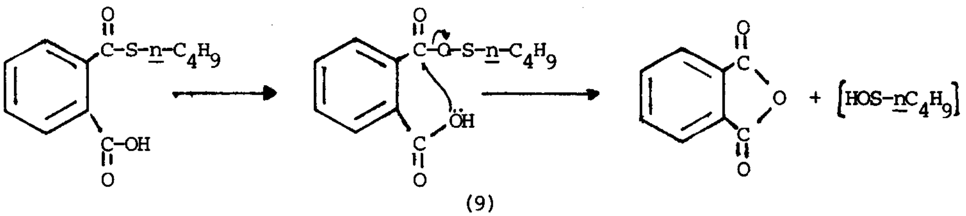
Since we assume the intermediate formation of an acyl sulphenate (6), the isolation of such compounds would be of considerable interest[1,3]. This would in principle be possible if their resistance to hydrolytic attack were increased[3] and the amount of oxidant present at any stage of the reaction could be accurately controlled (see table II). For this purpose RuO_4 seemed to be an appropriate oxidant. Its mode of reaction remembers that of ozone, at least with alkenes[7,8]. We obtained a solution of the yellow form in CCl_4 according to the procedure of van der Engh[9]. A CCl_4 solution of the orange form was obtained by the technique described by Berkowitz and Rylander[10]. The oxidation of the thiolesters was carried out by dropwise addition of a 0.15 M solution of RuO_4 in CCl_4 to a solution of the thiolester in CCl_4 at -10^{o} with stirring. A black precipitate of RuO_2 formed immediatly. After each addition a sample was taken, the RuO_2 filtered off and extracted with the solvent. The obtained solutions were concentrated and analysed by ir and tlc. The reaction proceeds with rapid consumption of oxidant. It could be observed that in the cases where the brownish orange RuO_4 was used, only when the molar ration RuO_4:thiolester attained a value of 2:1 the disappearance of the thiolester was complete[11]. In no case it was possible to detect the formation of (5) or (6).

Table II - Acyl sulphones and mixed sulphonic acid carboxylic acid anhydrides obtained by oxidation of thiolesters with RuO_4

Thiolester		RuO_4	Product	ir (CCl_4) ν cm^{-1}	nmr τ
R	R'				
EtO-	$PhCH_2$	Yellow	acyl sulphone	1760,1335,1125	2.68(5H,s)5.60(2H,s) 5.65(2H,q)8.69(3H,t)
EtO-	$PhCH_2$	Orange	mix.anhyd.	1780,1760,1370 1170,1145	2.68(5H,m)5.65(2H,s) 5.66(2H,q)8.65(3H,t)
EtO-	p-C_6H_4-OMe	"	" "	1780,1760,1370 1160,1145	2.96(2H,m)3.23(2H,m) 5.55(2H,q)6.27(3H,s) 8.60(3H,t)
EtO-	cyclo-C_6H_{11}	"	" "	1780,1760,1370 1165,1145	5.60(2H,q)6.10(1H,m) 7.5-8.5(10H,m) 8.65 (3H,t)
EtO-	n-C_4H_9	"	" "	1780,1760,1380 1160,1145	5.55(2H,q)6.79(2H,t) 8.58(3H,t)8.20(4H,m) 9.01(3H,t)
CH_3-	$PhCH_2$	"	" "	1720,1370,1160	2.60(5H,m)5.60(2H,s) 7.78(3H,s)
Ph-	$PhCH_2$-	"	a)b) " " b)	1780,1370,1160	2.30(10H,m)5.60(2H,s)
o-C_6H_4COOH	n-C_4H_9	"	phtalic anhydride		

a) With yellow RuO_4 this compound gave a complex mixture from which benzoic acid was isolated;
b) together with non identified products.

The results summarized in table II are in agreement with the different reactivity of the two forms of RuO_4 as described in the literature[8]. The orange form, being less reactive seems to allow the time necessary for the initially formed S-acylthiol S-oxide (1) to rearrange to the isomeric acyl sulphenate (6), probably via a S→O acyl shift, before further oxidation takes place. Once formed this compound would further react with RuO_4 faster as the thiolester does. This could explain the fact that we were unable to detect its presence what is not surprising since analogous facts are described in the literature[12]. The formation of phtalic anhydride from the oxidation of n-butyl monothiolphtalate can be rationalized in terms of an intramolecular cyclization of the intermediate acyl sulphonate (9) (scheme III). This assumption is supported by the findings of others[1] and would be in agreement with the existence of this intermediate.



(9)

Scheme III

It is interesting to note that in the series of thiolcarbonate O,S-diesters the reaction with orange RuO_4 afforded the mixed anhydrides, although the corresponding S-acylthiol S-oxides are relatively stable compounds and not known to rearrange spontaneously. This leads to the conclusion that RuO_4 beside its oxidizing action, must in some way induce this kind of rearrangement. The mechanism of the oxidations of organic compounds with RuO_4 still lacks systematic investigation. Evidence favouring a radical mechanism where the chlorinated solvents $HCCl_3$ and CCl_4 play an important role has recently been reported for the oxidation of ethers[13]. However, further efforts in this field would be of inestimable value for the complete understanding of this increasingly important reagent in organic chemistry.

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