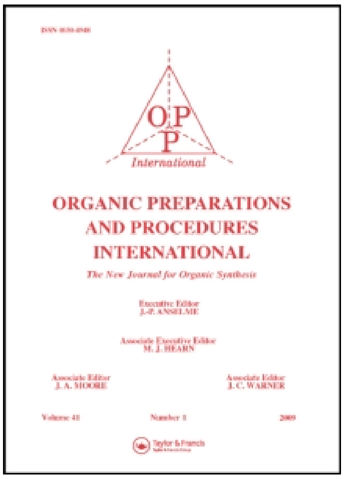

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REDUCTION OF SULFOXIDES WITH METHANE- AND p-NITROBENZENESULFINYL CHLORIDE BY OXYGEN TRANSFER REACTION

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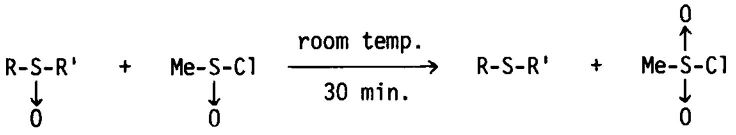
The reaction of sulfoxides with organic sulfinyl or sulfonyl chloride is little known except for the reactions of dimethyl sulfoxide with arenesulfonyl chloride[1] and with methyl chlorosulfinate.[2] In both cases, Pummerer reactions were found to take place. We have now examined a reaction of sulfoxides with organic sulfinyl chlorides, such as methanesulfinyl chloride and p-nitrobenzenesulfinyl chloride and found that a direct oxygen transfer occurred from the sulfoxide to the sulfur atom of the sulfinyl chloride.

The reduction of sulfoxides with methanesulfinyl chloride proceeded smoothly at room temperature to afford the corresponding sulfides with concomitant formation of methanesulfonyl chloride. The overall reaction is illustrated by the following equation.



$$\underset{\substack{\downarrow\\ \text{O}}}{\text{R-S-R'}} + \underset{\substack{\downarrow\\ \text{O}}}{\text{Me-S-Cl}} \xrightarrow[\text{30 min.}]{\text{room temp.}} \text{R-S-R'} + \overset{\substack{\text{O}\\ \uparrow}}{\underset{\substack{\downarrow\\ \text{O}}}{\text{Me-S-Cl}}}$$

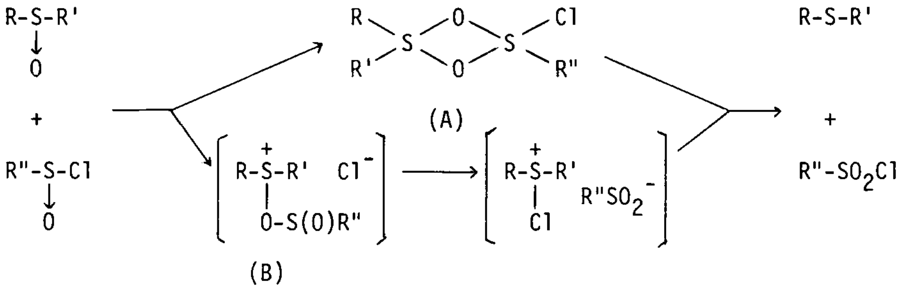
I II

a: R = R'= Me; b: R = Me, R'= Ph; c: R = R'= Ph;

d: R = Me, R'= CH_2Ph; e: R = Et, R'= CH_2Ph

An equimolar amount of methanesulfinyl chloride was added to a solution of any one of the sulfoxides (Ia-e, 3-5 mmol) in carbon tetrachloride and the mixture was kept standing at room temperature for 30 min. Then the whole CCl_4 solution was passed through a chromatography column packed with dry silica-gel to afford the corresponding sulfide (IIa-e) in good yields (80-90%). This reduction is applicable for dialkyl, aralkyl, diaryl and also benzylic sulfoxides. Moreover, use of an excess MeS(O)Cl is not harmful to the reduction, since the remaining excess MeS(O)Cl can be easily removed by the same work-up procedure mentioned above. Cyclic sulfoxides, such as thianthrene S-oxide (If) and phenoxathiane S-oxide (Ig), were also reduced with arylsulfinyl chloride, i.e., p-nitrobenzenesulfinyl chloride, in refluxing benzene for 4 hr to afford the corresponding sulfide (87-89% yield) and p-nitrobenzenesulfonyl chloride (36-50% yield).

The reduction may proceed through a formation of either a covalent type intermediate (A) or a sulfonium intermediate (B) as shown below.



Sulfilimines can also be reduced by treatment with methanesulfinyl chloride. When methyl phenyl N-p-toluenesulfonylsulfilimine (Ph-S(NTs)-Me) was allowed to react with an excess MeS(O)Cl in 30 ml acetonitrile for 3 days at room temperature, methyl phenyl sulfide and tosyl amide were obtained in 89% and 26% yield, respectively.

