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BORON PHOTOCHEMISTRY

XII *. THE ROLE OF IODINE IN THE PHOTOCYCLIZATION OF ANILINODIMESITYLBORANES

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Summary

The ratio of methyl group rearrangement to methyl group elimination during the photocyclization of anilinodimesitylborane is dependent upon the concentration of iodine present. At iodine concentrations of less than 10^{-3} *M*, the major product is a demethylated borazarophenanthrene, 7,9-dimethyl-6-mesityldibenz[*ce*][1,2]-azaborine (IV). At concentrations of iodine above 5×10^{-3} *M*, the major product is a methyl-rearranged borazarophenanthrene, 7,9,10-trimethyl-6-mesityldibenz[*ce*][1,2]-azaborine (V). The role of iodine was at least threefold: assisting in the production of a reactive cation-radical at low iodine concentrations, quenching the formation of the cation-radical at higher iodine concentrations, and actively assisting at the higher concentrations in the formation of a reactive species.

Introduction

In the past we have been concerned with the photochemical synthesis of substituted borazarophenanthrenes. A synthetic photocyclization route to yield simple, unsubstituted borazaro-, boroxaro-, and borathiarophenanthrenes was initially reported [1]. This route required the synthesis of *o*-iodo-substituted anilines as starting materials. We reported later that when elemental iodine was present in the reaction system consisting of noniodo-substituted anilinoboranes, containing a wide variety of other substituents in the anilino ring, the aminoboranes could be oxidatively photocyclized to furnish the corresponding borazophenanthrenes [2]. In the same paper we reported simultaneous elimination of a methyl group from 2,6-dimethylanilinodiphenylborane (I), yielding

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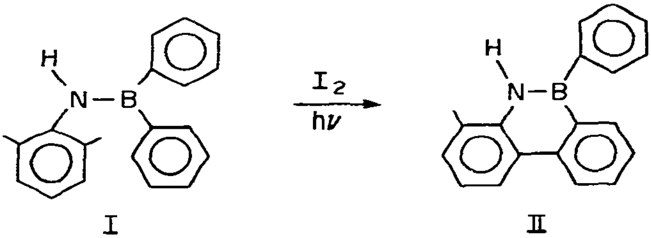
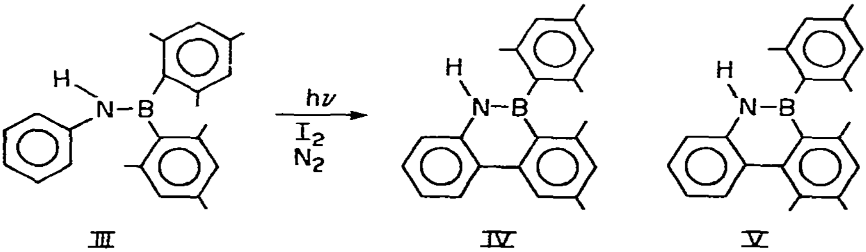
* For Part XI see ref. 28.

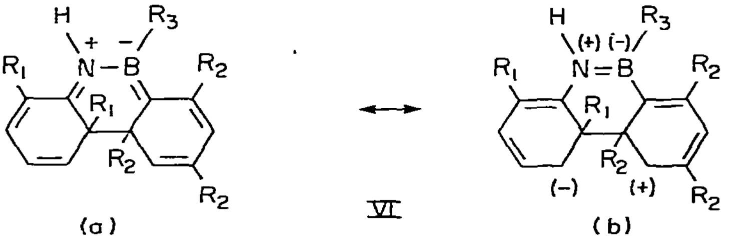
exclusively the 8-methylborazophenanthrene derivative II.



The photocyclization of the oxygen- and moisture-stable anilinodimesitylboranes (III) in the presence of iodine was later reported to produce a mixture of a demethylated phenanthrene-type derivative (IV) (12%) and a phenanthrene-type derivative (V) (88%) in which a methyl group had undergone a 1,2-shift [3].



It was postulated that during the photocyclization a reduced species (VI) was formed, which then was oxidized to form the aromatic system. In the excited state the charge-separated form VI (b) could conceivably make a substantial contribution to the overall structure and as such would be a controlling factor in determining whether a carbonium-ion-assisted methyl migration or an anion-assisted methyl elimination is to occur.



