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The First Synthesis of Aliphatic Sulfines from Thiono-esters

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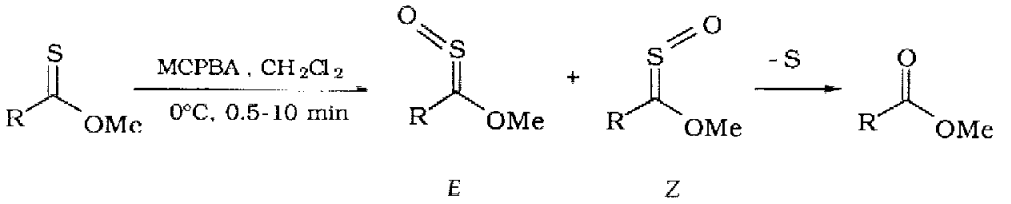
Abstract. Reaction of various thiono-esters with one equivalent of *meta*-chloroperoxybenzoic acid at 0°C in dichloromethane furnishes the corresponding sulfines, evidenced for the first time. These thiocarbonyl oxides are rather unstable at room temperature and give carboxylic esters, with loss of sulfur. The overall sequence provides an easy and quantitative C=S → C=O transformation.

Sulfines (thiocarbonyl oxides) are currently the subject of intense investigation.[1-4] Despite the initial assumption that aliphatic members cannot be prepared by direct oxidation of thiocarbonyl compounds[1,3,5,6], it is possible to achieve this for thioketones[7] and dithioesters.[8,9]

A DARC-Chemical Abstracts substructural retrieval showed that only three examples of thionester sulfines were known,[10,11] in the heterocyclic series. We decided to investigate the oxidation of a variety of thionesters,[12] to attempt the preparation of their sulfines and, if possible, evaluate their stabilities.

Reaction of thionesters **1-9** with one equivalent of *meta*-chloroperoxybenzoic acid, in dichloromethane, was carried out at 0°C for a short time (30 sec - 10 min). After work-up[13] chromatographic purification was avoided with immediate NMR analysis of the crude material. It was found to consist of a mixture of the sulfines **10-17** and the carboxylic esters **18-26** (table). ^{1}H NMR spectroscopy revealed the presence of both *E* and *Z* isomers of the sulfines. Methoxy signals were observed around 3.8 and 4.6 ppm respectively. For the cases of methyl

thiopivalate **4** and thiobenzoate **8** only the *Z* isomers were seen. The presence of sulfines was confirmed by ^{13}C NMR shifts of *ca* 210 and 215 ppm for the *E* and *Z* sulfinyl carbons respectively (entries 4-7, 9).



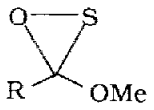
1-9 **10-17** **18-26**

The stabilities of sulfines were examined at room temperature by NMR. Their conversion into carboxylic esters **18-26**, with precipitation of sulfur, was observed. The reaction half time ranges from less than one to several hours. Sulfines, where R is a straight alkyl chain, decompose the most quickly, whereas hindered R groups (entries 4, 6 and 7) stabilize the sulfine moiety.

So, the synthetis of a variety of sulfines by direct oxidation of thionesters has been carried out for the first time. This was achieved even when the substrates are enethiolizable (entries 1, 3, 5, 6), in contrast to the expectation that divinyl disulfides would be formed.

It should be noted that the thiocarbonyl group is attacked selectively in the presence of a carbon-carbon double bond (entries 5-7).

Monitoring the crude mixture supports the view that sulfines are the primary oxidation products. Loss of sulfur is observed, followed by formation of the corresponding carboxylic esters. By analogy with previous speculation, we believe that the production of esters results from a thermally allowed electrocylization reaction of sulfines, intermediate formation of oxathiirane **27**, followed by loss of sulfur. We did not observe any rearrangement of intermediate **27**, in contrast to our recent results[8,9] with dithioesters (SR group instead of OMe).



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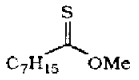
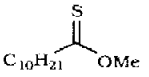
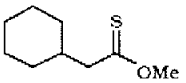
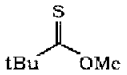
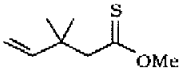
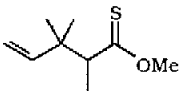
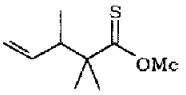
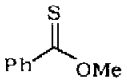
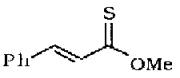
Due to quantitative formation of esters this sequence may be considered as an efficient C=S into C=O group transformation (for a review see ref. 14). It involves use of an equivalent of MCPBA and standing the product at room temperature overnight. An advantage is the avoidance of the use of heavy metals such as mercury or silver.

We have thus obtained various sulfines: aliphatic, α-unsaturated and aromatic ones. The rather short life of these sulfines however makes their use in synthesis difficult, unless they could be trapped by a reagent present *in situ* and compatible with the oxidation conditions.

Table. Oxidation of Thionesters with MCPBA.

Entry	Thionester	Sulfine		*E*/*Z* ratio	Sulfine NMR ^{1}H OMe *E*	*Z*	^{13}C C=S=O *E*	*Z*	Ratio sulfine/ ester	Ester
1		**1**	**10**	50 : 50	3.83	4.65			33 : 67[a]	**18**
2		**2**							0 : 100[b]	**19**
3		**3**	**11**	38 : 62	3.83	4.63			37 : 63[a]	**20**
4		**4**	**12**	0 : 100		4.62		208.9	65 : 35[a]	**21**
5		**5**	**13**	57 : 43	3.80	4.59	195.4	221.8	36 : 64[b]	**22**
6		**6**	**14**	88 : 12	3.80	4.56	201.4	224.3	97 : 3[c]	**23**
7		**7**	**15**	82 : 18	4.03	4.56	208.9	215.9	96 : 4[d]	**24**
8		**8**	**16**	0 : 100		4.70			10 : 90[a]	**25**
9		**9**	**17**	75 : 25	3.92	4.62	209.7		67 : 33[a]	**26**

a) The NMR spectrum was recorded 35-40 min after the end of the oxidation. b) The NMR spectrum was recorded 80 min after the end of the oxidation. c) The NMR spectrum was recorded 105 min after the end of the oxidation. d) The NMR spectrum was recorded 95 min after the end of the oxidation.

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12. Thionesters **1-9** were prepared according to the following methods. Reaction of carboxylic esters with Lawesson reagent in xylene at reflux for 24 hr furnished[15,16] thionesters **1**, **3**, **8** and **9** with respective yields of 49 %, 54 %, 66 %, 42 %. O-Methyl undecanethioate **2** was synthesized in a 41 % yield by treatment of the trimethylsilyl-keteneacetal from methyl undecanoate with hydrogen sulfide.[17] Reaction of pivalonitrile with acidic methanol and basic sulfhydrolysis of the resulting imidoester[18,19] led to O-methyl 2,2-dimethylbutanethioate **4** (yield: 26 %). 4-Unsaturated thionesters **5-7** were obtained with the aid of a Claisen rearrangement: O-methyl thioacetate, propanethioate and 2-methylpropanethioate were first prepared according to ref. 19 and then S-allylated by deprotonation with LDA and reaction with appropriate allylic halides; resulting ketenedithioacetals undergo thio-Claisen rearrangement[20] at room temperature over several hours or days to afford thionesters **5-7**.
13. The reaction mixture was diluted with dichloromethane, washed three times with an aqueous solution of sodium hydrogenocarbonate and then with brine. The organic phase was dried over magnesium sulfate and then concentrated by evaporation of dichloromethane. NMR analysis of the crude material was effected as soon as possible.
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