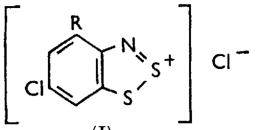
The Action of Sulphur Monochloride on *o*-Nitroanilines and *o*-Phenylenediamines: The Formation of 2,1,3-Benzothiadiazoles

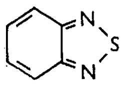
By P. Hope and L. A. Wiles

o-Phenylenediamines react with sulphur monochloride forming 2,1,3-benzothiadiazoles. In acid solution the nitro-group of *o*-nitroanilines oxidises sulphur monochloride to thionyl chloride, and the phenylenediamine thus formed reacts with these sulphur compounds giving the corresponding benzothiadiazole.

THE products formed by the reaction of sulphur monochloride on nitroanilines depend on the relative positions of the amino- and nitro-groups. *p*-Nitroaniline forms *p*-chlorobenzenethiazathiolium chloride (I; R = H) by the so-called Herz reaction,[1] while *m*-nitroaniline gives a tar from which no recognisable compound has yet been isolated.[2] From *o*-nitroaniline Blomquist and Diuguid [3] obtained a small amount of a dichlorinated Herz product (I; R = Cl), and we have now also isolated, in low yield, 2,1,3-benzothiadiazole (II), with *o*-phenylenediamine and thionyl chloride as intermediates. This is a novel reaction of sulphur monochloride.



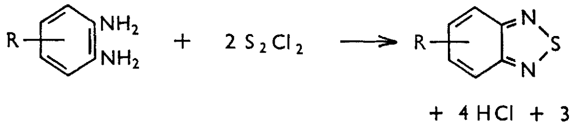
(I)



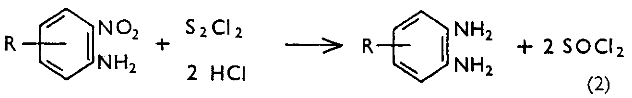
(II)

2,1,3-Benzothiadiazoles have previously been made from *o*-phenylenediamines by the reaction of sulphur dioxide,[4] thionyl chloride,[5] or sulphinylaniline,[6] $C_6H_5{\cdot}NSO$. In the present work sulphur monochloride gave 2,1,3-benzothiadiazoles from *o*-phenylenediamine and its 4,5-dichloro-, 4-nitro-, and 4,5-dimethyl derivatives (reaction 1). The yield of 2,1,3-benzothiadiazole from *o*-phenylenediamine and sulphur monochloride was only 27% in contrast with a yield of 84% using thionyl chloride.[7] Sulphur monochloride is oxidised by sulphur trioxide to thionyl chloride,[8] and we suggest that the nitro-group in *o*-nitroanilines has the same function. Moreover, *o*-nitroaniline is reduced to *o*-phenylenediamine by lower valency sulphur species such as sulphide and dithionite ions.[9] As a side-reaction the amino-group will react with sulphur monochloride to give hydrogen chloride, so that with *o*-nitroanilines (R = H, 4-Cl, or 4-NO_2) reaction (2) followed by reactions (3) and (1) may occur.

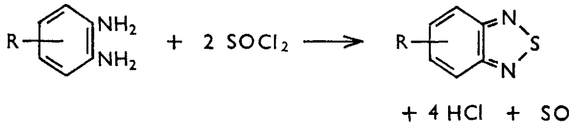
From each *o*-nitroaniline the corresponding *o*-phenylenediamine was isolated in trace amounts by thin-layer chromatography, and thionyl chloride was obtained from the reaction of 4-chloro-2-nitroaniline and sulphur monochloride. An alternative to reaction (2) is reaction (4), but this is discounted as the literature has no record of such a conversion, and we detected no *o*-dinitrobenzene.