R_1 = H; R_2 = CH_3; R_3 = mesityl
R_1 = CH_3; R_2 = H; R_3 = mesityl

The reactive intermediate (VI) is not unlike those proposed by others [4—7] for cyclization processes. We have undertaken the present study to better understand the mechanistic aspects, particularly that of iodine, in the photocyclization of anilinodimesitylboranes. There has been considerable work by others on the photophysics and photochemistry of iodine, including: the homolytic cleavage of iodine upon irradiation [8—11]; the formation of cyclohexyl radicals upon irradiation of pure cyclohexane and cyclohexane solutions of iodine at concentrations below 10^{-4} *M* [12]; the formation of a contact charge-transfer (CT) complex between atomic iodine and solvent [8—12]; the formation of ion-radical $I_2^{\cdot-}$ at concentrations above 10^{-4} *M* iodine [12—13]; and the observation of I_2 dimers and higher iodine oligomers at concentrations above 10^{-3} *M* [14—22].

In these publications only neutral radical transient intermediates are reported in cyclohexane solutions of iodine below 10^{-4} *M*, and increasing concentrations of radical-ion intermediates and iodine dimers, etc., are observed at concentrations above 10^{-4} *M*. We concluded that, in reactions involving iodine as a catalyst, the type of products, and/or their yields, will change as the iodine concentration is increased.

The results reported here are particularly interesting since it has now been found that the ratio of the demethylation (IV) and rearrangement (V) products is dramatically dependent upon the iodine concentration in the range of 10^{-3} to 5×10^{-3} *M* iodine. At concentrations of less than 10^{-3} *M* iodine, the photocyclization reaction occurs to give predominantly demethylated product IV. At concentrations greater than 5×10^{-3} *M* iodine, the major product formed is V due to methyl-group migration.

Experimental

All solvents used were Eastman spectro grade and were redistilled before use. The preparations of 2,6-dimethylanilinodiphenylborane and the anilinodimesitylboranes were described previously [2,3].

The course of the photocyclization reactions was followed by UV spectroscopy using a Cary model 15 spectrophotometer and by gas-liquid chromatography using a 10-ft long, 1/4-inch diameter column containing 5% Dexil on Chromosorb AW-DMGS in an F and M model 700 gas chromatograph. The irradiation technique used has been described [2,3].

Nine potential cyclizing agents were tested: triphenylpyrylium perchlorate, Reinecke salt, mercuric chloride, cupric sulfate, benzophenone, benzoquinone, tetracyanoethylene, tetracyanoquinodimethane, and iodine. All of the reagents were soluble or partly soluble in the solvents used except cupric sulfate, which was soluble in methanol, partly soluble in dimethoxyethane, and ground into a powder and held in suspension by agitation in the other solvents. Anilinodimesitylborane III (5×10^{-4} *M*) was used in a 1 : 1 mole ratio to each of the potential cyclizing agents tested. The values listed in Table 1 are approximate quantum yields of production of the indicated products as found by gas-liquid chromatography of the solutions after 3 min of irradiation.

The rate of consumption of iodine as measured by UV analysis during the photolysis of a 10^{-4} *M* solution of iodine in cyclohexane is shown in Fig. 1, curve a. The rate of consumption of iodine during a typical reaction is shown in Fig. 1, curve b, for a cyclohexane solution of III and iodine, both at 10^{-4} *M*. Fig. 1, curve c, is a typical plot relating irradiation time to the production of IV in a solution containing 10^{-4} *M* III and 10^{-4} *M* iodine. The short induction period observed in all runs is not shown.

Quantum yields for the production of IV and V were calculated using the initial slope (after the induction period) of similar curves obtained from the irradiation of solutions containing combinations of 10^{-2}, 10^{-3}, and 10^{-4} *M* iodine and anilinoborane. The results are shown in Fig. 2.

TABLE I

QUANTUM YIELD OF V

Solvent	C_6H_{12}	THF	CH_3CN	tBuOH	IPOH	$CHCl_3$	DME	MeOH
Cyclizing Agent								
I_2	0	0	0	.002	.002	.002	.004	0
TCE	0	0	0	0	0	-	0	0
Benzoquinone	0	0	0	0	0	-	0	0
Benzophenone	0	0	0	0	0	-	0	0
Cupric Sulfate	-	0	0	0	0	-	0	0
Mercuric Chloride	0	0	0	0	0	-	.001	0
TCNQ	0	0	0	0	0	-	0	0
Reinecke Salt	0	0	0	0	0	-	0	0
Pyrylium Salt	0	0	0	0	0	0	0	0

