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Photochemical Electrocyclization of Thermally Stable Triarylamine Radical Cations

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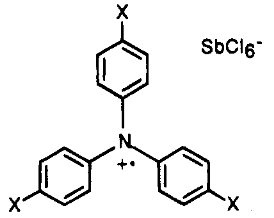
Introduction

Pericyclic reactions of radical cations constitute an area of great theoretical interest within physical organic chemistry.[1] Although most published investigations have so far focused on thermal rearrangements, a few examples of photoinduced processes have also been reported.[2] Conducted primarily in rigid low temperature matrices, these include electrocyclic ring openings,[3−6] electrocyclic ring closures,[7,8] a cycloreversion,[9] double bond migrations,[10,11] and cis−trans isomerizations.[12−14] The emerging pattern of reactivity found in excited state pericyclic reactions of radical cations suggests that Woodward−Hoffmann selection rules are often obeyed, as in closed shell substrates.[15] However, a study of the photoinduced electrocyclic ring opening of cyclobutene radical cation has recently challenged the inference that orbital symmetry arguments are applicable universally in these reactions.[3] Non-pericyclic chemical reactions catalyzed by excited radical ions at electrode surfaces[16,17] and in solution[18−24] have been the topic of several investigations, and photoexcited radical cations have been employed as single electron oxidants in several specific catalytic cycles.[18−22,24]

While examining the use of excited substituted triarylamine radical cations as oxidants in photoinduced electron transfer reactions, we have discovered a new photochemical reaction; namely, a cyclization followed by aromatization. Substituted triphenylamine radical ions are known to be photoactive, since their solutions bleach when exposed to light,[25] but the products, mechanism, and efficiency of the relevant photochemical reaction have not been established. The visible light induced 1,5-electrocyclic ring closures of the tris(4-bromophenyl)amine (**1a**) and tris(4-methoxyphenyl)amine (**1b**) radical cations in deoxygenated CH_2Cl_2 are described herein.



1a: X = Br
1b: X = OMe

Experimental Section

Reagents. Tris(4-bromophenyl)amine (**2a**) (Aldrich) was used without further purification. Methylene chloride (Baker) was distilled from CaH_2 prior to use. Tris(4-bromophenyl)aminium hexachloroantimonate (**1a**) (Aldrich) was purified by dissolution in CH_2Cl_2 and precipitation upon addition of diethyl ether. Tris(4-methoxyphenyl)amine (**2b**) was prepared and purified by the procedure of Bacon and Rennison[26] and was oxidized to the aminium salt by treatment with antimony[25] pentachloride.

Spectral Measurements. Absorption spectra were recorded on a Hewlett-Packard 8451-A diode array spectrophotometer equipped with a Hewlett-Packard 7470 plotter. ^1H NMR were recorded on a Nicolet QE-300 spectrometer. Gas chromatography−mass spectrometry analyses were performed on a Varian 3400 gas chromatograph (GC) interfaced with a Finnigan MAT 700 MS instrument using a 25 m DB-5 capillary column.

Steady State Photolysis of Substituted Triarylamines. **1a** (0.050 g) was dissolved in 300 mL of freshly distilled CH_2Cl_2. The dark blue solution was deaerated in a Pyrex tube by bubbling with a slow argon stream for 0.5 h. The resulting solution was sealed and irradiated in a Rayonet RPR-100 merry-go-round photoreactor equipped with phosphor-coated low pressure mercury arcs blazed at 350 nm for periods of up to 12 h. (The Pyrex vessel filters out all wavelengths shorter than 310 nm, and the output of the lamp is negligible below 320 nm, assuring that no direct excitation of the neutral precursor can take place.) Identical dark control reactions were covered by aluminum foil during side-by-side irradiations. The progress of the photolysis, monitored by following the bleaching of the **1a** absorbance at 716 nm, was stopped at 10% conversion of the aminium salt. Quantum yields were determined against potassium ferrioxalate as an actinometer.[27] After termination of the photolysis, the solvent was removed under reduced pressure. The resulting solid was extracted with diethyl ether (50 mL × 3) to separate the starting material and the photoproducts. The pale yellow extracts were combined and dried over $MgSO_4$, and solvent was removed by simple distillation. GC/MS analysis of the resulting solid (2.2 mg) showed two products, **2a** (GC retention time = 12.81 min, MS M^+ (*m/e*) 485, 483, 481, 479) and the cyclized product *N*-(4-bromophenyl)-3,5-dibromocarbazole[28] (GC retention time = 11.59 min, MS M^+ (*m/e*) 483, 481, 479, 477). Integration of the ^1H NMR (in $CDCl_3$) of the isolated

