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Comparison of Oxidative and Excited State Cyclizations of *N*-Benzyldiphenylamines to *N*-Benzylcarbazoles

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Abstract: Pulse radiolysis of a family of *N*-benzyldiphenylamines in aerated cyclohexane results in oxidative cyclization products, i.e., the corresponding *N*-benzylcarbazoles, as does direct photolysis at 254 nm. Chemical oxidation and bulk electrolysis lead to benzidine formation as the major product, with the competing cyclization pathway becoming minor. Photoinduced electron transfer sensitization induces formation of a radical ion pair in which back electron transfer quenches net reaction. No significant amounts of products deriving from bond cleavage of an intermediate cation radical could be detected in any of the reactions. AM1 calculations show lower barriers for the initial cyclization through a triplet state than through an intermediate cation radical or dication.

Introduction

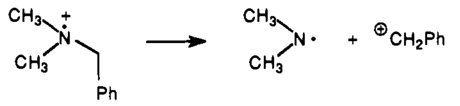
Photoinduced electron transfer between neutral reactants produces initially a singly oxidized and singly reduced radical cation−radical anion pair.[1,2] These intermediates exhibit dramatically altered chemical reactivity when compared with their neutral precursors, although the utility of such photodriven redox reactions rests in the ability to predictably control the ensuing dark reactions of the redox-activated radical ion intermediates. For example, cleavage of carbon−carbon[3] and carbon−heteroatom[4] bonds in radical ions is often strongly favored over comparable cleavages in their neutral precursors.[5] Alternatively, in some cases highly exothermic back electron transfer within the radical ion pair can serve as a source for singlet or triplet excited states. Although radical ions have been recognized as important intermediates in both chemical and biochemical transformations,[6] nearly no work is yet available to define the chemical efficiency of competing pathways or the intramolecular partitioning between different modes of chemical reaction. Nor is it yet clear how the environment in which a radical ion is produced can influence its subsequent chemistry.

Secondary and tertiary amine cation radicals are particularly interesting molecules to probe such effects, for they present several possible reaction modes.[7] Literature precedent exists for the cleavage of an N−H bond[8] in secondary amine cation radicals (by proton transfer within an exciplex), eq 1, or for the cleavage of an α-C−H bond[9] in tertiary amines bearing *N*-alkyl groups, eq 2.

$$R_2\overset{+\bullet}{N}H \rightarrow R_2N^\bullet + H^+ \tag{1}$$

$$R_2\overset{+\bullet}{N}CH_3 \rightarrow R_2NCH_2^\bullet + H^+ \tag{2}$$

Cleavage of an N−C bond has also been observed in *N,N*-dimethylbenzylamine, eq 3.[4c] In addition, cyclization has been



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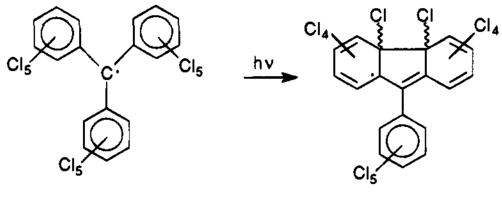
reported both in the ground states of diarylethylene radical cations[10] and upon photoexcitation of stable neutral radicals, e.g., perchlorotriphenylmethyl, eq 4,[11] an inert free radical that



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is isoelectronic with the triarylamine cation radical. Triplet states of diarylamines (conceivably produced by reduction (electron trapping) of the amine cation radical) have also been reported to cyclize to dihydrocarbazoles,[12] eq 5.

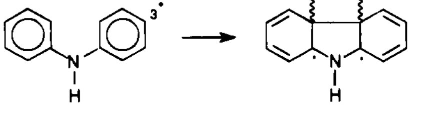

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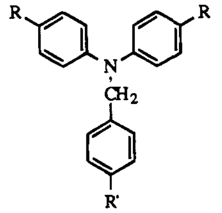
Table 1. Cyclic Voltammetric Oxidative Peak Potentials[a] for **1** in CH_3CN

amine	E_p (V vs SCE ± 50 mV)[b]
1a	+0.86
1b	+0.93
1c	+0.88
1d	+0.60

[a] Measured on a stationary Pt electrode as 0.02 M solutions in N_2-saturated CH_3CN containing 0.1 M $TBABF_4$ at 25 °C at a scan rate of 200 mV/s. [b] The observed potentials were referenced to a ferrocene internal standard.

In this work, we have investigated the reactions of a series of cation radicals of aromatic benzyldiphenylamines **1** prepared by several modes of oxidation (electrochemical oxidation, chemical oxidation, pulse radiolysis, and direct and sensitized photolysis). We hoped that the cation radicals **1** might be sufficiently stable to permit kinetic resolution of one or more of these possible competing pathways and that the substituents present on **1** might shift the observed reactivity in a predictable way.



1a: R, R, R' = H; **1b**: R, R = H, R' = F

1c: R, R = H, R' = OCH3; **1d**: R, R = OCH3, R' = H

Here, we describe the contrasting chemical reactivity encountered upon producing substituted benzyldiphenylamine radical cations in several different reaction environments, along with a semiempirical calculational study aimed at explaining the observed reactivity. Rather than yielding products derived from the intermediates expected from eqs 1 and 2, exposure of **1a**–**d** to ionizing radiation (3 MeV) in deaerated cyclohexane produced a transient dihydrocarbazole, in parallel to the reactivity envisioned as the first step in eq 5. Upon exposure to oxygen, these transients are converted in high yield to isolable carbazoles in reactions that are also observed, albeit in lower chemical yield, upon electron transfer photosensitization with $Ru(bpz)_3(PF_6)_2$ or upon chemical oxidation with ceric ammonium nitrate. Our exploration of several routes for producing the family of relatively stable cation radicals **1** illustrates how the local environment and the means for generation of a reactive intermediate can actually dictate its subsequent chemical fate.