QUANTUM YIELD OF IV

Solvent	C_6H_{12}	THF	CH_3CN	tBuOH	IPOH	$CHCl_3$	DME	MeOH
Cyclizing Agent								
I_2	.007	.001	.001	0	0	0	0	0
TCE	.006	.001	.002	0	0	-	0	0
Benzoquinone	.001	.001	.001	.002	.001	-	0	0
Benzophenone	0	0	0	0	0	-	0	0
Cupric Sulfate	X	0	0	0	0	-	0	0
Mercuric Chloride	.001	.001	.001	.001	.002	-	0	0
TCNQ	0	.002	0	0	0	-	0	0
Reinecke Salt	0	0	0	0	0	-	0	0
Pyrylium Salt	0	0	–	0	0	0	0	0

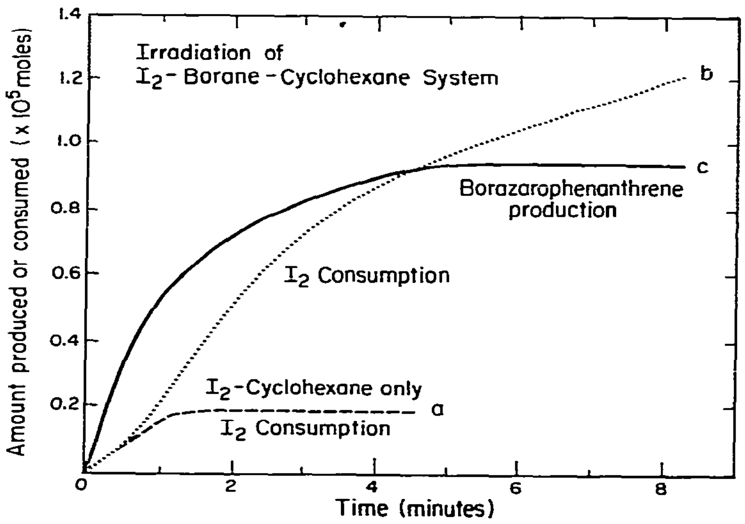


Fig. 1. Changes in the concentration of iodine and borazarophenanthrene upon irradiation.

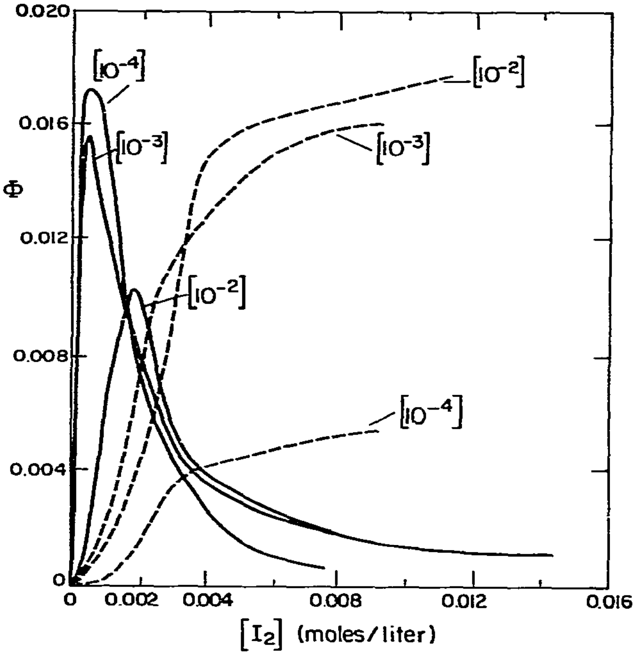


Fig. 2. Quantum yields of production of IV (———) and V (- - - - -) versus iodine concentration.

A cyclohexane solution containing 10^{-2} M of borane III and 10^{-2} M of iodine was irradiated to give a 58% chemical yield of V. The solution was titrated with 0.01 N sodium thiosulfate to determine the amount of unreacted iodine. Gas-liquid chromatography and mass spectrometry were used to determine the presence of iodinated products.