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[1] For a general reference, see: Bauld, N. J.; Belville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A.; Reynolds, D. W.; Wirth, D. D.; Chiou, H.-S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, *20*, 371.

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photoproducts showed a 75% chemical yield of reduced starting material **2a** [δ 6.32 (d, 6 H, J = 6.5 Hz), 6.84 (d, 6 H, J = 6.6 Hz)] and 20% *N*-(4-bromophenyl)-3,5-dibromocarbazole (**3a**) [δ 7.60–6.40 (m, 10 H)].

Visible light irradiation was accomplished with an Oriel 1000 W Hg arc lamp (Model 6604) source. Unwanted IR and UV light was removed by a water filter and a Schott 450 nm long band pass filter, respectively.

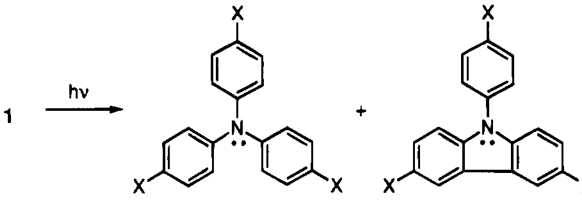
Photolysis of **1b** under identical conditions produced, after isolation of the photoproducts (2.6 mg), 69% **2b** (GC retention time = 15.07 min, MS M$^+$ (*m/e*) 335), ^{1}H NMR δ 6.29 (d, 6 H, J = 6.8 Hz), 6.38 (d, 6 H, J = 6.9 Hz), 3.73 (s, 9 H)) and 19% *N*-(4-methoxyphenyl)-3,5-dimethoxycarbazole (**3b**) (GC retention time = 14.10 min, MS M$^+$ (*m/e*) 333), ^{1}H NMR δ 7.60–6.40 (m, 10 H), 3.70 (s, 6 H), 3.68 (s, 3 H)).

Authentic samples of **3a** and **3b** were prepared by the method of Lamm and co-workers.[28] Coinjection of the authentic samples with the photolysis products produced a single eluting peak. Photoproducts **5** and **6** were identified by GC/MS and ^{1}H NMR spectroscopy.

Transient Absorption Spectroscopy. Time-resolved flash photolysis experiments were conducted on a Q-switched Nd:YAG laser (Continuum Surelite model 30A-P). Absorptive transients were monitored with a conventional 150 W Xe lamp, PTI monochromator, and Hamamatsu R928 photomultiplier arrangement. Signals were passed to a Tektronix model 540 digitizing oscilloscope interfaced to a personal computer.

Results and Discussion

UV photolysis of a deoxygenated **1a** solution was conducted in a sealed Pyrex tube with phosphor-coated low pressure mercury lamps blazed at 350 nm. This arrangement effectively prevents direct excitation of **2a** or any of the photobleached products. The photolysis was continued until 10% of the **1a** had been consumed, as monitored at its 716 nm visible absorption maximum. Analysis of the photolysis mixture shows that photoreduction and photocyclization are the primary photochemical processes, for GC/mass spectrometry reveals the reduced parent and a product with two fewer protons, eq 1, that coelutes with an authentic sample of the corresponding carbazole.



