diiodide. We are currently examining other carbohydrate precursors and the accompanying stereochemical consequences of this reaction and will report these studies in due course.

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Intramolecular Photochemical Addition Reactions of ω-Styrylaminoalkanes

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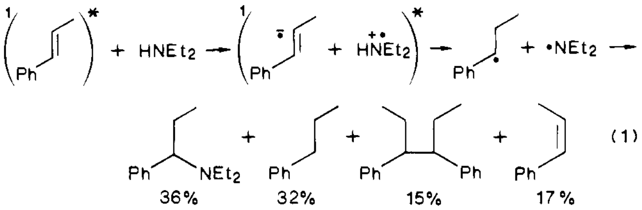
Intramolecular arene–olefin and enone–olefin photochemical cycloaddition reactions have attracted considerable interest as methods for the construction of strained polycyclic natural and unnatural products.[1] Intramolecular arene–amine and enone–amine photochemical addition reactions provide potential routes to nitrogen-containing heterocycles; however, these reactions have received relatively little attention. The intramolecular addition reactions of several secondary phenanthrylalkylamines have been reported by Sugimoto et al.,[2] and Aoyama and co-workers[3] have investigated the reactions of several tertiary styrylalkylamines, amides, and ureas. Recently Xu et al.[4] have reported the cyclization reactions of some α-silyl amine–α,β-unsaturated ketone and ester systems. To date, such reactions have been limited to the formation of five- and, less often, six-membered rings. However, since intramolecular exciplex formation has been observed for ω-aryl-α-(dimethylamino)alkanes with as few as 1 and as many as 11 methylene groups separating the chromophores,[5] it occurred to us that intramolecular arene–amine photochemical addition might provide a route to cyclized products with a wide range of ring size. We report here our preliminary results for a series of *N*-methyl-ω-(β-styryl)aminoalkanes, which serve to establish the versatility of the intramolecular styrene–amine cyclization reaction.

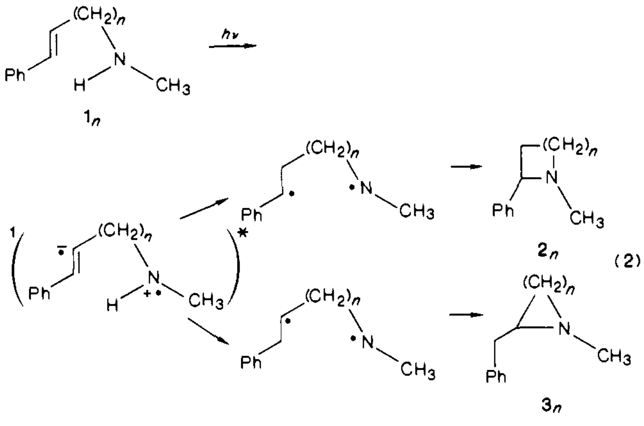
The intermolecular photochemical addition of amines to styrenes was initially reported by Cookson et al.[6] We find that the fluorescent singlet state of *trans*-1-phenylpropene (τ = 7.5 ns, Φ_f = 0.34) is quenched by diethylamine with a rate constant of 1.2×10^{10} M^{-1} s^{-1},[7,8] near the rate of diffusion in cyclohexane solution. Singlet quenching results in the formation of a single adduct, 1-phenylpropane, and the dimer of the 1-phenylpropyl radical (mixture of diastereomers, eq 1).[9] As was previously observed



(1)

for the reactions of singlet *trans*-stilbene and 9-cyanophenanthrene with secondary amines,[10] addition occurs in both polar and nonpolar solvents. While no exciplex fluorescence is observed, it appears likely that radical pair formation occurs via a charge-transfer-stabilized exciplex (eq 1).