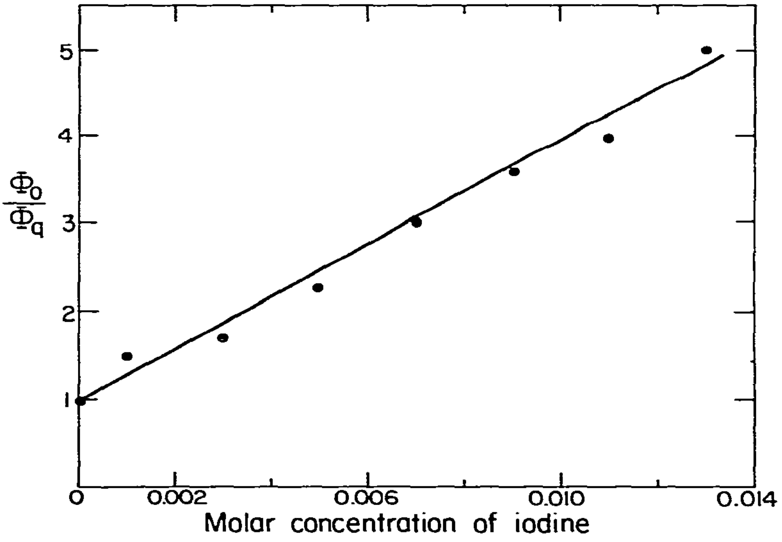


Fig. 3. Fluorescence quenching $[\Phi_q]$ of III by iodine.

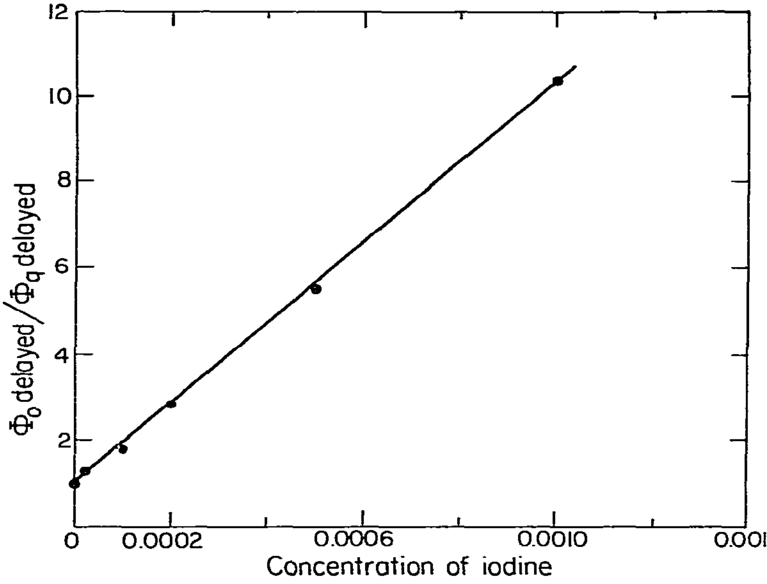


Fig. 4. Delayed fluorescence quenching [Φ_q delayed] of III by iodine.

Fluorescence quenching measurements were made by adding increasing amounts of iodine to solutions of III prior to degassing. The actual concentrations of iodine remaining after the degassing procedure were calculated based upon the absorption at 550 nm as measured by a Cary model 14 spectrometer. The fluorescence measurements were made with the apparatus described by Doty et al. [23]. The quantum yields of fluorescence (Φ_0) and delayed fluorescence (Φ_0(delayed)) were measured. In Figs. 3 and 4, the ratios Φ_0/Φ_q and Φ_0(delayed)/Φ_q(delayed) were plotted versus the iodine concentration, where Φ_q and Φ_q(delayed) represent the quantum yields of fluorescence of III measured in iodine solutions.

Results and discussion

Combinations of solvents and cyclizing agents were tested to determine the optimum combination for the production of compounds IV and V as listed in Table 1. Solutions of III in cyclohexane, tetrahydrofuran, acetonitrile, t-butyl alcohol, or isopropyl alcohol, containing small quantities of tetracyanoethylene, iodine, mercuric chloride, or benzoquinone, when irradiated produced at least a small amount of IV. The elimination of a methyl group during the photocyclization process, forming IV, occurred to a significant extent only in the presence of iodine or tetracyanoethylene in cyclohexane.

Concentrations of tetracyanoethylene below 5×10^{-5} *M* in cyclohexane were nearly as effective as the iodine-cyclohexane combination. However, tetracyanoethylene lost its cyclizing ability at concentrations above 5×10^{-5} *M* and was ineffective in producing V at any concentration, even in polar solvents. At the low iodine concentrations used in this series (5×10^{-4} *M*), only the methyl-rearranged product V was obtained in chloroform, isopropyl alcohol, t-butyl alcohol, and dimethoxyethane but was completely absent in nonpolar solvents. These results suggest the formation of a polar intermediate during the cyclization of III to V. V could be produced in cyclohexane by increasing the iodine concentration. In fact, the best yields of both IV and V were obtained using iodine in cyclohexane.

