Photocyclization Reaction of 1,3,5-Tris(diphenylamino)benzene

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Intramolecular photocyclization of diphenylamine and N-methyldiphenylamine to produce carbazoles in the presence or absence of oxygen has been studied extensively. [1-7] It has been shown that the photocyclization reaction takes place via the lowest excited triplet states of the diphenylamines, which undergo ring closure to yield triplet dihydrocarbazoles, leading to the formation of carbazoles. However, the mechanism of the steps from the dihydrocarbazole biradicals to the final product carbazoles has not been clarified. In particular, it has not been clearly understood how molecular oxygen operates in the formation of carbazoles.

We report here photocyclization of 1,3,5-tris(diphenylamino)benzene (TDAB) which has dual reaction sites for the ring closure. It is of interest to investigate its photochemical reaction process, and the study is expected to provide information on the mechanism for the formation of carbazoles.

TDAB was synthesized by the Ullmann reaction of 1,3,5-tris(phenylamino)benzene with iodobenzene in the presence of copper powder and potassium hydroxide in decalin at 170 °C, and purified by silica-gel column chromatography, followed by recrystallization from benzene/hexane, mp 256-257 °C. Photochemical reaction was carried out using a merry-go-round apparatus at room temperature. The reaction solution ([TDAB] = 1.0 x 10^{-3} mol dm^{-3}) was irradiated with a 500 W high-pressure mercury lamp. Quantum yields were measured with a potassium ferrioxalate actinometer by irradiation with monochromatic light of 313 nm ([TDAB] = 5 x 10^{-4} mol dm^{-3}).

Direct irradiation of a benzene solution of TDAB with light of the wavelength longer than 313 nm for 20 h under constant bubbling of oxygen produced 2,4-bis(diphenylamino)-N-phenylcarbazole (1) in ca. 70 % yield. The quantum yield for the formation of 1 was 0.07. By contrast, no appreciable reaction took place in the degassed system. When oxygen was bubbled into the solution only before irradiation, the photochemical reaction took place but gradually stopped. These results indicate that oxygen plays an important role in the photocyclization reaction.

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The product 1 was purified by silica-gel column chromatography, followed by repeated recrystallization from benzene/EtOH (1:1 vol ratio) to give colorless prisms, mp 210-211 °C. 1 was identified by various spectroscopies, mass spectrometry, and elemental analysis.

The quantum yield for the formation of 1 in the presence of piperylene ([piperylene] = 1 x 10^{-2} mol dm^{-3}), which acts as a triplet quencher, decreased to 0.03. The triplet-sensitized reaction of TDAB by selective excitation of benzophenone ([benzophenone] = 1.5 x 10^{-1} mol dm^{-3}) with monochromatic of 380 nm from a 500 W Xe lamp also gave 1. These results indicate that the photocyclization of TDAB proceeds via the excited triplet state of TDAB. The exclusive formation of 1 instead of 1-N-carbazolyl-3,5-bis(diphenylamino)benzene (2) can be explained in terms of the stability of an intermediate involved. The stability of the dehydrocarbazole biradicals leading to 1 and 2 does not seem to be different from each other. It is suggested that the reaction involves the intermediacy of the dihydrocarbazole radical cation generated by electron transfer from the dihydrocarbazole biradical to oxygen and that the formation of 1 is due to the radical cation intermediate leading to 1 being more stabilized than that leading to 2.

References