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Preparation of a Series of *N*-Aryl-*S,S*-diphenylsulfilimines by Nucleophilic Attack of *S,S*-Diphenyl-sulfilimine on Activated Halogenoaromatic Compounds

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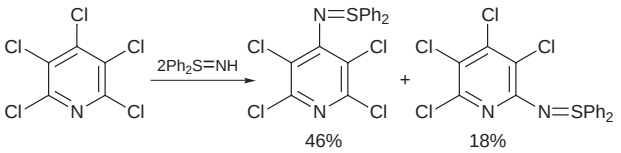
Some *N*-aryl-*S,S*-diphenylsulfilimines, most of which are novel compounds, are prepared and characterised, using a method based on nucleophilic attack of diphenylsulfilimine on activated aryl halides, especially polyhalogenated heterocyclic aromatic compounds.

There are several possible methods for the preparation of sulfilimines, most of which depend on the reaction of a sulfide with an *N*-halo compound[2,3] or with an amine or amide in the presence of an oxidising agent.[4] Such methods require formation of the S=N bond in the reaction sequence. We have investigated an alternative route in which the *N*-arylsulfilimine is generated from nucleophilic attack (*via* nitrogen) of an *N*-unsubstituted sulfilimine (2 equivalents required) on an activated aryl halide, thus developing a method in which the S=N bond is pre-formed. A typical reaction is shown in Scheme 1.



Scheme 1

The feasibility of the reaction depends on the sulfilimino nitrogen atom being a good nucleophilic centre: this point has been discussed by us earlier.[10] The preparations in this work have been the subject of various patent applications.[11] *S,S*-Diphenylsulfilimine is commercially available. The range of starting materials, the conditions of the reaction and the products obtained are given in Table 1.

The reaction has wide scope and does not depend, as do most previous methods, on the preliminary introduction of a nitrogen (amino) function into the aryl moiety. Chlorinated substrates are much less reactive than fluorinated analogues;[10] long reaction times give rise to diphenyl sulfide as a side product. The most useful solvent was found to be THF, which allowed the side-product, *S,S*-diphenylaminosulfonium chloride, to be removed by filtration and recycled by regeneration of the sulfilimine. Alcohol solvents, used at high temperatures, compete with the sulfilimine as nucleophilic species.

Product distributions may be rationalised by consideration of how reactivity at the 2- and 4-positions is affected by halogen groups other than the one displaced, and any activating aza nitrogen atoms.

Table 1 Preparation of *N*-aryl-*S,S*-diphenylsulfilamines[a]

Substrate	Solvent	*t*/h	Product(s)	Yield(%)
1-Chloro-4-nitrobenzene	BuOH	24	No reaction	
2-Chloro-3-nitropyridine	EtOH	7	2-Sulfilimino	76
2-Chloro-5-nitropyridine	THF	4	2-Sulfilimino	81
2-Chloro-3,5-dinitropyridine	THF	0.5	2-Sulfilimino	100
Pentachloropyridine	THF	4	4-Sulfilimino	46
			2-Sulfilimino	18
2,6-Dichloropyrazine	THF	18	2-Sulfilimino	95
2,4-Dichloropyrimidine	THF	8	4-Sulfilimino	48
4,6-Dichloropyrimidine	THF	8	4-Sulfilimino	72
2,4,6-Trichloropyrimidine	THF	4	2-Sulfilimino	36
			4-Sulfilimino	53
2,4,5,6-Tetrachloropyrimidine	THF	4	4-Sulfilimino	55
			2-Sulfilimino	15
Pentafluoropyridine	THF	6	4-Sulfilimino	84
2,3,5,6-Tetrafluoropyridine	THF	4	2-Sulfilimino	95

[a] In refluxing solvent.

Techniques used: UV–VIS, ^{1}H, ^{13}C and ^{19}F NMR, EI-MS, TLC

Schemes: 4

References: 24

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