The consumption of iodine during photolysis

Irradiation of a solution containing only iodine in cyclohexane caused a decrease in intensity of the iodine absorption at 550 nm until a nearly steady state was achieved (Fig. 1, curve a). This result was expected, since irradiation of iodine in cyclohexane has been reported to produce small amounts of iodocyclohexane, and irradiation of iodocyclohexane has been reported to produce a charge-transfer complex with atomic iodine $[C_6H_{11}I,I^\bullet]$ [12]. An equilibrium would be established if the primary mode of reaction for the latter species is:

$$2[C_6H_{11}I,I^\bullet] \rightarrow 2C_6H_{11}I + I_2$$

When equal volumes of cyclohexane solutions containing 10^{-2}, 10^{-3}, or 10^{-4} *M* III were treated with known amounts of iodine and the solutions were irradiated, the iodine concentration decreased initially as if no borane were present (Fig. 1, curve b). However, an increase in the rate of disappearance of iodine soon occurred which was independent of the borazarophenanthrene production (Fig. 1, curve c). When formation of the borazarophenanthrene ceased, nearly 90% of the initial iodine was still present. Analysis of the reaction medium showed that 70—80% of the consumed iodine had been incorporated as iodocyclohexane. The iodinated products found to be present by gas chromatography-mass spectroscopy techniques included iodocyclohexane, iodomesitylene, iodinated and diiodinated III, two isomers of iodinated V, and one of iodinated IV. No iodomethane was detected. Further irradiation resulted in an increase in the amount of iodinated products and a decrease in the borazarophenanthrene and iodine present.

In a reaction producing 2×10^{-3} *M* borazarophenanthrenes IV and V, less than 3×10^{-5} *M* acid was detected (presumably HI), and represented less than 1% of the total iodine consumed. It would be concluded from these results that the iodine consumption is not a part of the photocyclization reactions yielding either IV or V, but results from subsequent reaction of iodine with other photoproducts and solvent.

This conclusion is supported by the observation that irradiation in the long-wavelength (450 nm) band of iodine, where atomic iodine ($I^\bullet$) has been shown to form the contact CT species C_6H_{12}—$I^\bullet$ as a transient, does not result in the production of either IV or V. On the other hand, the irradiation of a solution of III in the presence of 10^{-4} *M* iodine with 313 nm light, where iodine has nearly zero absorption and III has an extinction coefficient of almost 1000, resulted in cyclization to form IV.

Relationship of product ratios to iodine concentration

The quantum yields of production of IV and V at the various concentrations of III in cyclohexane were calculated and plotted versus the iodine concentration (see Fig. 2). Concentrations of iodine greater than 2×10^{-3} *M* favored methyl group rearrangement with formation of V, whereas concentrations of iodine lower than 10^{-3} M favored methyl group elimination with formation of IV as the major product.

The initial increase in the quantum yield of IV below 2×10^{-4} M iodine appears to be a normal increase due to an increase in the number of reactive species. The decrease in the quantum yield of IV above 10^{-3} M iodine may be due to the interaction of iodine dimers, trimers, etc., with reactive species of III or may be related to a decrease in the amount of light absorption by the B—N bond because of the increased concentrations of iodine and its polymers, the production of which is not linearly related to the iodine concentration [10].

When the iodine concentration was varied in dimethoxyethane solutions, IV was produced in iodine concentrations below 5×10^{-5} M, with a maximum quantum yield at an iodine concentration of 10^{-5} M, whereas V was produced in dimethoxyethane at concentrations of iodine greater than 5×10^{-5} M, with a peak quantum yield near 10^{-4} M iodine. This behavior resembles the iodine-cyclohexane system except that the peak quantum yields occur at much higher iodine concentrations in the cyclohexane solutions.

