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Reduction with Sulfur Dioxide

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REDUCTION WITH SULFUR DIOXIDE

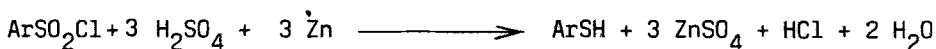
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Abstract A general method to reduce arene sulfonylchlorides to diarene disulfanes has been developed using sulfur dioxide and hydroiodic acid/quarternary ammonium salts as catalysts in a two - phase system.

INTRODUCTION

Zinc effectively converts arene sulfonylchlorides into arene thiols¹ which are industrially used as starting materials for the production of thioindigo dyes.



However, environmental problems arise from the separation and disposal of zinc salts formed since more than 500 kg of zinc sulfate per kmole arene sulfonylchloride have to be disposed of. Known metal-free procedures for the reduction of arene sulfonylchlorides include the use of hydroiodic acid^{2,3} and sodium hydrogensulfite in the presence of hydroiodic acid (20 - 50 mole%)⁴.

RESULTS AND DISCUSSION

For cost reasons sulfur dioxide and hydroiodic acid in catalytic amounts (1 - 5 mole%) have been used. As depicted in Table 1 unsatisfying yields of diarene disulfanes are obtained due to competing hydrolysis to arene sulfonic acids. However, addition of catalytic amounts of quarternary ammonium salts as co - catalysts results in a drastic increase in the yields of diarene disulfanes⁵.

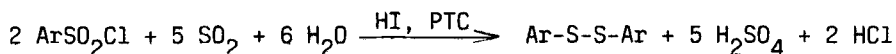


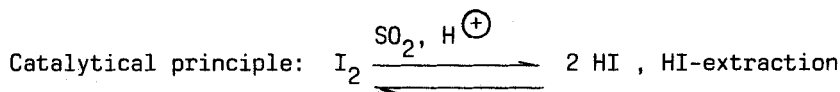
TABLE 1 Sulfur dioxide reduction of arene sulfonylchlorides with HI-and phase transfer catalysis

Arene sulfonylchloride	mole%HI	mole% $R_3N^+CH_3 Cl^-$	yield diarene disulfane
2,5-Dichlorobenzene sulfonylchloride	2	-	77 %
4-Chloro-2,5-dimethyl benzene sulfonylchloride	2	1	97 %
2,4-Dichloro-5-methyl benzene sulfonylchloride	5	-	-
	5	2	93 %
Naphthalene-2-sulfonylchloride	2	-	60 %
	2	1	93 %
8-Chloronaphthalene-1-sulfonylchloride	2	-	55 %
	2	1	90 %
	2	-	50 %
	2	1	96 %

* $R = C_8H_{17}$

The principle of sulfur dioxide reduction with hydroiodic acid catalysis can be applied to copper phthalocyanine tetrasulfonylchloride to give a green pigment - like disulfane which is then reduced with sodium hydrogensulfide to produce a water - soluble green sulfur dye⁶.

The observed catalytic effect can be explained by an extraction of hydroiodic acid by quarternary ammonium salts into the organic phase which consists of inert solvents like toluene or chlorobenzene. Formed iodine is reconverted to hydroiodic acid:



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