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The Reaction of Sulfenate Esters with Acyl Chlorides. Formation of Sulfenyl Chlorides, and Trapping Thereof with Alkenes.§

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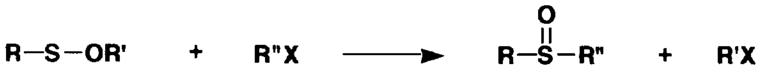
§ Dedicated to Professor Eberhard Wenschuh on the occasion of his retirement.

Abstract: The reaction of aryl sulfenate esters with acyl chlorides is described: the formation of sulfenyl chlorides and carboxylic esters occurs, and the reactive sulfenyl chlorides are trapped with cyclohexene as the β-chloro-sulfides.

The chemistry of sulfenate esters has received considerable attention over the years.[1] These compounds are potentially capable of undergoing reactions with electrophiles analogous to the Arbuzov reaction of phosphites and related compounds.[2] Reports of such chemistry, however, are rare and we were interested to explore the generality of this (the "Thio-Arbuzov" reaction), as illustrated in Scheme 1.[3]

Scheme 1. ("Thio-Arbuzov" reaction)



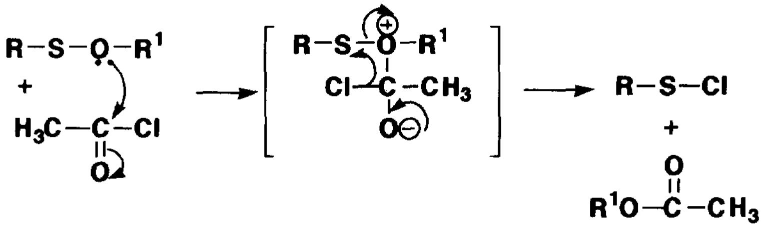
$$\mathrm{R{-}S{-}OR'} + \mathrm{R''X} \longrightarrow \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}R''} + \mathrm{R'X}$$

R = Aryl, NR_2, OR, SBu^t
R' = CH_3, Menthyl
R" = Benzyl, Alkyl, Allyl, propargyl

Our early attempts with alkyl and benzyl halides failed, and as the general order of reactivity of electrophiles in the Arbuzov reaction is acyl >> benzyl > alkyl we have examined the reactions of sulfenate and thiosulfenate esters with acid chlorides.[4]

In practice, these reactions proceed *via* acylation on oxygen, rather than on sulfur, with formation of a carboxylic ester and a sulfenyl chloride, Scheme 2, below.[5]

Scheme 2. "O" attack



Initially, formation of sulfenyl chloride was inferred by the characteristic red colour[1c] of the reaction solution, but isolation and quantification were best achieved by trapping with an alkene to give the β-chloro-sulfide. In addition all reactions were monitored by ^1H NMR and GC analysis. For the methyl esters, the Ar-S-OCH_3 singlet at 3.60-3.80 ppm disappeared and was replaced by either two singlets at 3.57 & 1.95 ppm due to methyl acetate (acetyl chloride reactions) or a singlet at 3.80 ppm due to methyl benzoate (benzoyl chloride reactions). Likewise monitoring the reactions of the menthyl sulfenate esters was again readily achieved by following the loss of the signal (dt) at 3.00-3.60 ppm H-3 of the menthyl residue and replacement by signals at 4.40 ppm (dt) for menthyl acetate, or at 4.80 ppm for menthyl benzoate. These results are summarised in Table 1.[6]

As can be seen from the table generally the β-chloro-sulfides[7] were obtained in good to excellent yields (49-95%). With the methyl sulfenates the carboxylic esters were readily removed by distillation. In the case of the menthyl sulfenates, reaction with benzoyl chloride at 100°C gave a mixture of the β-chloro-sulfide and menthyl benzoate which proved difficult to separate by distillation. The menthyl acetate and sulfides could easily be separated by distillation.

The above chemistry mirrors that of Si-O and S-N compounds (attack on oxygen and nitrogen respectively), reflecting the hard nature of the acyl group and its preference for the harder nucleophile, oxygen.[5,6] In a further attempt to encourage reaction on sulfur, rather than on oxygen, the reactions of thiosulfenate esters, RSSOR, with acyl halides were attempted. Once again, exclusive oxygen attack was observed and the corresponding thiosulfenyl chlorides were produced and trapped as the β-chloro-disulfides using cyclohexene see last two entries in Table 1.

