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INTERVENTION OF SULFINYL SULFONE IN THE OXIDATION PATHWAY OF THIOSULFONIC S-ESTER TO α-DISULFONE

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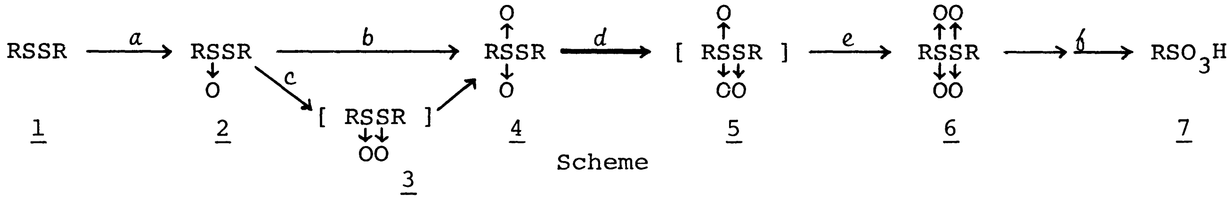
Sulfinyl sulfone was confirmed as a stable intermediate in direct NMR study on the oxidation of thiosulfonic S-ester with MCPBA in $CDCl_3$*, by comparing the chemical shifts with those of the authentic sample prepared by condensation method.*

Many studies have been carried out on the oxidation of organosulfur compounds bearing S-S linkage and the following oxidation pathway(Scheme) has been suggested.1) However, both compounds 3 and 5(parentheses) have neither been detected nor isolated, but have long been suggested to be formed during the oxidation of 2 and 4.



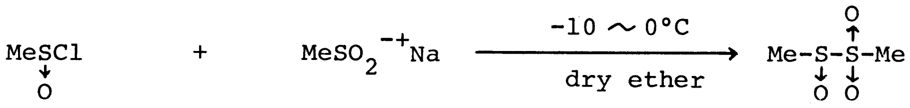
Scheme

We have shown recently that thiosulfinic S-ester(2) can be oxidized directly to thiosulfonic S-ester(path *b*) with nucleophilic oxidant such as $NaIO_4$,2) whereas oxidation of 2 to 4 is considered to proceed via path c when the oxidant is an electrophilic one such as peroxy acid or H_2O_2,3) although α-disulfoxide(3) is believed to be too unstable to be observed.3b) However, the path *d* has not been well-elucidated yet in this oxidation scheme.

We now wish to report that in the oxidation of thiosulfonic S-ester(thiolsulfonate) formation of sulfinyl sulfone(5) can be observed as a first mono-oxidation product in the NMR spectrum during the oxidation with MCPBA.

Although some symmetrical sulfinyl sulfones have been prepared by treating sulfinyl chlorides with alkali sulfinates, no sulfinyl sulfone has been obtained in the direct oxidation of 4.

When S-methyl methanethiosulfonate($MeSS(O)_2Me$, 4a)(0.5 mmole) was treated with an equimolar amount of MCPBA in $CDCl_3$(400 - 500 µl) at 27°C, two new methyl signals appeared at both 2.94 and 3.27 ppm at the initial stage of oxidation in the NMR spectra, besides both methyl peaks of 4a at 2.59 and 3.30 ppm, respectively. These two peaks were then identified as those of the corresponding sulfinyl sulfone (A) by comparison of these chemical shifts with those of authentic sample which was prepared independently by the reaction of methanesulfinyl chloride and sodium

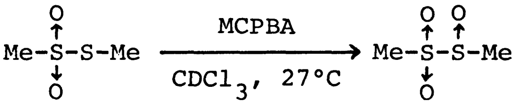


$$\underset{\substack{\downarrow\\ O}}{MeSCl} + MeSO_2^{-}{}^{+}Na \xrightarrow[\text{dry ether}]{-10 \sim 0^\circ C} Me-\underset{\substack{\downarrow\\ O}}{S}-\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}-Me$$

[A]

methanesulfinate in dry ether, as shown in above equation.4a,5a) The sulfinyl sulfone(A) showed the chemical shifts of two methyl groups at 2.94 and 3.30 ppm, respectively, which corresponds exactly to those of the new product in the oxidation of 4a. Results are illustrated in Fig. I and II.5b) Since further continuous oxidation led to obscure NMR spectra due to the large amount of precipitated *m*-chlorobenzoic acid(MCBA) formed in the reaction, the reaction mixture was filtered. However, the filtrate showed a slightly complicated NMR spectrum as shown in Fig. II,7) revealing that the intermediate A decomposed(very likely with moisture). In fact, keeping the reaction mixture in the tube at r.t. for long time caused eventually the same complicated NMR spectrum, in keeping with the observation that there was no NMR signals of the sulfinyl sulfone besides methanesulfonic acid9) in the oxidation of 4a with 30 % H_2O_2 in CD_3COOD at 27°C. Therefore, the sulfinyl sulfone, formed in the oxidation, must be unstable in the acidic media and decomposes readily under the hydrolytic condition.