Results and Discussion

Electrochemistry. Cyclic voltammograms (CV) for amines **1a**–**d** show quasi-reversible oxidation waves at about +1.1 V vs SCE, Table 1. As shown for **1a** in Figure 1, an additional reversible, oxidation–reduction couple appears at slightly less positive potentials on subsequent scans, reflecting an electrochemical behavior for **1a**–**1d** similar to that reported earlier for triphenylamine.[13] That this second couple can be seen only after the first anodic sweep suggests that it is generated by a secondary chemical reaction of the oxidized amine, possibly attributable to benzidine formation.[14] As required by this mechanism, oxidation to the radical cation is followed by a rapid dimerization and deprotonation, producing the dication, eq 6.

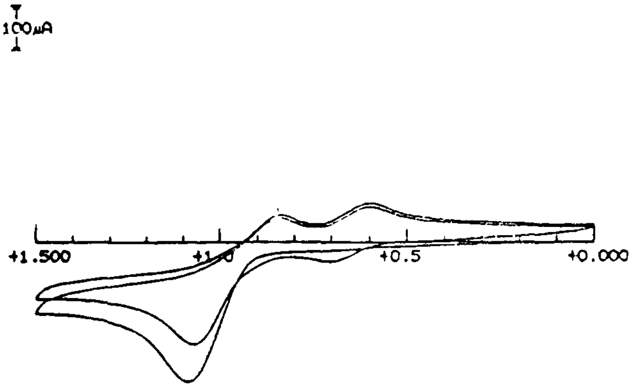
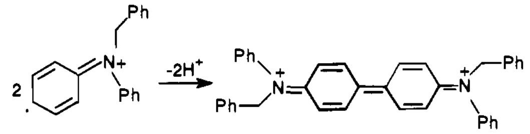


Figure 1. Cyclic voltammogram of **1a** measured on a stationary Pt electrode as a 0.02 M solution in N_2-saturated CH_3CN containing 0.1 M $TBABF_4$ at 25 °C at a scan rate of 200 mV/s.



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The dimeric product exists at the dicationic oxidation level because the oxidation of the initially produced benzidine takes place at a less positive potential than required for the oxidation of its amine precursor. An alternative coupling of the radical cation with a neutral amine, followed by rapid oxidation of the coupled product (also produced at a significant overpotential), would be kinetically and electrochemically indistinguishable from the radical cation dimerization pathway. No redox waves characteristic of a benzidine were observed in the electrochemical oxidation of **1d** in which methoxy groups at the para position of the phenyl rings block dimerization. Thus, the radical cation of **1d** is more stable, and its cyclic voltammogram more reversible, than the radical cations of **1a**–**c**.

Upon preparative anodic oxidation, followed by a reductive workup, the major isolable product derived from **1a** was the substituted benzidine **2**, formed as in eq 6. The dominance of the dimerization pathway for the radical cation produced by electrooxidation on a metal electrode is probably caused by the high concentration of cation radicals formed locally during the electrolysis.

Chemical Oxidation. Chemical one-electron oxidation of several trialkyl amines has been achieved with cerium(IV) ammonium nitrate.[15] The amine radical cations produced by this single electron oxidant usually react by σ bond fragmentation and by attack by water or molecular oxygen to form, as primary products, fragmented aldehydes and ketones.[13] However, Ce(IV) oxidation of benzylamines **1a**–**d** gave no evidence of C–N or α-C–H bond cleavage, for the products expected from these processes could not be detected by gas chromatography. Instead, a substituted carbazole is formed in the Ce(IV) oxidation of **1d**, and both carbazole and a second group of products, tentatively identified as the substituted benzidines on

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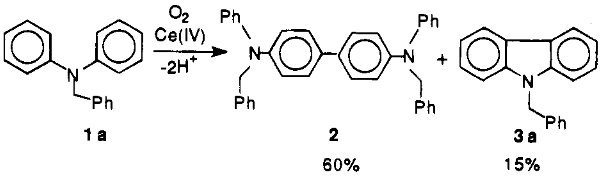
the basis of absorption spectra and GC/MS analysis, are obtained with **1a**−**c** (see below).

Chemical oxidation of amines **1a**−**c** in acetonitrile containing $Ce(NH_4)_2(NO_3)_6$ (6×10^{-5} M) produced a series of rapid color changes. These conditions are amenable to the formation of cation radicals, for the spectrum of the cation radical of triphenylamine (TPA) at 650 nm can be observed in a parallel experiment. In fact, however, no absorption maxima attributable to the radical cations of **1a**−**c** could be observed upon monitoring these reaction mixtures by absorption spectrophotometry, presumably because of rapid dimerization of the radical cations to the corresponding benzidines **2**, an assertion which was confirmed both by product isolation and by the appearance of an absorption maximum at 464 nm characteristic of the benzidine radical cation.[16] The detection of substituted benzidines in the Ce(IV) oxidations of **1a**−**c** suggests that dimerization, followed (or preceded) by disproportionation or reduction, competes with cyclization to a carbazole precursor. In addition, the corresponding *N*-benzylcarbazole derivatives **3** (ca. 15% chemical yield, based on starting material consumed) are formed upon treatment with a 10-fold excess of Ce^{4+}, along with the corresponding benzidine (ca. 60% yield), as shown for **1a** in eq 7.



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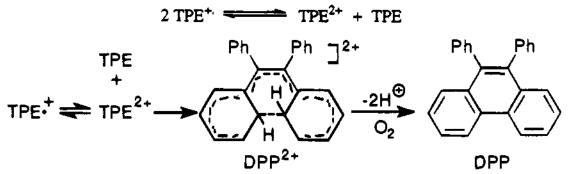
This route to cyclization of the radical cation of **1a** may be parallel to that of the tetraphenylethylene (TPE) radical cation in acetonitrile[10] in which 9,10-diphenylphenanthrene (DPP) is formed, eq 8. This conversion has been suggested to take place



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by disproportionation of the radical cation to a dication, which cyclizes to an intermediate that loses two protons. Thus, it is conceivable that the reactivity of the radical cation of **1a** in eq 7 reflects dimerization and cyclization either through the radical cation or by further oxidation to the dication by an excess of chemical oxidant.