Meanwhile, a similar oxygen transfer reaction was found to take place between sulfoxides (If and Ig) and p-nitrobenzenesulfenyl chloride in refluxing benzene to afford the sulfides IIf and IIg in good yields together with p-nitrobenzenesulfinyl chloride which was converted, during the work-up hydrolysis procedure, to the corresponding disulfide, thiolsulfonate and sulfonic acid. However, this reduction with arenesulfenyl chloride can be applicable only for the cyclic sulfoxide such as If and Ig, bearing no alpha-proton, since the reaction of the sulfoxides Ia and Id (which have alpha-protons) with arenesulfenyl chloride afforded the unsymmetrical disulfides (ca. 70% yield) in refluxing benzene.

Oxygen transfer from the sulfoxide to some other sulfur compounds is known only in the reaction between sulfoxide and sulfide.[3,4,5] A similar oxygen transfer reaction is known between heteroaromatic N-oxides bearing a N-O semi-polar bond and p-nitrobenzenesulfinyl chloride or p-nitrobenzenesulfenyl chloride at an elevated temperature to afford deoxygenated heteroaromatics presumably via a radical pathway.[6,7,8]

EXPERIMENTAL

Reaction of Sulfoxide with Methanesulfinyl Chloride. Typical Procedures.

a) To a 50 ml solution of benzyl methyl sulfoxide (Id, 770 mg, 5 mmol) in CCl_4 methanesulfinyl chloride (550 mg, 5.5 mmol) was added dropwise at room temp. and the CCl_4 solution was kept standing for 30 min. Then the whole CCl_4 solution was passed through a chromatography column packed with dry silica-gel (30 g) to afford benzyl methyl sulfide (IId, 560 mg) in 82% yield.

b) When an equimolar mixture of dimethyl sulfoxide and MeS(O)Cl in CCl_4 solution was kept standing for 30 min, the dimethyl sulfide formed and CCl_4 were distilled in vacuo and the methanesulfonyl chloride which remained, was identified by comparison of the IR and NMR spectra with those of an authentic sample.

Reaction of Methyl Phenyl N-p-Toluenesulfonylsulfilimine with Methanesulfinyl Chloride. — The sulfilimine (600 mg, 2 mmol) was allowed to react with MeS(O)Cl (400 mg, 4 mmol) in 30 ml acetonitrile at room temp. for 3 days. The tosyl amide precipitated was filtered (90 mg, 26% yield) and the resultant CH_3CN solution was passed through a chromatography column packed with dry silica-gel to afford methyl phenyl sulfide (220 mg) in 89% yield.

Reaction of Sulfoxide with p-Nitrobenzenesulfinyl Chloride.[9] Typical Procedures. a) A benzene solution of thianthrene S-oxide (If, 2.3 g, 10 mmol) and the sulfinyl chloride (2.1 g, 10 mmol) was heated under reflux for 4 hrs, and the benzene solution was washed with water. From the benzene layer, thianthrene (IIf, 1.9 g) and p-nitrobenzenesulfonyl chloride (1.1 g) were obtained in 87 and 50% yields, respectively. From the aqueous layer, p-nitrobenzenesulfonic acid (0.2 g, 1 mmol) was obtained by its conversion to the thiuronium salt.

b) In the reaction of the cyclic sulfoxide Ig with the sulfinyl chloride under the same condition, phenoxathiane (IIg), the sulfonyl chloride and the sulfonic acid were obtained in 89, 36 and 30% yields, respectively.

Reaction of Sulfoxide with p-Nitrobenzenesulfenyl Chloride.[10] Typical Procedure. — When a benzene solution of the sulfoxide (If and Ig) and the sulfenyl chloride was heated under reflux for 4 hrs, followed by the same work-up as in the previous experiment, the corresponding sulfide (IIf and IIg) was obtained in 87-89% yield together with the disulfide, the thiolsulfonate and the sulfonic acid in 46-52, 30-31 and 15-20% yields, respectively.

Reaction of Sulfoxides with 2,4-Dinitrobenzenesulfenyl Chloride.

a) When benzyl methyl sulfoxide (Id, 260 mg, 1.7 mmol) was allowed to react with the sulfenyl chloride (390 mg, 1.7 mmol) in 30 ml CH_3CN under reflux for 2 hrs, then a small amount of undissolved material was filtered off and the filtrate was condensed *in vaccuo*, a crystalline mass was obtained. This mass was washed with a cold benzene-hexane solution to afford unsymmetrical disulfide, i.e., methyl 2,4-dinitrophenyl disulfide, (300 mg) in 72% yield.

b) When an equimolar mixture of dimethyl sulfoxide (Ia) and the sulfenyl chloride was refluxed in CH_3CN for 3 hrs, methyl 2,4-dinitrophenyl disulfide was obtained in 66% yield after the same work-up procedure.

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9. Since the preparation of p-nitrobenzenesulfinyl chloride is not widely known (S. Oae, K. Ikura and Y. Shimano, Yuki Gosei Kagaku Kyokai-shi, 28, 80 (1970), we now describe its synthesis in detail.

   A dry chlorine gas passed into an anhydrous chloroform (500 ml) containing p,p'-dinitrodiphenyl disulfide (50 g, 0.162 mole) and an anhydrous acetic acid (19.5 g, 0.325 mole) at ca.-5°C. When an evolution of hydrogen chloride was ceased, chloroform and acetyl

chloride formed was removed in vaccuo, and the resultant light-yellow cubic crystal was obtained. (55-63 g, 82.5-94.4% yield, mp. 58-60°C) The sulfinyl chloride thus obtained was used without further purification.

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