Similar results were also observed in the oxidations of both $PhS(O)_2SMe$(4b) and $PhSS(O)_2Me$(4c).10) One finds at the initial stage the signal at 2.93 ppm which increases to 70 % and then gradually decreased as the oxidation of 4b with MCPBA in $CDCl_3$ proceeds at 27°C. This peak at 2.93 ppm was then assigned to be that of the methyl group of $PhS(O)_2S(O)Me$(B), since it is in the region from 2.90($PhSS(O)Me$) to 3.15 ppm(4c).5b) This intermediate, B is somewhat more unstable than the sulfinyl sulfone A which can be prepared by condensation of



$$\mathrm{Me}-\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}-\mathrm{S}-\mathrm{Me} \xrightarrow[\mathrm{CDCl_3},\ 27^\circ\mathrm{C}]{\mathrm{MCPBA}} \mathrm{Me}-\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}-\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}-\mathrm{Me}$$

4a [A]

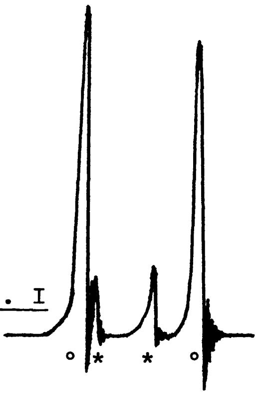


Fig. I

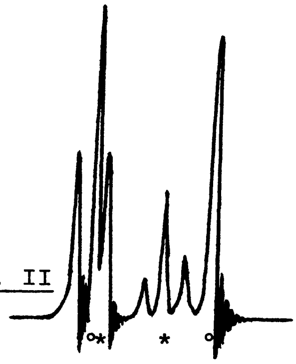


Fig. II

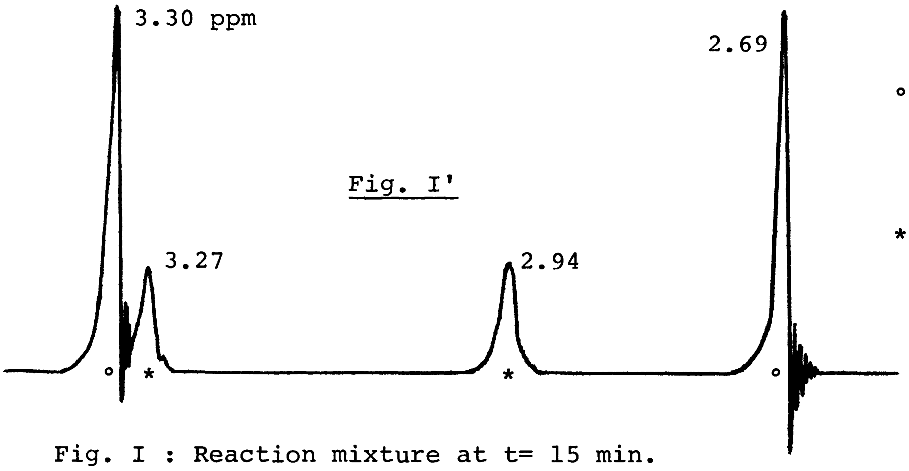
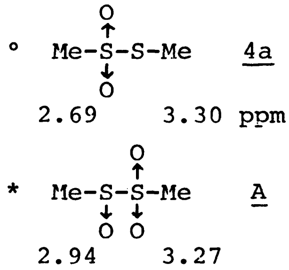


Fig. I'



$$^\circ\ \mathrm{Me}-\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}-\mathrm{S}-\mathrm{Me}\quad \underline{4a}$$

2.69 3.30 ppm

$$*\ \mathrm{Me}-\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}-\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}-\mathrm{Me}\quad \underline{A}$$

2.94 3.27

Fig. I : Reaction mixture at t= 15 min.
Fig. I': Six times expansion of Fig. I.
Fig. II: Filtrate of the reaction mixture at t= 30 min.

sulfinyl chloride and sodium sulfinate.

The NMR spectra taken during the oxidations of 4b and 4c with MCPBA give considerably complicated charts having ten or more signals, however, the NMR spectra during the oxidations of 4b and 4c with 30% H_2O_2 in CD_3COOD showed rather simple patterns at any intervals and the signals corresponding to those of the sulfinyl sulfones(B and C) did not appear on the charts, due to the facile hydrolyses of B and C in hydrolytic media.

Thus, the formation of sulfinyl sulfone as a stable intermediate in the oxidation of thiolsulfonate was confirmed by NMR. The oxidation, therefore, was found to be the reaction initiated by the electrophilic attack of the peroxy acid on the sulfenyl sulfur atom of thiolsulfonate.

REFERENCES AND FOOTNOTES

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5)a) The product, MeS(O)S(O)$_2$Me(A), as reported already,[4a)] was found to be different from sulfinic anhydride, MeS(O)OS(O)Me, based on the NMR chemical shifts and stretching absorptions in IR spectra of both compounds.

b) The chemical shift of methanesulfonyl moiety of A(3.27 ppm) appears at slightly higher field than that of 4a, despite of the expected lower chemical shift than that of 4a. However, this phenomenon has been already shown to be due to the anisotropic effect of the sulfinyl group of A, as reported.[6)]

6) Takata, T., Kim, Y. H., Oae, S., and Suzuki, K. T., Tetrahedron Lett., 1978 4303.

7) Although it could not be determined whether or not the peak at 3.41 ppm was that of α-disulfone, two peaks at 2.84 and 3.06 ppm were considered to belong to methanesulfinic and methanesulfonic acids, respectively, from the reported data.[8)]

8) Block, E., " Reactions of Organic Sulfur Compounds ", Academic Press, N. Y., 1978, p. 279.

9) An unidentified small peak at 2.36 ppm was also observed.

10) However, both sulfinyl sulfones, PhS(O)$_2$S(O)Me(B) and PhS(O)S(O)$_2$Me(C), could not be prepared in pure form by the condensation method(equation). Namely, both NMR spectra of the reaction mixtures after only filtration[4a)] showed ten or more signals in which those of the sulfinyl sulfones can be included. Actually, no unsymmetrical sulfinyl sulfone has been successfully prepared yet.

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