Formation of charge-transfer complexes

The absorption spectrum of III in the presence of iodine reveals a ground-state charge-transfer complex which absorbs at λ_{max} 350 nm ($\epsilon = 3500 \pm 1000$). By use of the method described by Foster [24], an equilibrium constant of $K = 6.9 \pm 0.6$ was measured for the ground-state charge-transfer complex of III with iodine. The amount of iodine complexed in a 10^{-3} M solution of III in cyclohexane at various iodine concentrations was measured directly against either a cyclohexane-iodine solution, or a cyclohexane solution of III, of equal molar concentration. By measuring the change in optical density at 360 or 280 nm and calculating the loss in density, the actual amount of iodine complexed could be calculated. Using the values obtained, the equation

$$K = \frac{[\text{complex}]}{[\text{III}][\text{I}_2]}$$

gives an equilibrium constant $K = 3.2$ l mol^{-1}. If a complex were to form between the iodine and a lone pair of electrons on the nitrogen atom of III in the usual manner for aromatic amines, a value of K in the range of 2×10^2 to 4×10^3 would be expected. A comparison of the values of K obtained for the iodine—III complex with those reported by Eubanks [25] suggests that a π-type complex is formed. This result is unexpected, since Eubanks reports aminoid complexes forming between aliphatic tetraalkyl aminoboranes and iodine. A model will show that it is highly unlikely that the mesityl groups produce a steric effect about the nitrogen so as to produce a low K value for a σ complex. To the contrary, steric interaction of the aromatic groups is relieved upon sp^2 hybridization of the nitrogen. Thus the aromatic groups present in III both sterically and electronically contribute to increase the double-bond character of the B—N bond system. The double-bond character has been demonstrated for the tetraalkyl aminoboranes using measurement techniques such as IR and NMR, which do not perturb the molecule appreciably [26,27], and has also been shown to play a major role in causing large Stokes shifts in the fluorescence spectra of anilinodimesitylboranes [28].

When the charge-transfer complex concentrations for the series in Fig. 2 were calculated and plotted versus the initial rates of production of IV and V, a random plot was obtained with no correlation between the ground-state CT complex and the rate of cyclization of either product. Furthermore, when a solution of I containing iodine was irradiated in the CT absorption band at 350 nm, no cyclization products were formed. These results indicate that excitation of the π-type ground-state charge-transfer complex is not a required step in the production of IV or V.

Interaction of iodine with the excited states of III; cation-radical formation

To determine whether iodine interacted with the excited state of III, the fluorescence and delayed fluorescence quenching ability of iodine were measured. We have reported that the anilinodimesitylborane series fluoresces with a quantum yield of fluorescence in the range of 0.07 to 0.18 and that a delayed emission corresponding to a delayed fluorescence was also observed at the same wavelengths as fluorescence [28]. The delayed emission was attributed to electron ejection-recapture emission. Figure 5 is the diagram which was used to explain the various properties of the observed luminescence spectra.

The prompt fluorescence of III from S'_1 has now been found to be quenched by iodine. A least-squares plot of Φ_0/Φ_q versus the iodine concentration gives a straight line with a slope of 296 l mol^{-1} and a correlation coefficient of 0.9917 (Fig. 3). The delayed emission via the CT state has been found to be quenched by much lower concentrations of iodine, and a plot of Φ_0(delayed)/Φ_q(delayed) versus iodine concentration gives a linear plot with a slope of 918 l mol^{-1} with a correlation coefficient of 0.9908 (Fig. 4). Therefore, both the excited CT state of the borane and the S'_1 state, as shown in Fig. 5, can interact with iodine.

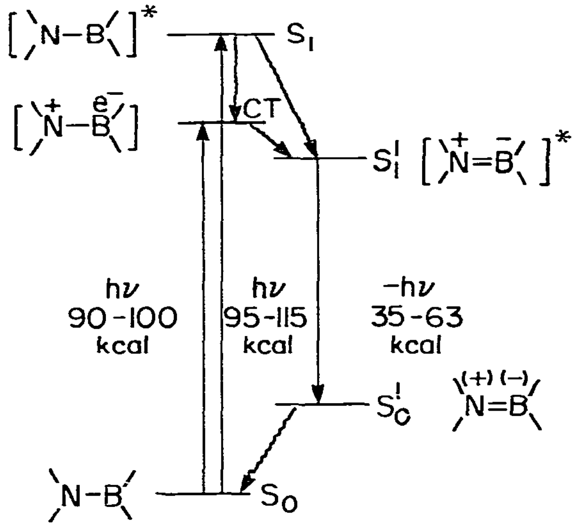
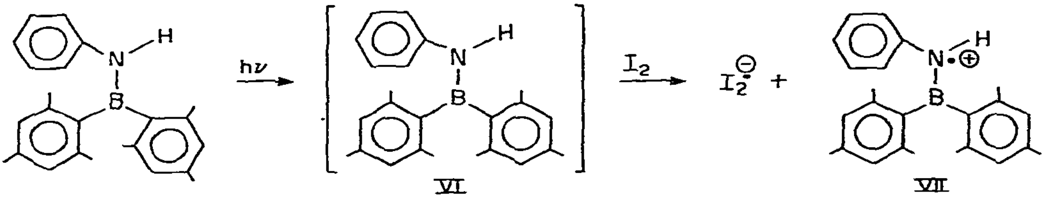


Fig. 5. Schematic of excited and ground states of anilinodimesitylboranes.