Upon treatment of **1d** (1.6×10^{-4} M) with 0.4−1.0 equiv of Ce^{4+}, a dark green solution (λ_{max} 750 nm) was observed immediately upon mixing, Figure 2. This band is assigned to the amine cation radical ($1d^{\bullet+}$) by comparison with that reported for the *N*,*N*,*N*-tris(*p*-methoxyphenyl)amine cation radical (λ_{max} 714 nm in acetonitrile).[17,18] In the presence of oxygen, carbazole **3d** is formed in low chemical yield (ca. 25% of consumed starting material) with a 10-fold excess of Ce^{4+}, eq 9, with trace amounts of the analogously substituted benzidine (λ_{max} 500 nm) being produced much more slowly than with **1a**−**c**.

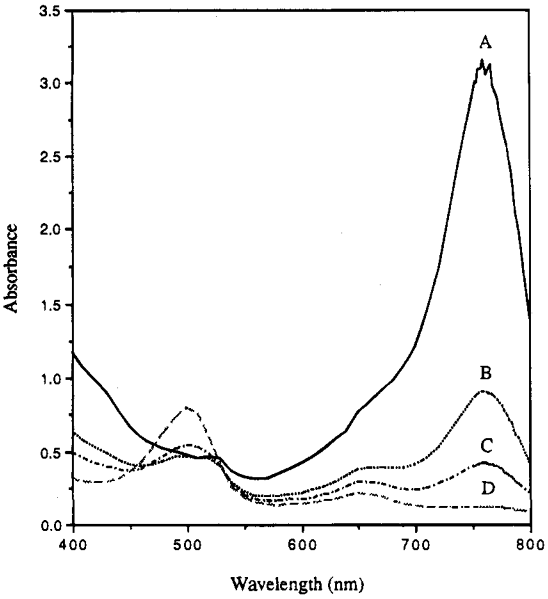
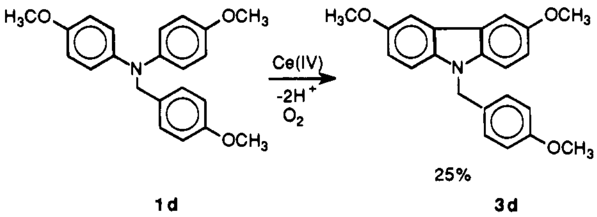


Figure 2. Absorption spectrum obtained by treatment of of **1d** (1.6×10^{-4} M) with 0.4−1.0 equiv of Ce^{4+}: (A) immediately; (B) 2 min; (C) 4 min; and (D) 12 min after mixing.



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Pulse Radiolysis. When produced by pulse radiolysis, the radical cations of **1a**−**d** participate in reaction pathways quite different from those observed upon electrochemical or chemical oxidation. Cyclization represents the principal reaction pathway, and dihydrocarbazoles can be observed as transients under deoxygenated conditions.

In the pulse radiolysis experiment, bombardment of an ionizable solvent with high-energy electrons produces solvent positive ions that can then react with solute, producing radical cations.[19,20] Radical cation formation from **1a**−**1d** in cyclohexane is energetically favorable because the ionization potentials of these amines (a range of 4.7−8.1 eV) are much lower than that of cyclohexane (9.9 eV).[21] Furthermore, ion recombination occurs within a few nanoseconds of energy deposition within the medium.[22] These "geminate ions" (or ion−electron pairs) formed in liquid cyclohexane have an inter-ionic distance shorter than the Onsager escape radius (r_c ¯ 300 Å),[23] such that the radical cation and the corresponding solvent radical anion or electron never escape each other's influence. The very rapid decay of correlated ion pairs ensures that considerable ion recombination takes place during the pulse. Geminate ion pairs have been suggested to account for approximately 90% of total charge recombination.[24] The lowest excited triplet or singlet states are formed by this fast and highly exothermic charge

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[17] The wavelength maximum for TPA radical cation in cyclohexane is 640 nm,[28] that of diphenylamine is 670 nm,[48] and that of tri(*p*-tolyl)amine is 670 nm.[49]

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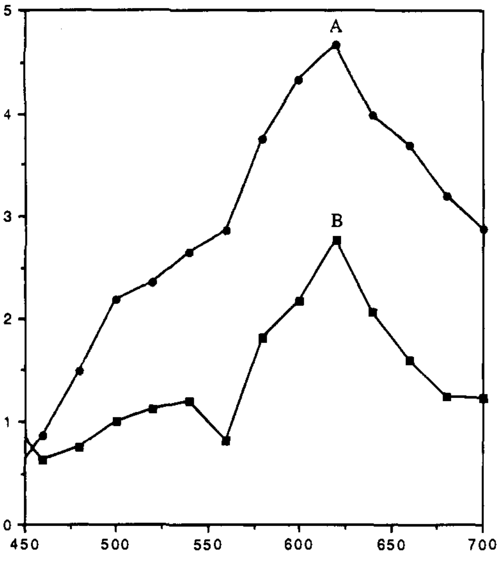


Figure 3. Absorption spectra of a deaerated solution of **1a** (10^{-3} M in cyclohexane) at two delay times after a 100 ns wide 3 MeV radiolysis pulse: (A) 8.4 μs; (B) 35.2 μs.

recombination (of the solute radical cation with either a solvent radical anion or a solvated electron).[24,25]

In an inert hydrocarbon solvent, the radical cation of triphenylamine produced by ionizing radiation has been reported previously to decay by back electron transfer through a singlet or triplet excited state,[26,27] ultimately producing *N*-phenylcarbazole.[28] The proposed mechanism for this transformation involves cyclization of a triplet excited state (produced by electron trapping by the initially formed radical cation, as discussed above) to an *N*-phenyldihydrocarbazole intermediate, followed by oxidation or disproportionation to the observed product.

