

PHOTOCATALYSED CYCLISATION OF AZOBENZENE

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RECENTLY we have observed that azobenzene when exposed to light in solutions containing high concentrations of sulphuric acid, undergoes oxidative cyclization to 3,4-benzocinnoline. Although fusion of azobenzene with aluminium chloride<sup>1</sup> is known to yield 3,4-benzocinnoline, no report of a photocatalysed cyclization of this type has appeared.

Azobenzene (200 mg) was dissolved in a mixture of ethanol (50 cc) and 24 N sulphuric acid (150 cc) and the solution exposed to sunlight for 5 hr. A benzene extract of the neutralized solution was then passed through a column of alumina, elution of the product being effected with a mixture of chloroform (10% v:v) and benzene. After evaporation of the solvent and crystallization from aqueous ethanol, 3,4-benzocinnoline (83 mg), m.p. 154<sup>o</sup> was obtained. Its identity was established by mixed melting point determination with an authentic sample<sup>2</sup> and comparison of ultra-violet absorption spectra in neutral and acidic solutions.

Spectroscopic studies have revealed that several other aromatic azo-compounds behave in a similar manner. The general applicability of the

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<sup>1</sup> A. Wolfram, E. Hausdorfer and L. Schornig, (Ger. Pat. 513, 206) Friedlander 17, 650 (1932).

<sup>2</sup> G.M. Badger, J.H. Seidler and B. Thompson, J.Chem.Soc. 3207 (1951).

reaction and its mechanism are being investigated and details will be published at a later date.

Azoxybenzene and 2-hydroxyazobenzene were found not to cyclize under these conditions and therefore the possibility of these compounds being intermediate in the transformation of azobenzene is precluded.

No significant difference could be detected between the rates of cyclization of cis- and trans-azobenzene and this was shown to be the result of cis  $\rightleftharpoons$  trans equilibration proceeding at a much higher rate than cyclization.