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CONVERSION OF o-BIPHENYLHYDROXYLAMINE TO CARBAZOLE

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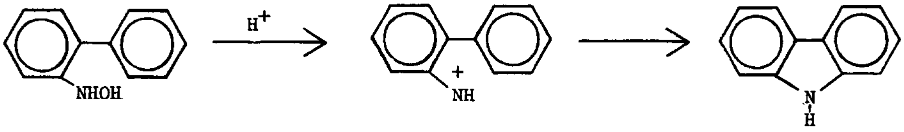
The synthetic and mechanistic importance of nitrenium ions has been clearly established.[1,2] Aryl nitrenium ions (anilenium ions) are usually produced from N-halo[3] or N-hydroxyanilines.[4] Intermolecular reactions of anilenium ions have received most attention while their intramolecular reactions are not as well studied. Carbazole[5] (II) or carbazole[6] analogs formed from cyclization of anilenium ions constitute the main area of intramolecular anilenium ion reactions and some discrepency exists in this area. Cyclization of o-phenylanilenium ion (A) formed from o-biphenylhydroxylamine (I) generated *in situ* under acidic conditions is suggested as a path for carbazole formation,[5] but o-biphenylhydroxylamine reportedly does not yield carbazole on reaction with acid.[7]

On reinvestigation of the reaction of I with acids, we have found that carbazole (10%) and tarry unworkable material is formed in 20% sulfuric acid, and reaction in liquid hydrogen fluoride yields carbazole (15%), azoxy-2-biphenyl (60%) and 2-amino-5-fluorobiphenyl (20%).[8] All compounds were identified by comparison with authentic material. We shall report later on the utility of this method for producing fluoroaromatic amines.



I A II

Facile conversion of I to azoxy-2-biphenyl may account in part for the low yield of carbazole and our inability to prepare I by a described procedure.[7] A new synthesis of I was accomplished by sodium borohydride (0.4 g, 10 mmoles) reduction of 2-nitrosobiphenyl[9] (5.0 g, 27 mmoles) in 500 ml of anhydrous ether under nitrogen atmosphere at 0°. The green color of the nitroso compound was discharged after about 8 hours and the mixture was poured into cold water and separated quickly. Removal of ether from the dried organic solution produced I as a yellow semisolid in 65% yield. Its identity was established by infrared spectroscopy[10] (3260 and 950 cm^{-1}) and a positive triphenyl tetrazolium chloride test.[11] Spectral analysis also showed the absence of 2-amino, 2-nitroso, 2-nitro, azo-2-, and azoxy-2-biphenyl. Thus this new arylhydroxylamine synthesis and the conversion of I to II add credence to reactions which produce II through the intermediacy of both I and A and promote the use of arylhydroxylamines for further studies in anilenium ion chemistry.

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