The transient absorption spectrum produced by pulse radiolysis of **1a** in a polymer matrix containing CBr_4 has a wavelength maximum of 660 nm (τ = 100 μs) and is assigned to the radical cation.[29] Upon pulse radiolysis in deaerated cyclohexane, however, even in the presence of an equivalent of CCl_4, broad absorptions centered at about 620 nm are observed instead for **1a**–**d**, as shown in the representative spectrum shown for **1a** and **1d** in Figures 3 and 4, respectively. These bands are assigned to the corresponding dihydrocarbazoles by comparison with the known spectrum of the dihydrocarbazole of triphenylamine in the same solvent[30] and their resemblance to other labile species observed in related oxidative cyclizations. Thus, when back electron transfer is not effectively blocked by solvent dissociation, the amine cation radical cannot be observed on a time scale slower than 100 ns.

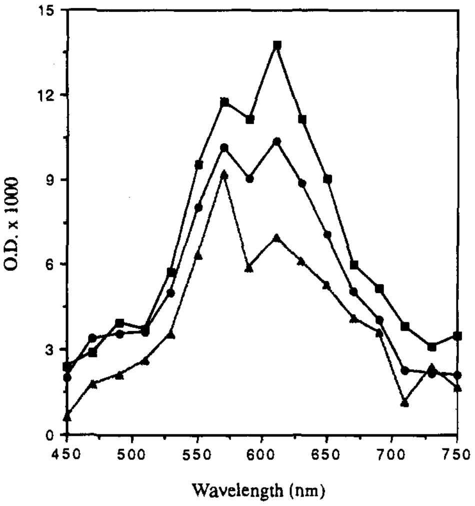


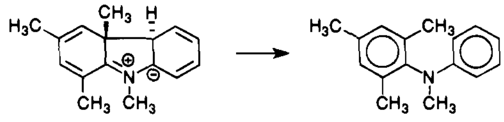
Figure 4. Absorption spectra of a deaerated solution of **1d** (10^{-3} M in cyclohexane) at three delay times after a 100 ns wide 3 MeV radiolysis pulse: (A) 20 μs; (B) 60 μs; and (C) 175 μs.

Table 2. Lifetimes and First-Order Decay Constants for Dihydrocarbazoles Produced by Pulse Radiolysis of Triphenylamine (TPA) and **1** in Cyclohexane

amine precursor	half-life (μs ($\pm$1 μs))	k_{obs} (s^{-1}) × 10^{-4}
TPA[a]	42	2.5
1a[b]	10	9.7
1b[a]	10	10
1c[b]	13	7.6
1d[b]	17	5.8

[a] Monitored at 630 nm. [b] Monitored at 650 nm.

These dihydrocarbazoles of **1a**–**d** are metastable and disappear in deaerated cyclohexane by similar first-order decay constants, Table 2. In the absence of a secondary chemical oxidant, the dihydrocarbazoles derived from **1a**–**d** are reconverted to **1a**–**d** by thermal relaxation. As a result, no carbazole products can be isolated after exposure to ionizing radiation in the absence of air. Similarly, the first-order decay of *N*,4a-dimethyl-4a,4b-hydro-1,3-dimethylcarbazole **4** in degassed methylcyclohexane has been ascribed to ring-opening to the amine ground state, eq 10,[31] and the dihydrophenanthrene produced in the photocyclization of *cis*-stilbene also thermally reverts to *cis*-stilbene in degassed solution.[32,33] In contrast, *N*-methyldihydrocarbazole **5** in degassed solution has been reported to disproportionate to *N*-methylcarbazole and N-methyltetrahydrocarbazole in a bimolecular process, eq 11.[31]



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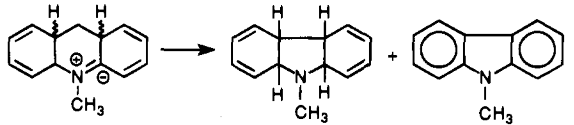

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No bimolecular decay was evident from a kinetic analysis of the dihydrocarbazoles produced from **1a**–**d** in deaerated cyclohexane, and although product isolation from a radiolytic mixture is difficult, only trace amounts of a product whose mass spectrum showed a molecular weight two mass units higher than the starting material (presumably a tetrahydrocarbazole) could be detected from an extensively electron-bombarded deaerated

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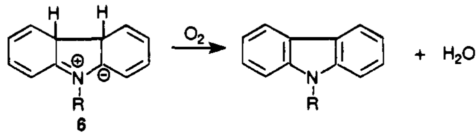
Table 3. Quantum Yields for Carbazole Formation from Direct Irradiation of Several Diphenylamines[a]

amine	Φ (±0.20)	amine	Φ (±0.20)
DPA	0.65	**1b**	0.64
7	0.68	**1c**	0.62
TPA	0.66	**1d**	0.64
1a	0.64		

[a] Oxygen-saturated solutions (ca. 10^{-3} M) in CH_3CN were irradiated at 254 nm in a Rayonet photochemical reactor.

solution of **1a**. Thus, reversion of the dihydrocarbazoles of **1a**–**d** to the corresponding diphenylamines appears to be more rapid, in the absence of oxygen, than disproportionation.

Under aerobic conditions, pulse radiolysis of **1a** in cyclohexane produced no observable visible-absorbing transients with lifetimes greater than the radiolytic pulse (100 ns). A plausible explanation is that in O_2-saturated solution either the triplet is quenched by O_2 (a very efficient triplet state quencher), the solvated electron is scavenged by oxygen, or the dihydrocarbazole **6** is oxidized as it is formed, eq 12. Air saturation of a radiolyzed solution of diphenylamine also causes the absorption assigned to dihydrocarbazole to vanish almost completely and its triplet lifetime to be reduced to 50 ns.[34] Hydrogen peroxide, the reductive by-product expected if molecular oxgen were to effect oxidation of an intermediate dihydrocarbazole to carbazole, was identified by iodometry.[35] Although quantitative analysis of the product mixtures obtained from pulse radiolysis is difficult, an extensively radiated sample of **1a** in O_2-saturated cyclohexane does show carbazole to be present.