The photophysical and photochemical behavior of a series of ω-(β-styryl)-α-(methylamino)alkanes (**1**$_n$, where n = 1–5) is summarized in Table I. Singlet lifetimes and fluorescence quantum yields are all smaller than the values for 1-phenylpropene, indicative of the occurrence of intramolecular quenching of the styrene singlet by the secondary amino group. No exciplex emission is observed for secondary or primary styryl amines; however, the tertiary analogues of **1**$_2$–**1**$_4$ display strong exciplex fluorescence.[11] Upon irradiation in dilute solution the styryl amines undergo trans,cis isomerization and intramolecular addition to yield mixtures of α-phenyl- (**2**) and α-benzylcycloalkylamines (**3**) (eq 2).[9] The ratios of adducts **2**/**3** and total adduct/isomerization obtained at moderate conversions (<30%) in acetonitrile solution are reported in Table I. At higher conversions, adducts account for >80% of consumed starting material for **1**$_2$–**1**$_4$, 50% for **1**$_5$, and 15% for **1**$_1$. Quantum yields for total adduct (**2** + **3**) formation from **1**$_2$, **1**$_3$, and *cis*-**1**$_3$ are 0.034, 0.11, and 0.19, respectively, and are lower for the other styryl amines. The total adduct yield is not strongly dependent upon solvent polarity; however, the adduct ratio is strongly solvent dependent. Values of **2**/**3** in cyclohexane solution for **1**$_2$, **1**$_3$, and **1**$_4$ are reported in Table I.



(2)

By analogy to the mechanism of intermolecular styrene–amine addition (eq 1), electronic excitation of the styryl amines **1**$_n$ is proposed to yield a locally excited singlet styrene that reacts with the amino group to form an intramolecular exciplex. The chain-length dependence of the singlet lifetime (Table I) for n = 3 < 2 < 4 < 5 reflects the tendency to form an exciplex, as

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Table I. Photophysical and Photochemical Behavior of Styryl Amines

amine	τ_s,[a] ns	Φ_f[b]	**2**/**3**[c]	(**2** + **3**)/isom[d]	yield,[e] %
trans-*N*-methyl-3-phenyl-2-propen-1-amine ($\mathbf{1}_1$)	<0.1	<0.005	>20	0.1	15
trans-*N*-methyl-4-phenyl-3-buten-1-amine ($\mathbf{1}_2$)	0.73	0.046	14 (3.0)	>10	63
trans-*N*-methyl-5-phenyl-4-penten-1-amine ($\mathbf{1}_3$)	0.51	0.021	2.4 (1.0)	3.0	57
trans-*N*-methyl-6-phenyl-5-hexen-1-amine ($\mathbf{1}_4$)	1.6	0.070	0.15 (0.8)	>10	82
trans-*N*-methyl-7-phenyl-6-hepten-1-amine ($\mathbf{1}_5$)		0.13	>8	1.0	30
cis-*N*-methyl-5-phenyl-4-penten-1-amine	0.35	0.015	2.4	>10	62
trans-5-phenyl-4-penten-1-amine	3.7	0.19	1.5	0.4	

[a] Fluorescence lifetime of 6×10^{-5} M styryl amine in nitrogen-purged cyclohexane solution at 300 K. Samples were excited at 308 nm with the frequency-doubled output of a synchronously pumped mode-locked dye laser, and fluorescence was selected with a prism monochromator and analyzed by means of a standard single-photon-timing apparatus using multiexponential least-squares fitting. The short-lived monomer emission accounted for >96% of the total fluorescence in all cases. [b] Fluorescence quantum yield determined under conditions of footnote *a* relative to styrene ($\Phi_f = 0.24^{8a}$). [c] Ratio of cyclic adducts from 0.005–0.01 M styryl amine in nitrogen-purged acetonitrile solution. Values in parentheses are for cyclohexane solution. [d] Ratio of total adduct to isomerization. [e] Yield of the major adduct (**2** or **3**) determined by GC analysis at moderate to high conversion (>50%).