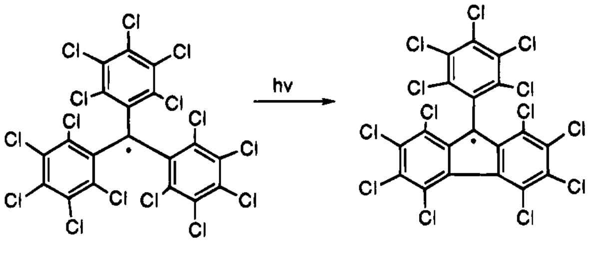
(1)

1a: X = Br **2a**: 75% **3a**: 20%

1b: X = OMe **2b**: 69% **3b**: 19%

Irradiation with visible light (>450 nm) also induces electrocyclic ring closure of the **1a** and **1b**. The quantum yields and chemical yields of products are invariant with the wavelength of exciting light. Because the D$_0$–D$_1$ transitions of **1a** (716 nm) and **1b** (726 nm) are found in this spectral region, this result suggests that photocyclization can occur through the lowest excited doublet state. It is unlikely that this photoinduced cyclization must occur through a high spin quartet since the quartet must lie at higher energy than the first excited doublet.[2] In sharp contrast, electrocyclic ring closures of the excited state of the closed shell neutral triarylamines take place from the high spin triplet states (and not a low spin excited singlets), as indicated by flash photolysis studies.[29] In particular, closed shell neutral **2a** and **2b** are known to photocyclize in their triplet excited states, although not all substituted triarylamines do so.[28] Strict precautions were taken to ensure complete removal of short wavelength UV light. In addition, photolysis of **2a**, under identical condtions of **1a**, did not produce **3a**. Therefore, we conclude that observed cyclization is an excited state process of the radical cation and not of its neutral precursor.

This type of electrocyclic ring closure is also well-documented for the lowest excited doublet state of isoelectronic diphenylmethyl radicals, both transient[30] and stable.[31] For example, we have previously shown that the thermally inert perchlorinated triphenylmethyl radical (**4**) undergoes 1,5 electrocyclic ring closure in the excited state, eq 2, and Meisel has implicated a parallel pathway in the excited of the parent trityl radical.[30] Fluorescence is also a competing deactivation pathway for the excited state of the perchlorotriphenylmethyl radical.[31] In substituted diphenylmethyl radicals, the propensity for excited state deactivation by ring closure is highly dependent upon steric crowding at the radical center.[30] In contrast to the observed photoreactivity in triphenylmethyl radicals, excited diphenylmethyl radicals relax primarily by fluorescence, and no competing photocyclization processes are observable.



(2)

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Accordingly, the photocyclization of triarylamine radical cations is not surprising, given its steric and electronic similarity with the closely related triarylmethyl radicals. Moreover, identical Woodward–Hoffmann selection rules for electrocyclic ring closure are expected for the triphenylmethyl radicals and their isoelectronic triarylamine radical cations.

The photocyclization of these excited radical cations is highly inefficient, with quantum yields of 0.00021 and 0.00013 being observed for **1a** and **1b**, respectively. These low quantum yields are presumably caused by rapid internal conversion of the lowest excited doublet states to the ground states in a process which is favored in these radical cations because of the low energy gap between the ground and lowest excited doublet states.[32] As mentioned above, these photocyclization quantum yields are excitation wavelength invariant. In contrast, stable **4**[31] and perchlorodiphenylmethyl[33] radicals exhibit wavelength-dependent photochemical ring closure efficiencies. It is interesting to speculate that the variation in quantum yields for **4** and perchlorodiphenylmethyl radicals may involve intersystem crossing to the quartet