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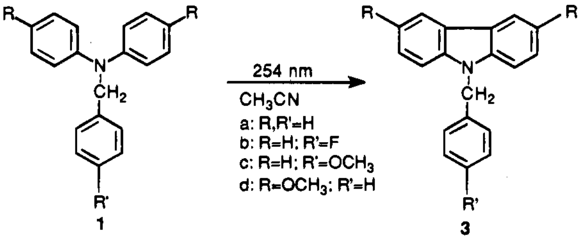
Steady State Direct Irradiation. Direct photolysis (254 nm) of **1a**–**d** (3×10^{-3} M) in N_2-saturated acetonitrile gives the corresponding carbazoles in very low chemical efficiency (ca. 1% based on consumed starting material after 10 h). In contrast, as had been previously reported for diphenylamine (DPA) irradiation, carbazoles **3a**–**d** are produced in O_2-saturated solution with high quantum efficiency (Φ ~0.64), eq 13, and similar results are obtained with *N*-methyldiphenylamine **7** and triphenylamine (TPA), Table 3. There was no dramatic influence of the attached substituent on the observed chemical yield of cyclization product.



1 **3**

(13)

A previous study of the direct photolysis of diphenylamine has implicated dihydrocarbazole formation from the triplet excited state.[12] The high frequency factor of 8×10^{11} s^{-1} observed in the ring closure in *N*-methyldiphenylamine was taken as evidence for a spin-allowed process leading to the triplet excited state of the corresponding dihydrocarbazole, followed by relaxation to the singlet state.[36] A similar intermediate (4a,4b-dihydrophenanthrene) has been proposed in the direct photocyclization of *cis*-stilbene.[37,38]

Table 4. Decay[a] of Amine Cation Radicals Producec by $Ru(bpz)_3$ Sensitization of **1a**–**c**

amine	k/ϵ (s^{-1}) × 10^{-4}
1a	7.5
1b	7.0
1c	7.1

[a] Monitored at 500 nm.

Sensitized Irradiation. As with electrochemical oxidation, irradiation of $Ru(bpz)_3(PF_6)_2$ (bpz = bipyrazine) in the presence of **1a**–**c** in N_2-saturated acetonitrile induces single electron oxidation of the amines by electron transfer sensitization. Transient absorption spectra of the radical cations of amines **1a**– were obtained upon flash excitation of $Ru(bpz)_3(PF_6)_2$ at 355 nm (10 ns laser pulse width, 16 mJ /pulse) in N_2-saturated acetonitrile containing these amines (ca. 10^{-4} M). The mixtures thus produced also exhibit a characteristic absorption maximum at about 480 nm that can be assigned to a strongly absorbing reduced $Ru(bpz)_3$ intermediate.[39]

The intermediates produced from **1a**–**c** decay in a second-order process by back electron transfer between the intermediate and the reduced Ru complex ($\epsilon \sim 1.2 \times 10^4$ M^{-1} cm^{-1}). Rate constants for these decays are listed in Table 4.[40] Only subtle dependence on substitutents was observed.

Analysis of the product mixture obtained upon steady-state irradiation of **1a** in the presence of this MLCT sensitizer did not reveal formation of benzylcarbazole or benzidine. Instead, nearly quantitative recovery of the starting material was observed. Thus, the major pathway for decay of the cation radical is likely back electron transfer to regenerate the neutral ground states of the sensitizer and amines. (Back electron transfer from the reduced ruthenium complex is not sufficiently energetic to generate an excited singlet or triplet state.) Although steady state photolysis of a mixture of dicyanoanthracene (DCA) and **1a** did produce carbazole in the presence of oxygen, transient absorption bands assignable to the DCA anion radical and the amine cation radical were not observed in a pulse experiment (presumably because inefficient cage escape of the geminate ion pair permits rapid back electron transfer to produce a reactive triplet state).

Calculations. Cyclization of diphenylamines to form carbazoles can occur, in principle, through three different routes: via (1) the triplet state, (2) the radical cation, or (3) the dication. AMPAC reaction path calculations[41,42] employing *N*-methyldiphenylamine **7** as a model compound for **1a** were employed to determine barriers for these possible reaction pathways. The AMPAC program was chosen for these calculations because

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(40) The parallel experiment could not be conducted for **1d** because of significant overlap of the absorption bands of the Ru complex absorption band and the amine at 355 nm.

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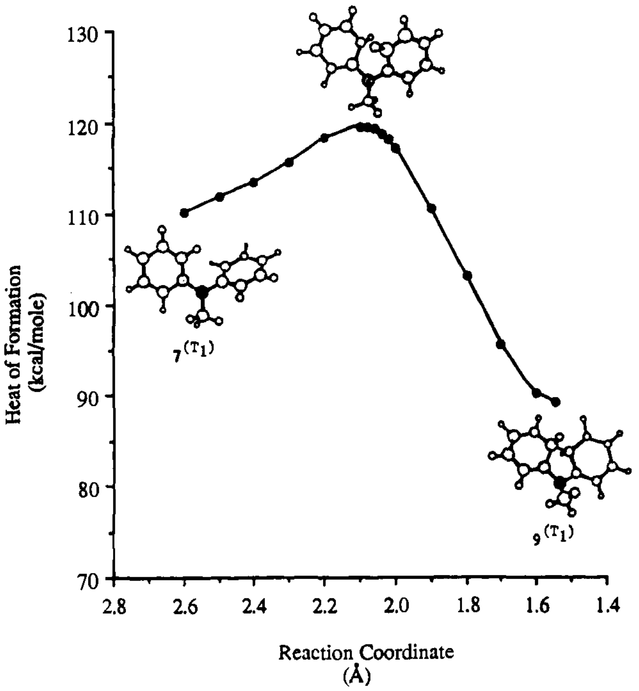
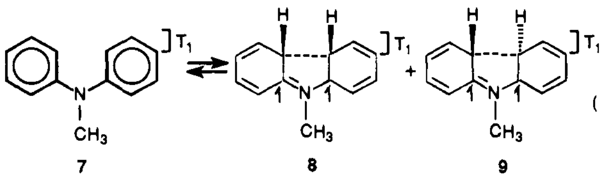


