

An Unusual Reaction of Diaryl Sulphones

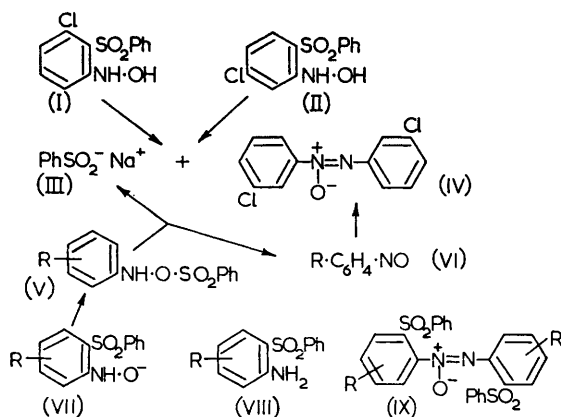
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In continuation of our studies of arylhydroxylamine derivatives,¹ we have prepared a number of 2-(hydroxyamino)diaryl sulphones, *e.g.* (I) and (II), by catalytic reduction of the corresponding nitro-compounds, and have examined their reactions with sodium hydroxide (20% in aqueous

dioxan) at 20° under nitrogen. The expected disproportionation^{1,2} occurred in all cases, and gave the amines (VIII) and the azoxy-derivatives (IX), but was accompanied by a remarkable reaction involving loss of the phenylsulphonyl group. Thus, the chlorophenylhydroxylamine derivative (I) afforded a precipitate of sodium phenylsulphinate (III) almost immediately, and a further quantity was detected in the aqueous alkaline solution by methylation to methyl phenyl sulphone (total yield, 44%). The associated product lacking the phenylsulphonyl group was 3,3'-dichloroazoxybenzene (IV) (30%). The same products, (III) and (IV), were obtained from the isomeric chlorophenylhydroxylamine (II) by a similar treatment with alkali.

This is apparently an intramolecular process, since 4-(hydroxyamino)diphenyl sulphone fails to undergo the reaction, and affords 4,4'-di(phenylsulphonyl)azoxybenzene almost quantitatively. We tentatively suggest a mechanism in which the rearrangement, (VII) → (V), proceeds *via* a five-membered transition state involving attack of



¹ M. F. Grndon, B. T. Johnston and W. L. Matier, *Chem. Comm.*, 1965, 67.

² E. Bamberger and F. Brady, *Ber.*, 1900, 33, 271.

—O⁻ on the sulphur atom of the sulphonyl group; the latter process is uncommon, but was invoked to rationalise a rearrangement of $\alpha\alpha$ -dichlorosulphones.³ The subsequent elimination, (V) \rightarrow (VI) + (III), is analogous to the formation of nitrosobenzene by reaction of *N*-phenyl-*N*-phenylsulphonylhydroxylamine with alkali.⁴ In the presence of a reducing agent such as the phenylhydroxylamine derivative (VII), the nitroso-compound (VI) is likely to furnish the azoxy-derivative (*cf.* IV), perhaps *via* a radical intermediate.⁵ We find, indeed, that although *m*-chloronitrosobenzene is unaffected by alkali alone at 20°, it is converted

into 3,3'-dichloroazoxybenzene (IV) after the addition of hydroxylamine.

Attack of hydroxide at the carbon atom of the C-S bond would yield sulphinate and phenolic products. Apparently none of the sodium phenylsulphinate arises in this way, since phenols were not detected. Furthermore, *o*-nitrosodiphenyl sulphone, *o*-nitrodiphenyl sulphone and 5,5'-dichloro-2,2'-di(phenylsulphonyl)azoxybenzene (*cf.* IX) gave no phenylsulphinate when treated with alkali, even though these compounds possess *ortho*-activating groups which might be expected to promote the hydrolysis.

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³ F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 5187; L. A. Paquette, *ibid.*, 1964, **86**, 4089.

⁴ O. Piloty, *Ber.*, 1896, **29**, 1559.

⁵ C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, 1965, 751; E. J. Geels, R. Konaka, and G. A. Russell, *Chem. Comm.*, 1965, 13.