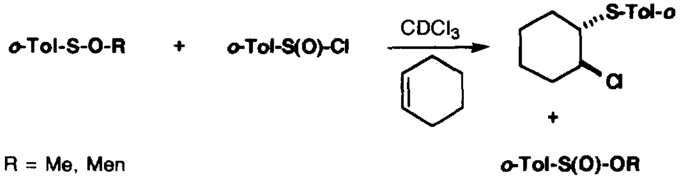
Other reactive electrophiles were also tried.[3] When sulfinyl chlorides were added to the sulfenates a very fast reaction ensued.[7,8] Again the characteristic red colouration indicating formation of a sulfenyl chloride was observed. These reactions are summarised in Scheme 3. NMR evidence indicated that the β-chloro-sulfides and carboxylic esters were produced quantitatively.

Table 1.

Temp.	Sulfenate	Acyl chloride	Added, Alkene (Sulfide, yield)	RC(O)R (yield)
0°C	PhSOMen	CH_3COCl	-[a]	MenOAc. (95%)
0°C	PhSOMen	CH_3COCl	*Trans* stilbene (49%)	MenOAc.[b]
0°C	PhSOMe	CH_3COCl	cyclohexene (68%)	MeOAc.[c]
0°C	*p*-TolSOMe	CH_3COCl	cyclohexene (95%)	MeOAc.[c]
0°C	*o*-TolSOMe	CH_3COCl	cyclohexene (83%)	MeOAc.[c]
0°C	*m*-TolSOMe	CH_3COCl	cyclohexene (87%)	MeOAc.[c]
100°C	PhSOMe	PhCOCl	cyclohexene (67%)	MeOBz.[c]
100°C	*o*-TolSOMe	PhCOCl	cyclohexene (68%)	MeOBz.[c]
0°C	*o*-TolSOMen	CH_3COCl	cyclohexene (93%)	MenOAc. (95%)
100°C	*o*-TolSOMen	PhCOCl	cyclohexene (94%)[d]	MenOBz. (94%)[d]
0°C	*t*-BuSSOMe	CH_3COCl	cyclohexene (84%)	MeOAc.[c]
100°C	*t*-BuSSOMe	PhCOCl	cyclohexene (64%)	MeOBz.[c]

a = No alkene added. b = Obtained quantitatively by ^1H NMR.
c = Obtained quantitatively by ^1H NMR, not isolated due to volatility.
d = Obtained as an inseparable mixture (See text). *NB* all new compounds gave satisfactory analysis and spectroscopic data.[7]

Scheme 3



In summary, we have demonstrated that in contrast to the corresponding phosphorus compounds, aryl sulfenates react with acyl and sulfinyl chlorides at oxygen, to give sulfenyl chlorides and the corresponding esters. The sulfenyl chlorides were readily trapped with alkenes such as cyclohexene, to form the β-chloro-sulfides in good yields. This could represent a new method for the *in situ* preparation of the highly reactive sulfenyl chlorides.

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6. The reaction of aminosulfenate esters with acyl chlorides has been reported, and gives similar results to those discussed here. Musin, B. M.; Ivanov, V. B.; Ivanov, B. E., *Akad. Nauk. USSR, Ser. Khim.*, **1988**, *7*, 1693; *Chem. Abstr.*, **1989**, *110*, 191880j. The reaction of sulfenate esters with TMSCl has also been studied and shown to go on oxygen exclusively see Harpp, D. N.; Friedlander, B. T.; Larsen, C.; Steliou, K.; Stockton, A., *J. Org. Chem.*, **1978**, *43*, 3481.
7. The β-chloro-sulfides all gave spectroscopic and analytical data consistent with the proposed structures. See Goering, H. L.; Relyea, D. I.; Howe, K. L., *J. Am. Chem. Soc.*, **1957**, *79*, 2502.
8. With the menthyl sulfenate (*o*-TolSOMen) the prepared sulfinate ester (*o*-TolS(O)OMen) was a mixture of diastereoisomers (1 : 1) by ^{1}H NMR. Trituration with methanol yielded the (S)-(-)-menthyl *o*-toluenesulfinate in 33% yield.

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