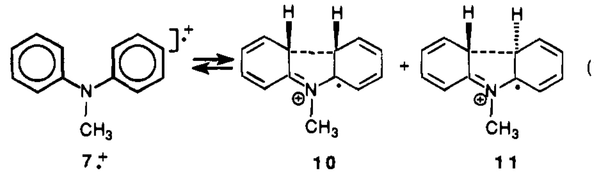
Figure 5. AM-1-calculated reaction path coordinate for the cyclization of the triplet of *N*-methyldiphenylamine **7**.

of the known utility of the MNDO method for open-shell systems and excited states[43] and the demonstrated superiority of the AM-1 package for analogous reaction path calculations.[44] These calculations indicate that the triplet pathway (amine (T_1) to dihydrocarbazole (T_1)) is favored energetically over that involving the radical cation or dication: ΔH (triplet pathway) = −9.6 kcal/mol, ΔH (radical cation pathway) = +35.4 kcal/mol, and ΔH (dication pathway) = +20.2 kcal/mol.

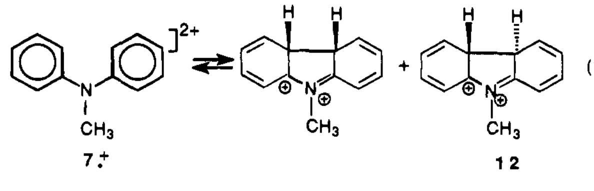
To locate the transition states (TS) for the cyclization of the triplet state of **7**, the distances between the "breaking" bonds in the triplet *cis*-fused isomer **8** and its *trans* isomer **9** (indicated by dotted lines) were "stretched" incrementally to attain the ring-opened amine, eq 14. The TS, and hence the potential barrier, was then found by using a force field calculation to minimize the gradient norm, Figure 5. Analogous calculations for the radical cation and the dication are summarized in eqs 15 and 16 and in Figures 6 and 7, respectively. In the transition state for the cyclization of the radical cation, the forming bond has a length of 2.00 Å, whereas the corresponding bond lengths in the triplet state and dication reactions are 2.20 and 2.10 Å, respectively. The optimized geometries for these isomers indicate that the *cis*-fused-triplet **8** is less stable by about 3 kcal/mol than the *trans*-fused isomer **9** and that the *cis*-fused radical cation **10** is less stable by about 3 kcal/mol than the corresponding *trans* isomer **11**. The dication, in contrast, cyclizes through a pathway with a much lower activation barrier to a more stable dicationic *trans*-fused product **12**.



(14)



(15)



(16)

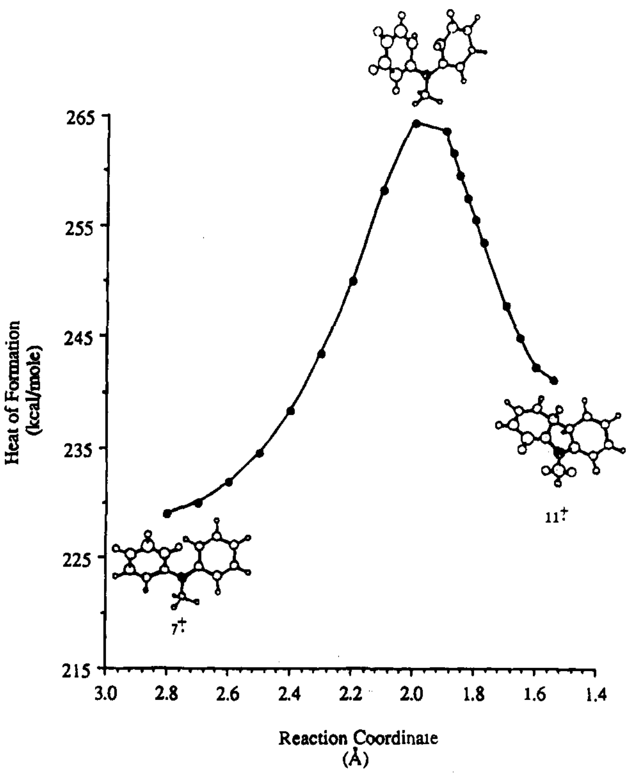


Figure 6. AM-1-calculated reaction path coordinate for the cyclization of the radical cation of *N*-methyldiphenylamine **7**.

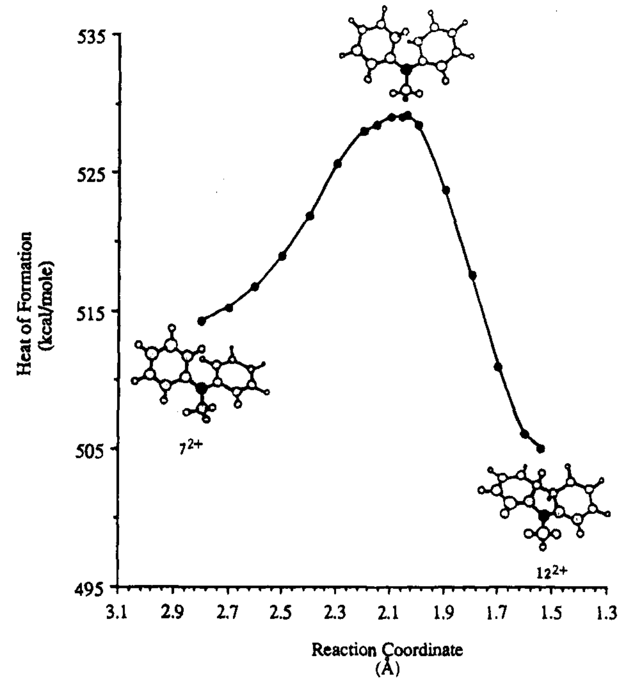


Figure 7. AM-1-calculated reaction path coordinate for the cyclization of the dication of *N*-methyldiphenylamine **7**.

