

α -CHLORINATION OF SULFOXIDES WITH SULFURYL CHLORIDE¹

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α -Chlorination of sulfoxides has been reported to occur when sulfoxides are allowed to react with tosyl chloride (1), NOCl (2), PhICl₂ (3) or *t*-BuOCl (4) in the presence of pyridine. We wish to report that the chlorination of sulfoxides with SO₂Cl₂ in CH₂Cl₂ in the absence of base yields α -chlorosulfoxides rapidly and generally in good yield. The reactions were carried out under anhydrous conditions at -78° for dialkyl sulfoxides and either -78° or 0° for aralkyl sulfoxides. The reaction time was generally less than 15 min. The monochlorinated sulfoxides are significantly less reactive toward sulfuryl chloride than their precursors thus allowing stepwise α -chlorination and ready isolation of either the mono- or dichlorinated sulfoxides.

The following example serves to illustrate the simplicity of method: Sulfuryl chloride (280 mg, 2.0 mmole) was added dropwise to a solution of 278 mg (1.72 mmole) of ethyl phenyl sulfoxide in 10 ml of methylene chloride at 0°. Thin layer chromatography indicated that the reaction was complete within 2 min. Standard workup and purification yielded 287 mg (89%) of α -chloroethyl phenyl sulfoxide (5,6). We have found that it is advantageous to add dry CaO to the reaction mixture. This generally increases the yield and purity of the product since the HCl formed during the reaction is removed thereby preventing sulfoxide decomposition via Pummerer-type rearrangements (7).



The chlorination of sulfoxides can also be carried out using chlorine in CH₂Cl₂ but this route is experimentally more difficult and thus less desirable for laboratory use. Curiously bromine does not react under condition in which chlorination is rapid, methyl phenyl sulfoxide being recovered after 24 h contact with Br₂ in CH₂Cl₂ at 25°.

Contrary to the other chlorination procedures (2-4) we found the present reaction to be generally non-stereospecific and where possible mixtures which contained considerable amounts

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of each diastereomer were obtained. For example, n.m.r. determination of the diastereomer ratio obtained from thiane-S-oxide and *n*-butyl methyl sulfoxide indicated near 1:1 ratios. Each diastereomer obtained from the latter sulfoxide was shown to be configurationally stable under the reaction conditions.

Sulfoxides which can be chlorinated at two possible positions show high positional selectivity and yield only the more highly substituted chlorides. *n*-Butyl methyl sulfoxide gave a 75% yield of the α -chloro-*n*-butyl derivative; no evidence of the isomeric sulfoxide was observed in the n.m.r. of the total crude product. Benzyl methyl sulfoxide gave only α -chlorobenzyl methyl sulfoxide, albeit in low yield. These results again differ from those obtained in the base-catalyzed reactions in which both possible positional isomers were obtained (2, 3). Dichlorination with SO_2Cl_2 afforded α, α' dichlorosulfoxides in preference to the α, α' isomers.

Work on the mechanism of the SO_2Cl_2 -sulfoxide reaction and comparison with those involving chlorinations in the presence of base is in progress and will be reported in due course.

TABLE

<u>Sulfoxide</u>	<u>Temp (°C)</u>	<u>Time (h)</u>	<u>Product</u>	<u>Yield (%)</u>
PhS(O)CH_3	0	0.25	$\text{PhS(O)CH}_2\text{Cl}$	83
$\text{PhS(O)CH}_2\text{Cl}$	25	12	PhS(O)CHCl_2	72
$\text{PhS(O)CH}_2\text{CH}_3$	0	0.25	PhS(O)CH(Cl)CH_3	89
$\text{PhS(O)CH(CH}_3)_2$	-78	0.5	$\text{PhS(O)C(Cl)(CH}_3)_2$	71
$\text{PhCH}_2\text{S(O)CH}_3$	-78	0.25	PhCHS(O)CH_3 Cl	25
$\underline{n}\text{-(C}_4\text{H}_9)_2\text{SO}$	-78	0.1	$\underline{n}\text{-C}_4\text{H}_9\text{S(O)CH(Cl)-}\underline{n}\text{-C}_3\text{H}_7$	85
$\underline{n}\text{-C}_4\text{H}_9\text{S(O)CH(Cl)-}\underline{n}\text{-C}_3\text{H}_7$	-78	0.5	$\underline{n}\text{-C}_4\text{H}_9\text{S(O)C(Cl)}_2\text{-}\underline{n}\text{-C}_3\text{H}_7$	70
thiane-S-oxide	-78	0.1	2-chlorothiane-S-oxide	76
$\text{CH}_3\text{S(O)-}\underline{n}\text{-C}_4\text{H}_9$	-78	0.1	$\text{CH}_3\text{S(O)CH(Cl)-}\underline{n}\text{-C}_3\text{H}_7$	75

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5. All sulfoxides had spectroscopic properties in agreement with the assigned structures.
6. The sulfone corresponding to the starting sulfoxide is a biproduct (generally less than 10%) obtained in the chlorination. Its formation is due to small amounts of water present in the reaction mixture and its yield can be increased by further addition of water.
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