

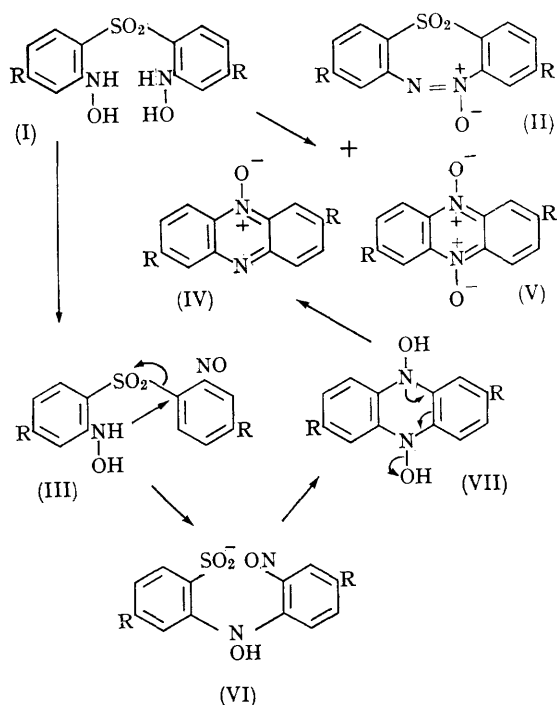
The Formation of Phenazines from Diaryl Sulphones: A Novel Smiles Rearrangement

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WHEN 2,2'-di(hydroxyamino)diphenyl sulphones (I; R=H, Cl, Me) are treated at 20° with sodium hydroxide (20% in aqueous dioxan), thiadiazepines and phenazine derivatives are formed. Thus 4,4'-dichloro-2,2'-di(hydroxyamino)diphenyl sulphone (I; R=Cl) afforded 4,4'-dichlorodibenzo-[b,f][1,4,5]thiadiazepine 5,11,11-trioxide (II; R=Cl) (35%), 2,7-dichlorophenazine 5-oxide (IV; R=Cl) (18%), and 2,7-dichlorophenazine 5,10-dioxide (V; R=Cl) (15%).

The phenazine oxides are formed, apparently, *via* a Smiles rearrangement, and we favour the pathway indicated in the scheme, in which a nitroso-hydroxyamino-compound (III) is the crucial intermediate. The concomitant formation of the thiadiazepine trioxides (II) is diagnostic of the presence of these nitroso-hydroxylamines (III). The latter may be derived, by oxidation or, more likely, by intermolecular disproportionation of the di(hydroxyamino)-sulphones (I). Analogously, phenylhydroxylamine is converted by alkali into aniline and azoxybenzene.¹ The unusual ease of the Smiles rearrangement (III→VI) can be attributed to powerful activation by the nitroso-group. Furthermore, the hydroxyamino-group is probably a particularly good nucleophile in this reaction, since the transition state can be stabilised by electron-donation from the oxygen atom adjacent to the nucleophilic nitrogen (the alpha effect²). The fate of the sulphino-group has not been established, but the process (VI)→(VII) may be analogous to the formation of chloromercuribenzenes and sulphur dioxide from sodium phenylsulphinates and mercuric chloride.³ For simplicity



of presentation, the hydroxyamino-intermediates have been written in their protonated forms, but the active species are probably anions derived by loss of protons from oxygen or nitrogen. Thus, the

¹ E. Bamberger and F. Brady, *Ber.*, 1900, **33**, 271.

² J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16.

³ W. J. Evans and S. Smiles, *J.*, 1935, 181.

phenazine dioxides (V) are considered to arise by radical oxidation of the dianion derived from intermediate (VII).

Similar products are formed by reduction of the di(hydroxyamino)-sulphones (I) with zinc and alkali. At 20°, the dichloro-derivative (I; R=Cl) furnished 2,7-dichlorophenazine (20%). A possible route to the phenazines might involve alkali-catalysed rearrangement followed by reduction of the oxides (IV) and (V); we have confirmed that phenazine 5-oxides and 5,10-dioxides are readily converted into phenazines by zinc and alkali.

These results have an important bearing on the

⁴ M. F. Grundon and A. S. Wasfi, *J.*, 1963, 1982.

alkaline reduction of 2,2'-dinitrodiaryl derivatives. 2,2'-Dinitrodiaryl ethers afford phenazines,⁴ and we find that the corresponding sulphides and sulphones behave similarly. For example, reduction of 4,4'-dichloro-2,2'-dinitrodiphenyl sulphone with zinc and sodium hydroxide in aqueous dioxan at 20° gave 2,7-dichlorophenazine in 25% yield. We believe that the reaction involves a Smiles rearrangement of a nitroso- or a nitro-hydroxylamine derived by partial reduction of the dinitro-compound.

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