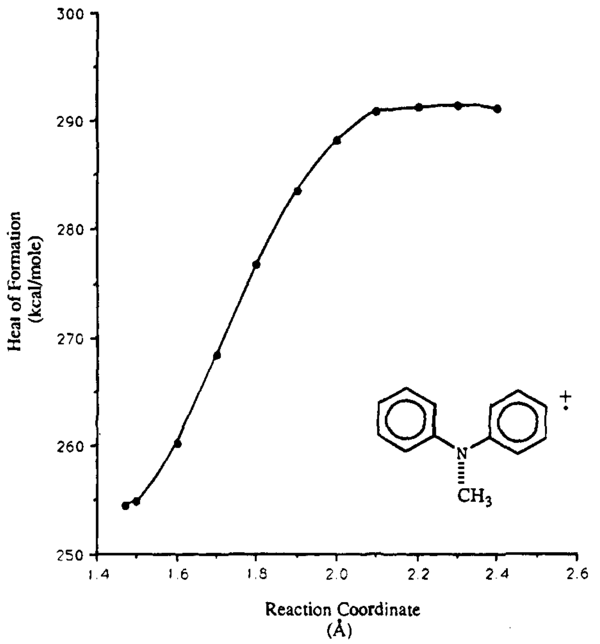


Figure 8. AM-1-calculated reaction path coordinate for the cleavage of C(1)−N(2) bond in the radical cation of *N*-methyldiphenylamine **7**.

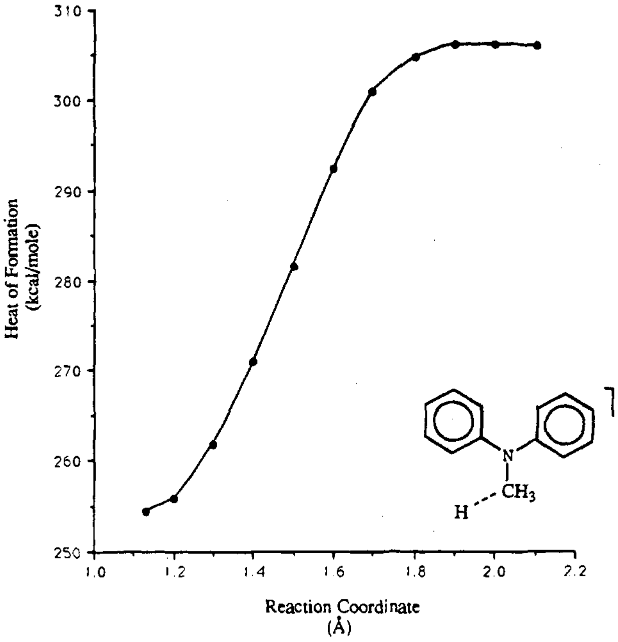


Figure 9. AM-1-calculated reaction path coordinate for the cleavage of the αC(1)−H(31) bond in the radical cation of *N*-methyldiphenylamine **7**.

With the radical cation of **7**, two bond breaking paths can also compete, in principle, with the cyclization: (1) cleavage of the methylene C−N bond (Figure 8) or 2) cleavage of the α-C−H bond (Figure 9). Calculations show that both routes encounter much larger barriers than that associated with the cyclization, as is consistent with the absence of any experimental evidence for bond cleavage.

These calculations thus rationalize the observed cyclization to a dihydrocarbazole through the triplet amine. However, AM1 calculations do not include solvent or solvent stabilization effects on various intermediates and transition states. With radical cations, enhanced solvation is known to decrease the barrier to cyclization,[45] and in particular, these calculations show no additional barrier beyond the thermicity of the reaction and may be very sensitive to local solvation effects. The prediction that cyclization via the triplet state dominates over the radical cation or dication pathways seems to agree with the experimental results obtained here. That is, carbazole yields are greater when the triplet is generated photochemically or by electron trapping within the radiolytic pulse than when the radical cation is generated chemically or electrochemically. Furthermore, these calculations suggest initial formation of a *trans*-fused dihydrocarbazole along the triplet surface.

Conclusions

N-Benzylcarbazoles are formed in lower yields from cation radicals produced by electrochemical and chemical methods than from those produced by pulse radiolysis or photoexcitation. The radical cations produced upon electrochemical or chemical oxidation dimerize to benzidines because of the high local concentrations of the intermediates generated under these conditions. In contrast, the radical cation produced by pulse radiolysis traps an electon (charge recombination with a solvated electron) within the radiolytic pulse to produce a triplet that can efficiently cyclize. Cyclization is the dominant pathway for the triplet produced by pulse radiolysis in deaerated cyclohexane, although thermal reversion to the ring-opened amine starting material reverses the photoreaction in the absence of oxygen. The rate of formation of dihydrocarbazole is only weakly dependent on the substituents present in **1a**−**d**. Likewise, substituents had only a minimal effect on the chemical yield of carbazole produced by steady state irradiation in aerated acetonitrile. The low net reactivity observed upon electron transfer sensitization by $Ru(bpz)_3(PF_6)_2$ results from quenching by back electron transfer from the reduced sensitizer to its paired radical cation, leading to the ground state neutrals.

Chemical oxidation and electrochemical oxidation of **1a**−**c** result in dimerization of these radical cations to yield benzidine products. In these oxidative transformations, substituents did influence the stability of the cation radicals and, hence, the attainable chemical yields. The cation radical of **1d**, for which benzidine formation is blocked, could be directly detected when generated by chemical oxidants. Its longer lifetime is also evidenced by the reversibility of its cyclic voltammetric oxidative scan.

Consistent with these experimental results, AMPAC calculations imply faster and more energetically favorable cyclization of N-substituted diphenylamines from the triplet state than from the cation radical or dication. Alternative cleavage pathways are also of higher energy.

