2-Azido-2′-nitrenobiphenyl

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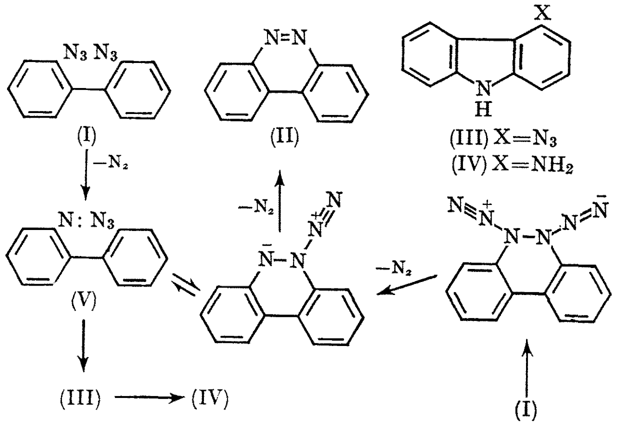
Summary An intramolecular formation of the azo-linkage accompanying the elimination of two moles of nitrogen from a bis-azide has been observed for the first time; however, the reaction is very inefficient even when the new N–N bond becomes part of an aromatic six-membered ring.

IT has been reported[1] that photolysis of 2,2′-diazidobiphenyl (I) gives neither a carbazole nor benzo[*c*]cinnoline (II). However, a re-investigation has established the formation of (II) (trace amounts) and 4-azidocarbazole (III) (50%, m.p. 118·5—120°) in the photolysis of (I). A solution of (I) in degassed n-heptane was irradiated at 2537 Å for 15 min. in a Rayonet Photochemical Reactor with 16 low-pressure mercury lamps. Product yield decreased with increasing irradiation time. Recovery of starting material decreased from 94% after irradiation for 15 min. to 50% after irradiation for 90 hr. This photostability is uncertain since an accumulation of an amorphous beige solid slowly coated the walls of the vessel and decreased light transmission. Comparison of R_f values with those obtained for an authentic sample from four different solvents confirmed the presence of (II). The previously unknown azide (III) was identified through reduction to 4-aminocarbazole (IV, m.p. 188—192°), a new compound independently prepared by reduction of 4-nitrocarbazole and converted into 4-benzamidocarbazole, m.p. 253—254°.[2] Trace quantities of (III) were isolated from the pyrolysis of (I) in acetic anhydride but in *o*-dichlorobenzene (IV) was produced (*ca.* 10%). These results appear to require that intramolecular N–N bond formation follows evolution of molecular nitrogen. Insofar as the formation of carbazole by either the photolysis or pyrolysis of *o*-azidobiphenyl proceeds from an intermediate nitrene,[3] the formation of (III) from (I) may be construed as diagnostic evidence for the intermediacy of 2-azido-2′-nitrenobiphenyl (V). The nitrene would not be required for the formation of (II) if an N–N bond is reversibly formed by azide–azide rather than by azide–nitrene intramolecular interaction. On the assumption that evolution of molecular nitrogen would rapidly follow or occur simultaneously with the formation of an N–N bond, the intermediacy of the nitrene (V) prior to N–N bond formation is preferred. This leads to the interesting conclusion that the C–H bond in the *o*′-position is a more effective nitrenophile than the azido-group in the same position.



Photolysis or pyrolysis of 2-azido-2′-nitrosobiphenyl gives benzo[*c*]cinnoline-*N*-oxide, presumably with 2-nitreno-2′-nitrosobiphenyl as intermediate.[4] Formation of 4-nitrosocarbazole was not reported. A discrete nitrene intermediate may be bypassed by an alternative mechanism in which the nitroso-group provides anchimeric assistance for the elimination of nitrogen.

The pyrolytic formation of (IV) from (I) may be accounted for by hydrogen abstraction either before or after cyclization. The latter is expected to occur more rapidly than the formation of 2-amino-2′-azidobiphenyl, which was not detected, from the nitrene (V). A comparable conversion of *o*-biphenylnitrene to carbazole rather than to *o*-aminobiphenyl has been reported.[3]

Financial assistance was received from NASA.

(*Received, April* 28*th*, 1969; *Com.* 591.)

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[1] L. Horner and A. Christmann, *Angew. Chem. Internat. Edn*, 1963, **2**, 599.

[2] B. M. Barclay and N. Campbell, *J. Chem. Soc.*, 1945, 530.

[3] A. Reiser, H. Wagner and G. Bowes, *Tetrahedron Letters*, 1966, 2635.

[4] L. A. Neiman, V. I. Maimind, and M. M. Shemyakin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1964, 1357.