Formation of Crossed Phenazine from the Reaction between Tetra-*p*-anisyl- and Tetra-*p*-tolyl-hydrazines in Liquid Sulphur Dioxide

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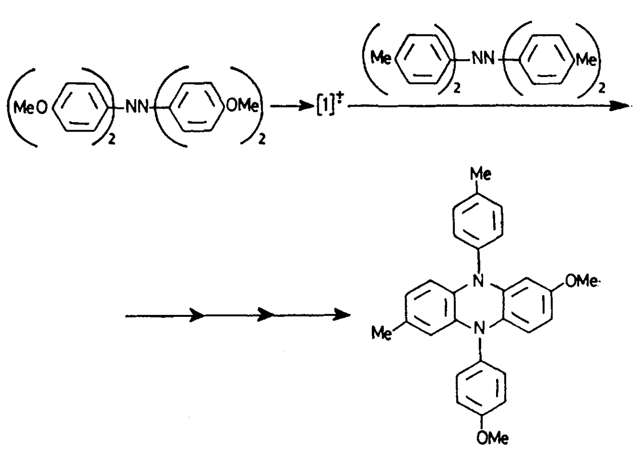
Summary On dissolving tetra-*p*-anisyl- and tetra-*p*-tolylhydrazines in liquid sulphur dioxide in the dark in the absence of oxygen, the tetra-*p*-anisylhydrazine cation radical was formed and 2-methoxy-7-methyl-5-*p*-anisyl-10-*p*-tolyl-5,10-dihydrophenazine was isolated from the reaction mixture.

Recently the cation radicals of tetra-*p*-anisylhydrazine (**1**) and tetra-*p*-tolylhydrazine (**2**) prepared by anodic oxidation, were found to give 5,10-dihydrophenazines.[1] Considering the stability of the di-*p*-anisylaminyl cation,[2] it is probable that the cation radical of (**1**) dissociates into the di-*p*-anisylaminyl radical and the di-*p*-anisylaminyl cation, which then attacks excess hydrazine to give the phenazine intermolecularly.

In the light of these reactions we expected the formation of a 'crossed' phenazine from the reaction of (**1**) and (**2**) in liquid sulphur dioxide. Liquid sulphur dioxide is well known to be a mild oxidant.[3] The reaction path is expected to be simple because of the absence of a proton source. When (**1**) was treated with sulphur dioxide, the formation of



its cation radical[1] was observed in the first stage of the reaction by the periodical measurement of e.s.r. and u.v. spectra, and then the cation radical of 2,7-dimethoxy-5, 10-di-*p*-anisyl-5,10-dihydrophenazine (**3**)[1] started to form and the intensity of this absorption increased during the reaction. After 24 h (**3**) and di-*p*-anisylamine (**4**) were obtained in yields of 10 and 40% respectively. The same behaviour was observed in the reaction of (**2**) with sulphur dioxide, although the reaction rate was slower than that of (**1**). After 48 h 2,7-dimethyl-5,10-di-*p*-tolyl-5,10-dihydrophenazine (**5**) (15% yield), and di-*p*-tolylamine (**6**) (65% yield), were isolated after work-up.

When the appropriate amount of degassed sulphur dioxide was added to a mixture of (**1**) and (**2**), the tetra-*p*-anisylhydrazine cation radical was formed immediately; u.v. and e.s.r. spectra very similar to those of the cation radical of (**3**) were then seen, and the reaction was continued for 24 h. Careful investigation of the mass spectrum of the crude products suggested the formation of (**3**), 2-methoxy-7-methyl-5-*p*-anisyl-10-*p*-tolyl-5,10-dihydrophenazine (**7**), and (**4**) and (**6**). The diphenylamines were separated from the dihydrophenazines by extracting with petroleum ether. Column chromatography on silica gel gave di-*p*-anisylamine and di-*p*-tolylamine in yields of 20 and 40% respectively. Compounds (**7**) [*m/e* 422; δ 2·18 (6H), 3·66 (6H)] and (**3**) were also obtained in 4 and 5% yields respectively using column chromatography on silica gel.

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