previously observed for fluorescent arene–tertiary amine intramolecular exciplexes.[5,11] Adduct formation quantum yields are largest for the styryl amines that form the most stable intramolecular exciplexes. The similar values of k_f for $\mathbf{1}_2$–$\mathbf{1}_5$ and 1-phenylpropene ($k_f = \Phi\tau_s \sim (5 \pm 1) \times 10^7\ \mathrm{s}^{-1}$) indicate that there is no significant ground-state interaction between the chromophores except in the case of the nonfluorescent allylamine $\mathbf{1}_1$.[12] It is interesting to note that the photophysical properties of *cis*- and *trans*-$\mathbf{1}_3$ are similar, while those of the primary amine analogues of $\mathbf{1}_3$ are more like those of 1-phenylpropene, indicative of inefficient intramolecular singlet quenching by the primary amino group. Primary amines are known to be much poorer electron-transfer quenchers than secondary or tertiary amines as a consequence of their higher ionization potentials.[10]

Following exciplex formation, transfer of the N–H hydrogen to the styrene β- or α-carbon yields the singlet biradical precursors of **2** and **3**, respectively (eq 2). The absence of intersystem crossing in the locally excited styrene or singlet exciplex is indicated by the nearly complete intramolecular quenching of styrene trans,cis isomerization in $\mathbf{1}_2$ and $\mathbf{1}_3$ and the ability of a triplet sensitizer (Michler's ketone) to affect trans,cis isomerization but not cyclization of *trans*- or *cis*-$\mathbf{1}_3$. Evidence for the singlet multiplicity of the biradical intermediate is provided by the stereospecific formation of the syn adduct $\mathbf{2}_3$-*d*, from $\mathbf{1}_3$-*N*-*d*, and the absence of D–H exchange of the vinyl hydrogens in recovered $\mathbf{1}_3$.[13] While cage escape accounts for over half of the 1-phenylpropyl radicals formed in the intramolecular reaction (eq 1), the biradicals formed in the intramolecular reaction either cyclize or revert to starting material, resulting in improved preparative yields for the intra- vs intermolecular reaction.

An intriguing feature of the intramolecular styrene–amine addition reaction is the formation of α-benzyl amines (**3**) as the major product from $\mathbf{1}_4$ and as a minor product from some of the other styryl amines. On the basis of biradical stabilities (eq 2) and the regioselectivity of the intramolecular reaction (eq 1), we had anticipated the regioselective formation of the α-phenyl amines (**2**). Among the factors that may influence the regioselectivity of intramolecular addition are (a) the conformational energy of the polymethylene chain, (b) N–H···C hydrogen bond formation in the exciplex,[14] (c) biradical stabilities, and (d) partitioning of the biradical intermediate between product and reactants. The increase in cyclization regioselectivity with increasing solvent polarity (Table I) indicates that solvation of the exciplex may also be an important factor. In the case of $\mathbf{1}_3$ the **2**/**3** ratio is also temperature dependent, decreasing from 2.4 at 30 °C to 6.2 at −40 °C in acetonitrile solution. Thus cycloaddition regioselectivity can be controlled by the appropriate choice of solvent and temperature. As noted by Aoyama et al.,[3b] hydrogen transfer in styryl amines is not limited to five- and six-membered transition states but has now been observed for four- to eight-membered transition states. In reactions such as these, where intramolecular exciplex formation precedes hydrogen transfer, extension to even larger ring sizes is limited only by the requirement that intramolecular exciplex formation compete with decay of the styrene singlet.

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3-Oxaplatinacyclobutanes. Synthesis and Intramolecular Cyclization of the First Bis(hydroxymethyl) Transition-Metal Complex

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The relevance of metallacyclic transition-metal complexes to organic synthesis is well documented.[2,3] While most investigations have focused on all-carbon metallacycles, recently effort has been directed toward metallacycles substituted with synthetically interesting heteroatoms such as oxygen and nitrogen. In these cases, involving early[3b,4] and late[5] transition metals, the heteroatom is invariably bonded directly to the metal. In contrast, metallacyclic complexes substituted with oxygen or nitrogen on ring positions away from the metal center have not been investigated, despite the potential for using such systems in organic heterocycle syn-

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