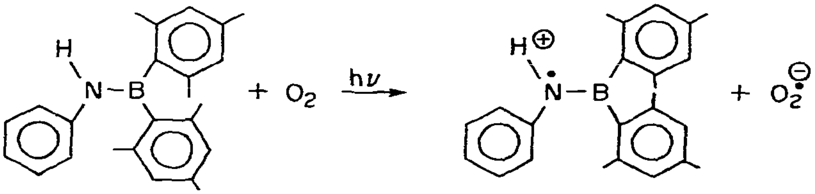
A proposed electron-transfer mechanism

The ease with which an electron is lost from the π-system of aromatic groups attached to boron has already been established [29]. Furthermore, there is spectroscopic evidence that highly charge-separated species are formed upon irradiation of the anilinodimesitylboranes [26]. If an electron transfer were to occur from a long-lived excited state of III to iodine, an intermediate radical such as VII would be produced.



Hancock and Dickinson [30] proposed an analogous amino-borane cation-radical, similar to the radical intermediate that Srinivasan and Hsu [31] proposed for the cyclization of *cis*-stilbene. We therefore propose that an electron-transfer reaction occurs between iodine and the intramolecular CT state of the borane to produce the radical intermediate VII, which can cyclize to produce IV.

The presence of oxygen at higher iodine concentrations (10^{-2} *M*) increases the ratio of IV to V from 0.1 in a nitrogen atmosphere to 0.17 in the presence of atmospheric oxygen. This slight increase in the production of IV and decrease in the production of V can be accounted for by assuming that oxygen accepts an electron to form $O_2^{\cdot-}$.

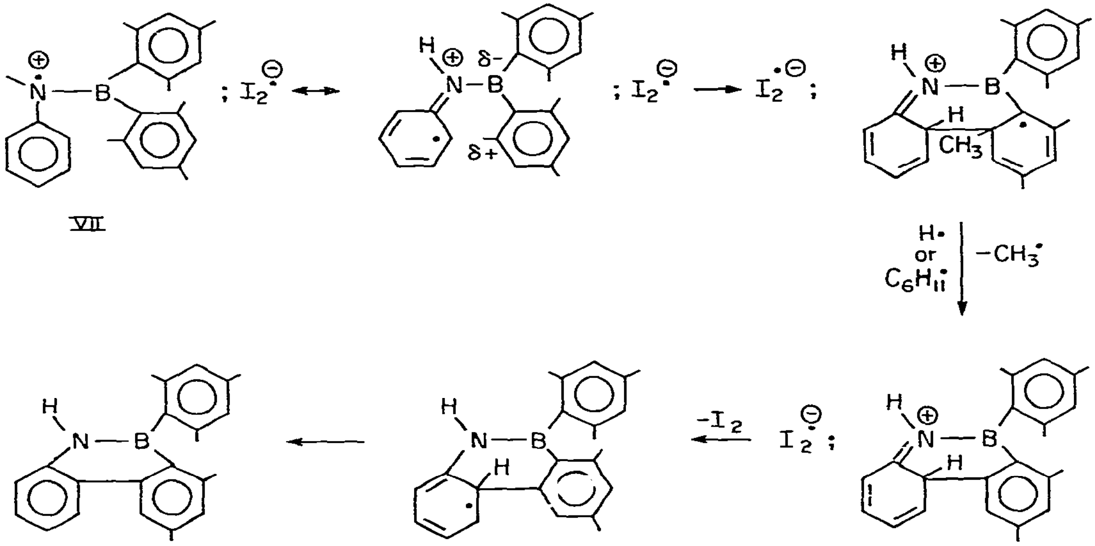


The oxygen-assisted electron abstraction from *N*-vinylcarbazole by electron-deficient olefins to form a reactive cation-radical intermediate has been reported [32] as a product-determining step.

