

## The Formation of Sulphones and Sulphonates from *p*-Aminophenols

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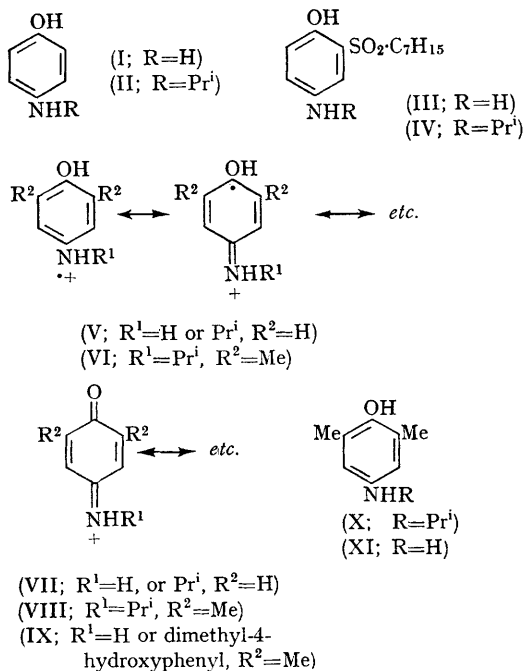
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THE current interest in derivatives of *p*-aminophenols<sup>1</sup> prompts us to report our findings on the oxidation of some *p*-aminophenols, which is an

extension of our work on the enzymic oxidation of *o*-aminophenols.<sup>2</sup> The laccase used was obtained from *Polyporus versicolor*.<sup>3</sup>

Laccase-catalyzed oxidation of the aminophenols (I and II) in solutions buffered to pH 5.0 containing sodium heptanesulphinates takes place readily in air and gives the sulphones (III), 81%, and (IV), 92%, respectively. These sulphones (25% and 15% respectively) have also been obtained by oxidation of the aminophenols (I and II) with ferric chloride in acidic solution. The structures of the sulphones were proved by synthesis from 5-acetamido-2-methoxybenzenesulphonic acid: the heptyl sulphone (III) was obtained by the methods described<sup>1</sup> for the methyl homologue, and (IV) was obtained by treating an ethanolic solution of (III) with acetone and hydrogen in the presence of 10% palladium on charcoal. These results are equivalent to those found for the oxidation of *o*-aminophenols<sup>2</sup> and indicate the intermediacy of either a protonated arylimino-radical (V) or a protonated iminoquinone (VII).

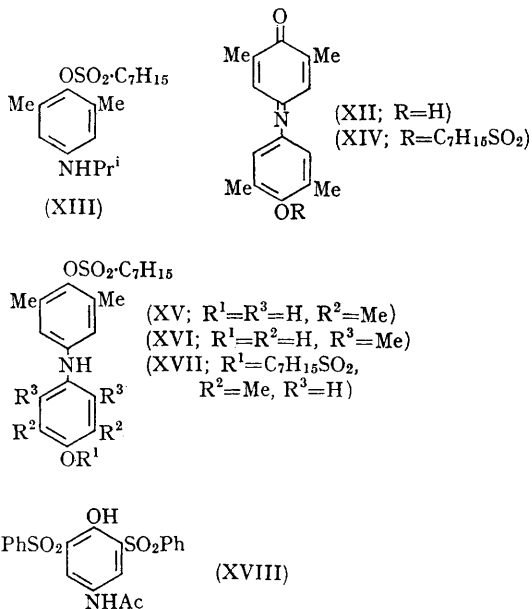
However, the reaction follows another course, leading to sulphonates, when the aminoxylenols (X and XI) are oxidised. Oxidation of (X) in solutions buffered to pH 5 containing sodium heptanesulphinates is rapid even in the absence of laccase, and the main product is the sulphonate



(XII). This is evidently the product from addition of heptanesulphinic acid to the protonated iminoquinone (VIII) by nucleophilic attack at oxygen. Aerial oxidation of the aminoxylenol (XI) at pH 5 is very rapid: ammonia is liberated and the main product is an indophenol, probably (XIII). When the oxidation is carried out in the presence of sodium heptanesulphinate production of the indophenol is inhibited and the main products are a sulphonate (XV or XVI) and a disulphonate (XVII). Structure (XVI) for the monosulphonate is supported by its n.m.r. spectrum. The monosulphonate probably arises in the same way as (XII), from an intermediate such as (IX), and the disulphonate probably by oxidation of (XV) to (XIV) followed by attack of sulphinate anion on the conjugate acid. Sulphonates have been isolated from only those *p*-aminophenols bearing alkyl substituents at both positions *ortho* to the hydroxy-group: nucleophilic attack at carbon is the preferred process for intermediates of type (VII).

Preliminary experiments have shown that the oxidation of *p*-aminophenol (I) in presence of sodium benzenesulphinate is a more complex process than in presence of sodium heptanesulphinate. From the complex reaction mixture from ferric chloride oxidation of *p*-aminophenol in presence of sodium benzenesulphinate, two disulphone monoacetates have been isolated after

acetylation. One is an *N*-acetyl compound [ $\nu_{\max}$  (CHCl<sub>3</sub>) 1700 cm.<sup>-1</sup>] probably of structure (XVIII), and the other is an *O*-acetyl compound [ $\nu_{\max}$  (Nujol) 1750 cm.<sup>-1</sup>] whose structure is under investigation.



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<sup>1</sup> R. F. Collins and M. Davis, *J. Chem. Soc. (C)*, 1966, 2196.

<sup>2</sup> K. Bailey and B. R. Brown, *Chem. Comm.*, 1967, 408.

<sup>3</sup> G. Benfield, S. M. Bocks, K. Bromley, and B. R. Brown, *Phytochemistry*, 1964, 3, 79.