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PHOTOBENZIDINE REARRANGEMENTS. I. REACTIONS OF 1,4-DIARYL-1,4-DIMETHYLTETRAZENES AND N,N'-DIMETHYLHYDRAZOBENZENE[1]

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The thermal decomposition of 2-tetrazenes is fairly well known.[2] In contrast, the photochemical behavior of 2-tetrazenes has received little attention. Child and coworkers obtained N-methylaniline (1) and N,N'-dimethylhydrazobenzene (2) by exposing solutions of 1,4-dimethyl-1,4-diphenyl-2-tetrazene (3) to either sunlight or a mercury lamp. Yields were not given.[3] Similarly, much more information is available about acid-catalyzed and thermal rearrangements of hydrazoaromatics than about light-catalyzed rearrangements.[4] During a study of the photochemistry of hydrazoaromatics we became interested in the photo reactions of analogous 2-tetrazenes. We now present a preliminary report on these two systems.

When a degassed 10^{-5}M solution of 3 in dry hexane was irradiated with the 300-nm lamps of a Rayonet Reactor (Model 100-A), several compounds were formed. Column chromatography on Silica gel (Brinkman 70-325 ASTM), with 1:1 benzene:cyclohexane elution, gave 2, mp 31-32°, in 43% yield.

A much cleaner reaction occurred on irradiation of 10^{-5}M solutions of 3 at 350 nm (band pass 6 nm) in a Bausch and Lomb monochromator (model 33-86-07). Only three products were formed: 1, 2, and N,N'-dimethyl-N-phenyl-p-phenylenediamine (4). These products were separated by tlc on Silica gel (Brinkman GF-254), with the use of authentic samples as monitors. Compound 2 was removed from the plate with ethanol and assayed by ultraviolet spectroscopy. The yield was 67%. Compound 4 corresponds with the p-semidine type rearrangement product of 2, obtained recently from acid-catalyzed rearrangement by White.[5] Similar irradiation of other 1,4-diaryl-1,4-dimethyl-2-tetrazenes bearing p,p'-substituents (di-Me, and di-Cl) gave the corresponding N,N'-dimethylhydrazoaryls in 70-75% yield. Yields were determined spectrophotometrically after tlc separation. These reactions were followed by ultraviolet spectroscopy. In contrast with reaction of 3, a clean isosbestic point was obtained during each of these reactions, indicating a simple conversion of the 2-tetrazene in these cases. The tetrazenes disappeared by a first-order process. Analysis of the rate data will be published later.

Irradiation of 2 at 300 nm in hexane gave two major products: 1, and the p-semidine (4), in yields of 24% and 46% respectively. We are aware of only one other report of a photobenzidine rearrangement; that in which o- and p-semidine were obtained in 0.25 % yield from hydrazobenzene.[6]

Our work shows that 1, 2 and 4 are obtained from 3; and that 1 and 4 are obtained from 2. Thus, it might appear that when 3 is irradiated 2 is formed first and converted next into 1 and 4. Undoubtedly, prolonged irradiation of a solution of 3 would result in this sequence. However, irradiation of solutions of 3 for short periods of time, during which 2 was shown in control experiments to be substantially unchanged, gave measurable amounts of all three products: 1, 2, and 4. Therefore, the tetrazene (3) is converted into N-methylaniline and the p-semidine directly, as well as being able, in principle, to go to these products via the hydrazo product (2).

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