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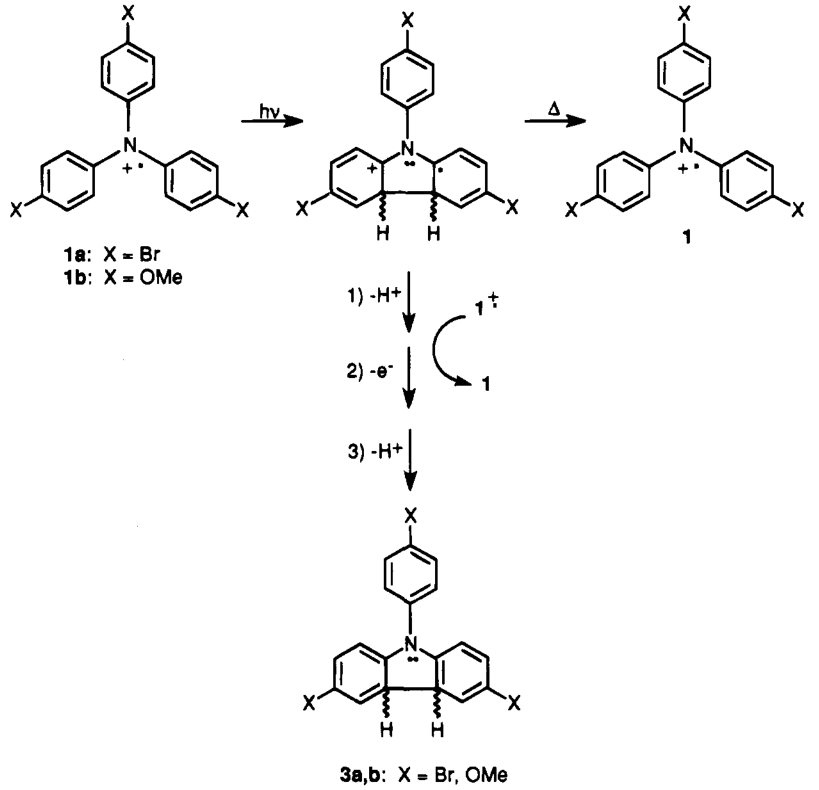
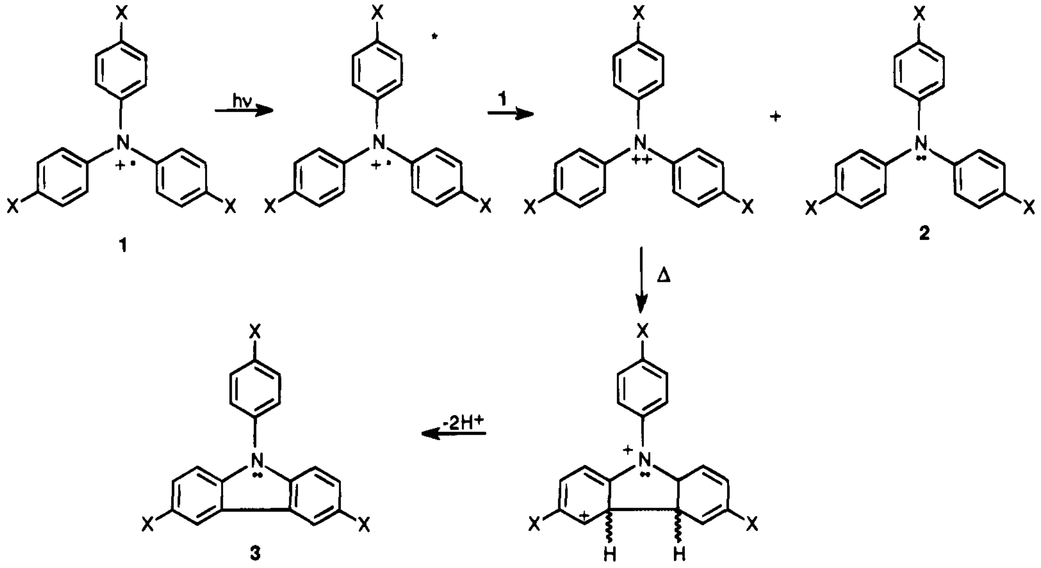
Scheme 1. Proposed Mechanism of the Pericyclic Photocyclization of Substituted Triarylamine Radical Cations in CH_2Cl_2 Solution



Scheme 2. Proposed Mechanism of the Photocyclization of Substituted Triarylamine Radical Cations by Photoinduced Electron Transfer



manifold upon excitation at shorter wavelengths. If so, **1a** and **1b** may not be able to access Q_1 from D_2 when excited by UV light (D_2 λ_{max} = 370 nm, 372 nm for **1a** and **1b**, respectively) either because Q_1 is of higher energy than D_2 or because intersystem crossing is slow relative to internal conversion to D_1.

