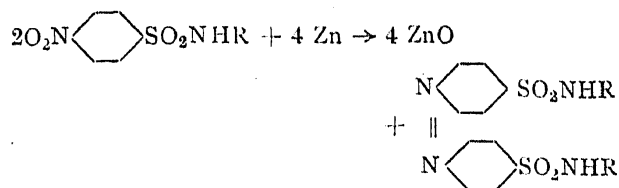


STUDIES IN THE SYNTHESIS OF  
SOME SUBSTITUTED BENZENESUL-  
PHONAMIDES. PART III.—A SIMPLE  
NEW METHOD OF SYNTHESIS OF  
SOME N-SUBSTITUTED AZOBENZENE  
4, 4'-DISULPHONAMIDES

MANY unsymmetrical azobenzene sulphonamides have been made by diazotising a suitable amine and coupling it with a second amino or phenolic compound.<sup>1</sup> But few symmetrical azobenzene-4, 4'-disulphonamides have so far been reported and these have been made by the sulphonation of azobenzene followed by conversion to the corresponding sulphochloride and treating the latter with a suitable amine to form substituted amides.<sup>2-4</sup>

It is surprising that no attempts have been made so far to directly reduce a nitrobenzenesulphonamide to the corresponding azo-bis compound in the manner of the preparation of azobenzene from nitrobenzene.

The present paper describes the successful application of this simple method to the production, in almost theoretical yields, of eight such azo-bis compounds using the corresponding nitrobenzenesulphonamides referred to in Part II, of this series.<sup>5</sup>



The substances analysed correctly for nitrogen by the modified Kjeldahl method of Part II.<sup>5</sup>

As, however, the nitrogen content of the azo and the corresponding hydrazo compounds is very nearly the same, the reduction equivalents of the compounds using stannous chloride were determined, thereby obtaining a positive confirmation of the azo structure of these compounds, the reduction equivalents of the hydrazo being double those of the corresponding azo compounds. For this purpose, a weighed quantity of the azo compound was boiled with an excess of standard stannous chloride solution in an atmosphere of carbon dioxide under reflux during about an hour till the azo compound completely dissolved. The excess of stannous chloride was titrated against standard iodine solution. In all cases the equivalents approximated to the theoretical value for the azo compounds showing the remarkable stability of the azo compounds to further reduction in spite of the excess of zinc used.

The accompanying table summarises the analytical data of the eight azo-bis compounds synthesised in this work.

Azo-derivative	Yield %	M.P. in °C.	Percentage of Nitrogen		Stannous Chloride Equivalent	
			Calcd.	Found	Calcd.	Found
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> NH <sub>2</sub> ] <sub>2</sub> <sup>2-4,6-7</sup>	95	307	16.4	16.28	85	86
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> NHC <sub>2</sub> H <sub>5</sub> ] <sub>2</sub>	87	248-49	15.21	15.19	92	94
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> NHC <sub>2</sub> H <sub>5</sub> ] <sub>2</sub>	85	230.5	14.13	13.85	99	111
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> NHC <sub>10</sub> H <sub>7</sub> (-α) ] <sub>2</sub>	85	267	9.45	8.91	148	160
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> NHC <sub>10</sub> H <sub>7</sub> (-β) ] <sub>2</sub>	96	265.5	9.45	9.14	148	156
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> N $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$ ] <sub>2</sub>	93	214-15	10.76	10.22	130	116
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> N $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$ ] <sub>2</sub>	97	212.5	10.21	9.86	137	146
[ = N. C <sub>6</sub> H <sub>4</sub> . SO <sub>2</sub> NH.C <sub>6</sub> H <sub>4</sub> .SO <sub>2</sub> NH <sub>2</sub> ] <sub>2</sub> <sup>4</sup>	80	312	12.9	2.2	162	161

The general procedure adopted was to treat the nitro-compound, suspended in sufficient alcohol, with three atomic proportions of powdered zinc and an excess of 30 per cent. aqueous sodium hydroxide solution. The mixture was refluxed for about five hours. The product separated as an insoluble sodium salt. The whole reaction mixture was evaporated to dryness, neutralised with 7 N sulphuric acid and filtered. The precipitate was well washed with water and then alcohol and in some cases crystallised from the latter, yielding orange-coloured crystalline substances.

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