Annelation with *N*-Arylsulphimides. Synthesis of 1,2,4-Benzoxadiazines

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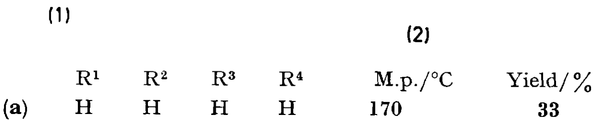
Summary Reaction of several *N*-aryl-*SS*-dimethylsulphimides (**1**) with *p*-toluonitrile oxide provides a simple synthesis of the 1,2,4-benzoxadiazine ring system (**2**).

SULPHIMIDES, $R_2S{=}NR$, which contain a nucleophilic nitrogen atom bearing a good leaving group, have so far been very little used in synthesis. We have investigated the reactions of *N*-aryl-*SS*-dimethylsulphimides (**1**) with several substrates containing an electrophilic carbon atom, and report here the formation of 1,2,4-benzoxadiazines (**2**) from the sulphimides and *p*-toluonitrile oxide.



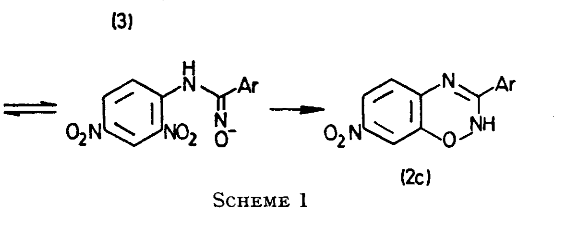
(1) (2)

	R¹	R²	R³	R⁴	M.p./°C	Yield/%
(a)	H	H	H	H	170	33
(b)	H	H	Cl	H	174—176	64
(c)	H	H	NO_2	H	192	27
(d)	H	NO_2	H	H	186	[a]
(e)	Ph	H	H	H	102—104	50
(f)	Cl	H	H	NO_2	174—175	40
(g)	H	H	H	NO_2	178	[a]

[a] (**1d**) gave a mixture of (**2d**) (41%) and (**2g**) (48%).

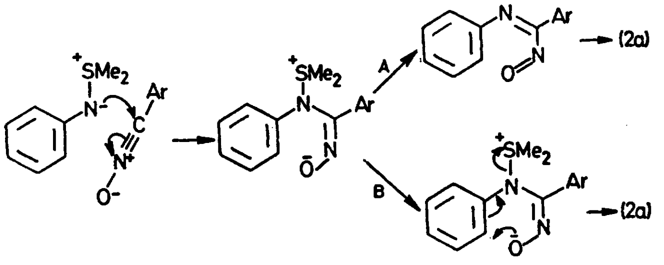
The sulphimides (**1**), which are isolable oils or low-melting solids, were prepared by the method of Claus and Vycudilik[1] from the corresponding aniline, dimethyl sulphoxide, and phosphorus pentoxide. They were found to react rapidly with *p*-toluonitrile oxide in dichloromethane at room temperatrue and gave the crystalline benzoxadiazines (**2**), which either precipitated from the reaction mixture or were isolated by thin layer chromatography. The benzoxadiazines could also be obtained directly from the anilines without isolation of the intermediate sulphimides; the yields of products were similar to those obtained when the sulphimides were isolated.

Very few 1,2,4-benzoxadiazines have previously been prepared,[2,3] and there is no general method for their synthesis. The 6-nitro-derivative (**2d**) is reported to be formed when the amidoxime (**3**) is heated with ethanolic potassium hydroxide.[2] We repeated this reaction and obtained a product which was very similar to compound (**2d**) derived from the *m*-nitrophenylsulphimide, but not identical with it. However, it was identical in all respects with the isomer (**2c**) formed from the *p*-nitrophenylsulphimide (**1c**); we conclude that the cyclisation of the amidoxime (**3**) is preceded by rearrangement, probably *via* a spiro Meisenheimer complex as shown in Scheme 1.†



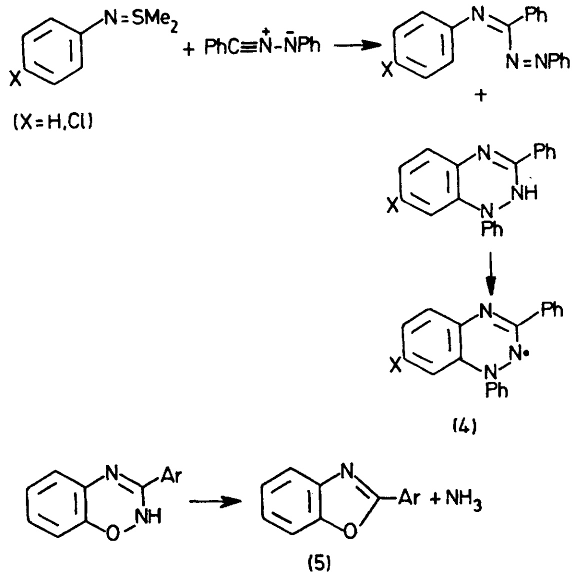
SCHEME 1

This reaction of *N*-aryl sulphimides contrasts with that between *N*-phenyl triphenylphosphimide and benzonitrile oxide, which results in cycloaddition to the phosphorus–nitrogen double bond of the ylide, followed by extrusion of triphenylphosphine oxide.[4] As in the case of the carbon ylides, the sulphur derivatives preferentially extrude a sulphide fragment rather than a sulphoxide. Two mechanisms can be envisaged for this reaction, and are shown in Scheme 2. One involves "backbone" displacement of dimethyl sulphide and electrocyclic ring closure of the resulting nitrosoimine (path A); the other (path B) involves displacement of dimethyl sulphide through the ring.



Scheme 2

In the corresponding reactions of the *N*-arylsulphimides with a nitrile imine, benzonitrile-*N*-phenylimide, two types of products were isolated; azo-imines and 1,2-dihydrobenzo-1,2,4-triazines (Scheme 3), the latter being partially oxidised during work-up into the stable radicals (**4**).[5] The azo-imines could be cyclised under the reaction conditions, indicating that they are probably the primary products and thus providing tentative evidence in favour of path A in Scheme 2.



Scheme 3

The chemistry of 1,2,4-benzoxadiazines remains to be explored; one remarkable reaction is their solution pyrolysis (in benzene or chlorobenzene), which gives high yields of the corresponding benzoxazoles (**5**) and ammonia.

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† Structures of the other nitrobenzoxadiazines reported in ref. 2 are, presumably, also wrong.

[1] P. Claus and W. Vycudilik, *Monatsh.*, 1970, **101**, 396.

[2] A. Werner and T. Herberger, *Ber.*, 1899, **32**, 2686.

[3] L. Semper and L. Lichtenstadt, *Annalen*, 1913, **400**, 302; H. Rheinboldt and O. Schmitz-Dumont, *ibid.*, 1925, **444**, 113; R. L. McKee, 'The Chemistry of Heterocyclic Compounds. Five- and Six-Membered Compounds with Nitrogen and Oxygen,' Wiley-Interscience, New York, 1962, p. 454.

[4] R. Huisgen and J. Wulff, *Tetrahedron Letters*, 1967, 921.

[5] *Cf.* H. M. Blatter and H. Lukaszewski, *Tetrahedron Letters*, 1968, 2701.