Two distinctive mechanistic proposals for photoinduced ring closure of the triarylamine radical cations to carbazole products are possible. The first mechanism, Scheme 1, takes place by photoinduced cyclization of the excited triarylamine radical cation, followed by sequential deprotonation–oxidation–deprotonation steps. A concerted elimination of H_2 from the dihydrocarbazole radical cation is precluded because the hydrogen atoms presumably would be in an anti arrangement if the preferred disrotatory cyclization mode in the lowest excited state is followed.[15] After deprotonation, the dihydrocarbazolyl radical is likely oxidized to the cation by **1**, although traces of residual molecular oxygen may also contribute to the required oxidation.

An alternative mechanism takes place by photoinduced electron transfer. In this mechanism, Scheme 2, absorption of light drives a net disproportionation reaction. Estimates of the free energy for this photoinduced electron transfer from the Rehm–Weller equation[34] shows this reaction to be exergonic by 15 kcal mol^{-1} for

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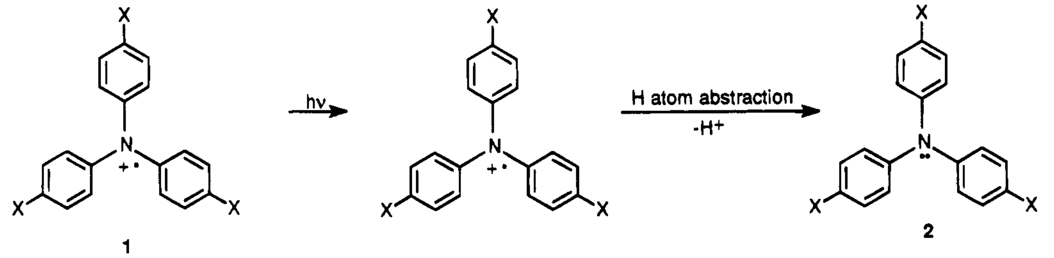
(34) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

Scheme 3. Photoreduction of Excited Triarylamine Radical Cations through Hydrogen Abstraction/Deprotonation

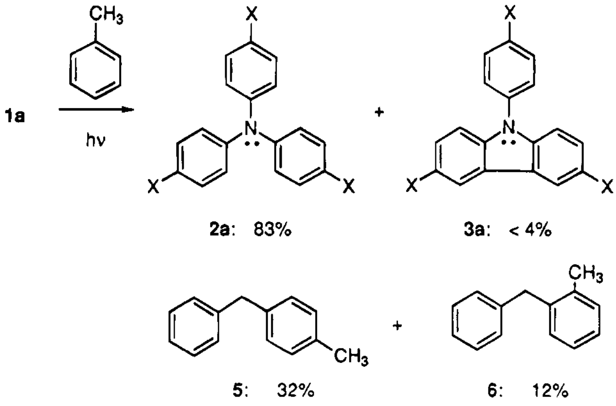


1a and by 20 kcal mol^{-1} for **1b**.[35] Thus, it is thermodynamically favorable for an excited state triarylamine radical cation to oxidize a ground state radical cation to a dicationic triarylamine species. The efficient thermal cyclizations of these triarylamine dications to the corresponding carbazole dications have been reported using electrochemical methods.[36]