Methyl elimination

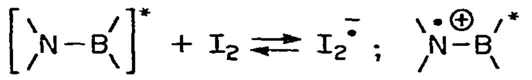
We have shown that 2,6-dimethylanilinodiphenylborane photocyclizes with elimination of methane to produce II [2]. We have now found that the methyl elimination from the aromatic ring attached to nitrogen is independent of iodine concentration and that methyl migration cannot be made to occur in the 2,6-dimethylanilinodiphenylborane system I. This is in contrast to the photocyclization of anilinodimesitylborane III, in which methyl elimination is dependent upon the concentration of iodine. Attempts to use liquid N_2 to trap any methane produced, to determine its presence by gas chromatographic techniques using a flame ionization detector, or to detect its presence using mass spectrometry gave dubious results. Thus, methane has not been identified as a product of the photocyclization of III to form IV. However, the homolytic cleavage of a methyl group is not expected to be quenched at low concentrations of iodine. This fact was substantiated by Ebert et al. [12], who reported that low concentrations of iodine do not quench the radical processes in cyclohexane. We have not detected any methylated products in reactions involving iodine.

The sequential steps in the cyclization process are visualized as:



Methyl migration

The formation of $I_2^{\bar{\cdot}}$ upon irradiation increases as the iodine concentration is increased [12]. The iodine anion radical produced enters into the following equilibrium:



This suppresses the formation of the cation-radical VII, resulting in a decrease in the yield of methyl-eliminated product IV. The decay of the excited state via the cation-radical VII is thus prevented or delayed, allowing the excited state VI to have more time to decay via other routes. The quantum yield of fluorescence and the chemical quantum yield of IV decrease as the iodine concentration increases. The quantum yield of V, however, increases concurrently. The role played by iodine, therefore, must involve a role beyond that of its part in the equilibrium process leading to the cation-radical VII. This is particularly required in light of the fact that the quantum yields of V in 10^{-2} and 10^{-3} *M* III at iodine concentration of 5×10^{-3} *M* are as great as, or greater than, those obtained for the production of IV at 10^{-3} *M* iodine. A decrease in the quantum yields with increasing iodine would be predicted if a strictly equilibrium-determining role was being played by iodine. The facile interaction of iodine with the excited CT and S'_1 states makes it conceivable that, in addition to the limiting affect on the formation of the cation-radical VII, iodine is exerting a heavy-atom effect which enhances intersystem crossing. This is in contrast to the formation of phenanthrene from stilbene, where formation of a dihydro intermediate via the triplet has been ruled out on energetic as well as experimental grounds [33]. The production of IV via the cation-radical VII and the secondary role of iodine as an intersystem crossing agent seem to be further substantiated by the observations that only IV is produced when tetracyanoethylene is used as the cyclizing agent and that V has not been observed in these reactions under any solvent or concentration conditions.

We proposed [3] an overall contribution of a charge-separated resonance form to the structure of the dihydro intermediate (VI b) to account for the difference between elimination from the anilino ring versus the methyl migration on the mesityl ring.

Such charge-separated excited states are not novel and have been proposed by several authors [34—36]. We have not observed the presence of the dihydro intermediate in these systems when iodine was present, suggesting that the dihydro intermediate VI, if formed, is a transient species which undergoes rapid conversion to the borazarophenanthrene.

Conclusion

We have reported that the photocyclization of anilinodimesitylborane in the presence of less than 10^{-3} *M* iodine occurs with the production of a demethylated phenanthrene derivative. When the photocyclization is carried out in the presence of greater than 5×10^{-3} *M* iodine, a methyl-group-rearranged phenanthrene derivative is formed. The role of iodine in these photocyclization reactions is at least threefold: First, at low concentrations, iodine acts as an electron acceptor, aiding the formation of a reactive cation-radical. Second, at higher concentrations, an iodine anion-radical, which is reported to be formed directly upon irradiation of either I_2, I_4, or higher polymers of iodine, can suppress the formation of the reactive aminoborane cation-radical. Third, at the higher concentrations, iodine must also be promoting a required reactive intermediate. Such an intermediate facilitates formation of a methyl-group-rearranged product. This effect may be accomplished by enhancement of intersystem crossing by way of a heavy-atom affect. A π-type charge-transfer complex of iodine with III has been observed. However, no connection of this complex with the photocyclization process has been established. Further studies on the kinetics and on the flash photolysis or pulse radiolysis of this system are essential to further elucidate the role of iodine and determine the nature of the intermediate products, as well as to elucidate the cause of the short induction period at the start of each irradiation. No attempt has been made to detect the radical cation VII by electron spin resonance techniques.

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