Experimental Section

Diphenylamine (Baker), 4,4′-dimethoxydiphenylamine (Aldrich), benzyl chloride (Mallinkrodt), 4-methoxybenzyl chloride (Aldrich), 4-fluorobenzyl chloride (Aldrich), and 1.6 M *n*-butyllithium in hexanes (Aldrich) were used as received. Cyclohexane and acetonitrile (Aldrich, HPLC grade) were filtered and distilled through a 0.5 μm filter.

Preparation of Para-Substituted *N*-Benzyldiphenylamines 1a−c. Amines **1a**−**c** were prepared by treatment of diphenylamine with the appropriately substituted benzyl chloride.[46]

1a: mp 89−90 °C; ^{1}H-NMR ($CDCl_3$) 5.00 (s, 2H), 6.93−7.33 (m, 15H); UV absorption (CH_3CN) λ_{max} (nm) 242 (ϵ = 6000); mass spectrum, *m/e* (rel intensity): 91 (81.67), 168 (49.84), 182 (13.18), 259 (100.0); HRMS *m/e* calcd for $C_{19}H_{17}N$ 259.3607, found 259.3610.

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1b: recrystallization from hot ethanol to afford white needles; mp 97–101 °C. ^{1}H-NMR ($CDCl_3$) δ 4.95 (s, 2H), 6.94–7.32 (m, 14H); UV absorption (CH_3C N) λ_{max} (nm) 244 (ϵ = 6050); mass spectrum, *m/e* (rel intensity) 277 (100); HRMS *m/e* calcd for $C_{19}H_{16}NF$ 277.1267, found 277.1268.

1c: recrystallization three times from hot ethanol to afford white needles; mp 71–72 °C. ^{1}H-NMR ($CDCl_3$) δ 3.77 (s, 3H), 4.93 (s, 2H), 6.82–7.23 (m, 14H); UV absorption (CH_3CN) λ_{max} (nm) 240 (ϵ = 6100); HRMS *m/e* calcd for $C_{20}H_{18}NO$ 289.3875, found 289.3877.

1d: A slightly orange viscous oil was obtained by treating *N,N*-bis(*p*-methoxyphenyl)amine with benzyl bromide in glycerol. The residual oil was purified by column chromatography on neutral alumina with 3:10 ethyl acetate:hexanes (v/v) as eluent: ^{1}H-NMR ($CDCl_3$) δ 3.74 (s, 6H), 4.86 (s, 2H), 6.76–7.35 (m, 13H); ^{13}C-NMR ($CDCl_3$) δ 55.23, 55.57, 56.44, 113.86, 114.57, 121.85, 127.87, 131.47, 142.55, 154.23, 158.41; UV absorption (CH_3CN), 310 (ϵ = 7000); mass spectrum, *m/e* (rel intensity) 319 (100); HRMS *m/e* calcd for $C_{21}H_{21}NO_2$ 319.1572, found 319.1579.

Electrochemical Measurements. Electrochemistry was performed on a BioAnalytical System 100 electrochemical analyzer. All electrochemical measurements were carried out under N_2 at 25 °C in anhydrous acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate (Southwestern Analytical Co.) as the supporting electrolyte. The concentration of amines used was ca. 10^{-3} M. The electrochemical cell consisted of a platinum wire as the counter electrode, Ag/AgCl as the quasi-reference, and a platinum button as the working electrode.

Steady State Photolysis. A. Sensitized Irradiationl. An acetonitrile solution of $Ru(bpz)_3(PF_6)_2$ (with an optical density of approximately 0.6) that was also 0.1 M in amine **1a–d** was purged with N_2 for 5 min. Steady state sensitized irradiation of the resulting deaerated solutions was conducted in a Rayonet photochemical reactor equipped with low-pressure mercury arcs blazed at 350 nm. The reaction mixture, having been extracted into ether and filtered through silica gel to remove the sensitizer metal complex, was analyzed on a Hewlett-Packard 5890A capillary gas chromatograph equipped with a flame ionization detector. Benzidine and carbazole products of **1a** were identified by co-injection with authentic samples,[47] and those derived from **1b–d** by quantitative gas chromatography/mass spectroscopy.

B. Direct Irradiation. Approximately 10^{-3} M solutions of amines **1a–d** in acetonitrile were irradiated with low-pressure mercury bulbs (254 nm) in a Rayonet photochemical reactor. After irradiation, the reaction mixture was analyzed by gas chromatography as described above.

Flash Photolysis and Pulse Radiolysis Measurements. A 10^{-3} M solution of **1a–d** in nitrogen- or oxygen-saturated cyclohexane or in N_2-saturated CCl_4 in a quartz flow cell with a 2.4 cm analyzing pathlength was irradiated with an electron pulse (width 100–200 ns) from a 3 MeV van de Graaff accelerator or with a Q-switched Nd: YAG laser (Continuum Surelite) that provided 10 ns pulses at 355 nm (6 mJ/pulse) by passing the incident pulse through a harmonic generating crystal.

Transient absorption was monitored using a 150 W Xe lamp, grating monochromator, and photomultiplier tube arrangement. Time-resolved absorption spectra, obtained by averaging 50 transients, were recorded on a Tektronix TDS 540 digitizer interfaced with a personal computer for data analysis.

Product analysis of extensively radiolyzed samples was conducted as described above for the steady state irradiations.

Chemical Oxidation of 1a–1d. To a 10 mL sample of a 10^{-5} M solution of $Ce(NH_4)_2(NO_3)_4$ in CH_3CN was added an acetonitrile solution (10^{-5} – 10^{-6} M) of amines **1a–d**. The resulting solution was monitored on a Hewlett-Packard diode array absorption spectrometer. At the completion of the reaction, water was added to dilute the ceric salts and the resulting solution was extracted with ether. The organic layer was then analyzed as above by gas chromatography or by gas chromatography/mass spectroscopy as discussed above.

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