Several attempts to further distinguish between these mechanisms of ring closure by laser flash photolysis measurements were unsuccessful. No transient species were observable, presumably because insufficient concentrations of transient species are produced, given the low quantum yields discussed above. Furthermore, it is impossible to distinguish the mechanisms in Schemes 1 and 2 by concentration dependence studies without independent knowledge of the absolute rate constants of the two rate-determining steps: both involve bimolecular trapping of a key transient by the ground state substrate. Nevertheless, this photocyclization is a rare example of a photochemical reaction that can be induced either by excitation of the neutral precursor with UV light or of the corresponding radical cation with visible light. The only other example of such a photochemical reaction in fluid solution is the tetraphenylhydrazine radical cation benzidine rearrangement reported by Svanholm and Parker.[37]

The reduced starting material is also a major product. Integration of the ^{1}H NMR spectrum of the photolysis mixture showed that the reduced starting material was recovered in 75% yield on the basis of the amount of the reacted **1a**, eq 1. As mentioned previously the photocyclized product accounts for 20% of the remaining consumed starting material. If photocyclization through the dication were the only photochemical process, a 1:1 ratio of reduced aminium to cyclized carbazole product would be expected, eq 1. Because a higher yield of neutral amine is isolated, a second pathway must be available for the direct reduction of the excited radical cation. Reduction of **1a** or **1b** during workup and isolation of photoproducts is conceivable, but when **1a** or **1b** is subjected to the product isolation conditions, no reduced or cyclized products are observed. We are unable to determine the species oxidized concomitantly with the observed reduction to **2a** (or **2b**), although a likely candidate is the solvent, probably via hydrogen atom abstraction, followed by deprotonation, Scheme 3.

It is well established that excited radicals are better hydrogen atom abstractors in the excited state than in the ground state.[38] The importance of excited state hydrogen atom abstraction by **1a** was probed by introducing an additional hydrogen atom source to the photolysis solution. Excellent hydrogen atom donors such as tributyltin hydride or triphenylmethane cannot be used because of an efficient competing thermal reaction: **1a** is instantly reduced when mixing together solutions of the hydrogen atom donor and **1a**. Toluene, a better hydrogen atom source than CH_2Cl_2, is thermally unreactive with **1a** for periods greater than 1 day as monitored by visible absorption spectroscopy. The photodecomposition efficiency of **1a** in CH_2Cl_2 is increased approximately 4-fold upon the addition of 1 M toluene: the product ratio of uncyclized-to-cyclized products in the photolysis of **1a** in CH_2Cl_2 is 3.75, eq 1, whereas this ratio is raised to >20 in the presence of 1 M toluene, eq 3. The benzyl radical produced by photoinitiated hydrogen atom transfer from toluene is oxidized further to the benzyl cation by **1a** (benzyl radical $E_{1/2}^{ox}$ = 0.73 V,[39] **1a** $E_{1/2}^{ox}$ = 1.05 V vs SCE[36]). The benzyl cation is ultimately trapped by toluene to give *p*-benzyltoluene (**5**) and *o*-benzyltoluene (**6**) in a combined 44% isolated yield. Thus, hydrogen atom abstraction by excited **1a** from toluene ultimately produces **2a**. The excited doublet states of **1a** and **1b** are deactivated by two possible photochemical routes and by two possible photophysical pathways (fluorescence and nonradiative decay).



(3)

Conclusions

Photochemical electrocyclization of **2a** and **2b**, previously reported to take place upon ultraviolet excitation of the neutral species, also takes place upon visible excitation of the corresponding radical cations. The quantum yields of ring closure are considerably lower for

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[35] Calculated from the oxidation potentials for the triarylamines (radical cation and dication) reported in ref 36 and the 0,0 transition energies of the radical cations given in ref 32.

[36] Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1087.

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the radical cations than those of the neutral parents. The lack of photocyclization efficiency presumably derives from competing internal conversion shortening the lowest excited doublet state lifetime. Two ring cyclization mechanisms (proceeding through the excited cation radical or through the dication produced by photoinduced electron transfer) are plausible, although the observed stoichiometry does not correlate quantitatively with either route. The excited states of these triarylamine radical cations are reactive toward hydrogen atom donors, as evidenced by the high yield of reduced starting material also isolated.

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