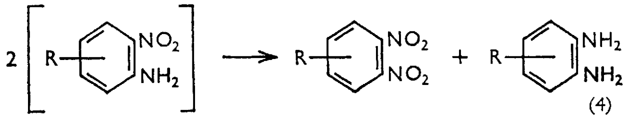
(1)



(2)



(3)



(4)

EXPERIMENTAL

The *o*-nitroanilines and *o*-phenylenediamines were obtained commercially. Infrared (i.r.) spectra were recorded on a Perkin-Elmer Infracord Spectrophotometer, and melting points were determined on a Kofler hot-bench apparatus.

TABLE 1

2,1,3-Benzothiadiazoles obtained from *o*-nitroanilines and sulphur monochloride

o-Nitroaniline	2,1,3-Benzothiadiazole	M. p.	Lit. m. p.	Yield (%)
Unsubstituted	Unsubstituted	43°	44° [7]	8
4-Chloro *	5-Chloro	—	57·5 [10]	10
4-Nitro	5-Nitro	125	128 [10]	3

* In this experiment toluene was the solvent. Distillation gave thionyl chloride, recognised by its i.r. spectrum, and a residue of 5-chloro-2,1,3-benzothiadiazole as a pale yellow oil. It was identified by nitration as 5-chloro-4-nitro-2,1,3-benzothiadiazole, m. p. 141° (lit.,[11] 141°) (Found: C, 34·2; H, 0·7; Cl, 15·7; N, 19·3. Calc. for $C_6H_2ClN_3O_2S$: C, 33·4; H, 0·9; Cl, 16·5; N, 19·5%).

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[1] For a review of the Herz reaction see W. K. Warburton, *Chem. Rev.*, 1957, **57**, 1011.

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[6] A. M. Khaletsky, V. G. Pesin, and Chi Chun Chao, *Proc. Acad. Sci.* (*U.S.S.R.*), *Sect. Chem.*, 1956, **31**, 106.

[7] A. M. Khaletsky and V. G. Pesin, *J. Gen. Chem.* (*U.S.S.R.*), 1950, **20**, 1983.

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Formation of 2,1,3-*Benzothiadiazoles from* o-*Nitroanilines.*—The *o*-nitroaniline (1 mole) and sulphur monochloride (2 moles) were heated under reflux in benzene solution (12 hr.). The solution was evaporated and the residue extracted with ether. The ether solution was treated with hydrochloric acid, and the acid extracts yielded traces of the *o*-phenylenediamine when submitted to thin-layer chromatography on Eastman Chromatogram sheets using benzene and then ethanol as the solvent phases. Evaporation of the ether extract gave the 2,1,3-benzothiadiazole, which was separated by distillation from large amounts of the unchanged *o*-nitroaniline. It was identified by mixed melting point or by its i.r. spectrum. The results are given in Table 1.

TABLE 2

2,1,3-Benzothiadiazoles obtained from *o*-phenylenediamines and sulphur monochloride

					Analysis							
					Found (%)				Calc. (%)			
o-Phenylenediamine	2,1,3-Benzothiadiazole	M. p.	Lit. m. p.	Yield (%)	C	H	N	S	C	H	N	S
Unsubstituted	Unsubstituted	42°	44° [7]	27	52·8	3·2	20·6	23·2	53·0	2·9	20·6	23·5
4,5-Dichloro	5,6-Dichloro	110	112—113 [12]	44	35·0	1·2	15·2	15·5	35·1	1·0	14·8	15·6
4-Nitro	5-Nitro	128	128 [10]	47	39·0	1·9	24·5	18·7	39·8	1·7	23·2	17·7
4,5-Dimethyl	5,6-Dimethyl	81	86 [13]	70	58·9	4·9	15·5	21·1	58·5	4·9	17·1	19·5

Formation of 2,1,3-*Benzothiadiazoles from* o-*Phenylenediamines.*—The *o*-phenylenediamine (1 mole) and sulphur monochloride (2 moles) were heated under reflux in benzene solution (12 hr.). The residue, after evaporation of the solvent, was extracted with chloroform and the solution treated with hydrochloric acid to remove unchanged amine. Evaporation of the chloroform gave the 2,1,3-benzothiadiazole, which was purified by distillation or recrystallisation from ethanol. The results are given in Table 2.

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