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Arene–Iminium Salt Electron-Transfer Photochemistry. Mechanistically Interesting Photoaddition Processes

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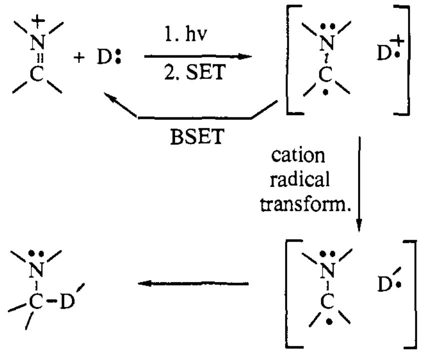
Abstract: Studies of the electron-transfer photochemistry of arene–iminium salt systems have been explored. Fluorescence quenching investigations have demonstrated that a series of arenes including substituted toluenes and benzenes quench the fluorescence of a variety of 2-aryl-1-pyrrolinium perchlorates. Quenching rate constants in these cases correlate with the ΔG_{SET} values as expected for quenching by reversible electron-transfer pathways. In addition, nonconjugated iminium salts quench the fluorescence of a host of arenes with k_q values which parallel those predicted on the basis of electron-transfer free energy calculations. Photoaddition reactions of toluene, benzyltrimethylsilane, benzyltrimethylstannane, and 2-aryl-1-pyrrolinium salts have been explored. Likewise, electron-transfer-induced, excited-state reactions of toluene and benzyltrimethylsilane with 1,2-dimethyl-1-pyrrolinium perchlorate have been investigated. The results of these photoreactions have been interpreted in terms of steric, electrofugal group, and solvent effects upon the rates of competitive pathways available to initially formed radical cation pair intermediates. Finally, the photochemistry of benzyltrimethylstannane is described.

Through previous, extensive investigations we have been able to demonstrate that the photochemistry of iminium salt systems is dominated by processes initiated by single electron transfer from a variety of neutral donors to excited states of systems containing conjugated $R_2N^+{=}CR_2$ chromophores.[1] The results of these studies have pointed out the utility of reactions promoted by electron transfer between alkene π-donors and iminium salts in sequences targeted at the construction of interesting N-heterocyclic and carbocyclic ring systems, some of which are found as key structural units in natural product systems.[2] These efforts have also provided examples which show how photoinitiated electron-transfer routes can be used to probe structural and electronic features of interesting cation radical species[3] and in the regiocontrolled generation of novel radical and diradical intermediates.[4,5]

More recent studies in our laboratories have focused on the photochemistry of arene–iminium salt systems in which the aromatic π-donors contain hydrogen, trialkylsilyl, or trialkylstannyl substituents at benzylic positions. Communications have appeared in which our preliminary observations related to mechanistic[6] and synthetic[7] aspects of these photochemical processes are summarized. In this paper, the complete details of exploratory and mechanistic investigations of photoaddition reactions occurring via photoinitiated electron-transfer pathways in arene–iminium salt systems are described.

The general strategy we have employed in developing new reactions and in enhancing reaction efficiencies for donor–iminium salt photochemical processes, promoted by excited-state electron transfer, is embodied in the simplified mechanistic sequence depicted in Scheme I. Our premise has been that donor systems can be designed such that the derived cation radical species can undergo fast secondary reactions which effectively compete with energy-wasting back electron transfer (BSET) and other reaction modes (e.g., radical coupling) and which generate neutral radical precursors of products. This would result in the potential for high chemical and quantum efficiencies for excited-state reactions following these pathways. In addition, the scope of these excited-state reactions would be broadened if the capability existed for their initiation by excitation of either the donor or iminium salt acceptor groupings or through photosensitization by an electron acceptor or donor sensitizer.[8] Accordingly, with the correct combination of electrochemical potentials and excited-state energies, similar radical cation pair or diradical cation intermediates could be produced in thermodynamically driven electron-transfer processes[9] for either excited donor–ground-state iminium salt or ground-state donor–excited iminium salt systems. Thus, the flexibility would exist for having extended conjugation needed for light absorption in either one of the electron-transfer partners.

Scheme I



Exploratory studies have been conducted to probe these features of electron-transfer-promoted photoreactions of iminium salts. These efforts have focused on the photoaddition (the current studies) and photocyclization (following paper) processes of arene–iminium salt systems stimulated by excitation of either component. In addition, we have examined how the chemoselectivity of these processes is governed by the nature of reaction

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[1] (a) Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130. (b) Mariano, P. S. *Tetrahedron Suppl.* **1983**, *12*, 3845. (c) Mariano, P. S. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed; Plenum: London, 1984.

[2] (a) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136. Stavinoha, J. L.; Mariano, P. S.; Leone-Bay, A.; Swanson, R.; Bracken, C. *J. Am. Chem. Soc.* **1981**, *103*, 3148. (b) Tiner-Harding, T.; Ullrich, J. W.; Chiu, F. T.; Chen, S. F.; Mariano, P. S. *J. org. Chem.* **1982**, *47*, 3360. Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228. (c) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1985**, *50*, 5667.

[3] Somekawa, K.; Haddaway, K.; Mariano, P. S.; Tossell, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3060.

[4] (a) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C., Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6855. (b) Chen, S. F.; Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1983**, *105*, 6160.

[5] Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.

[6] Lan, A.; Quillen, S. L.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6439.

[7] Ho, G. D.; Lan, A. Y.; Mariano, P. S. *Tetrahedron Lett.* **1985**, 5867.

[8] In theory, electron transfer to or from an electronically excited, neutral photosensitizer from or to respective donor or iminium salt functions followed by secondary electron transfer could result in generation of the same types of radical ion intermediates as are generated in the direct electron-transfer process (eq i and ii below). Of course, the spacial relationships between the α-amino and donor cation radicals (i.e., contact, solvent sparated, or free) could very well depend upon the method used for ion radical generation.

$$[\mathrm{Sens}]^* + R_2N^+{=}CR_2 \xrightarrow{\mathrm{SET}} R_2\ddot{N}{-}\dot{C}R_2 + \mathrm{Sens}^{\cdot+} \xrightarrow{\mathrm{D}} \mathrm{Sens} + \mathrm{D}^{\cdot+} \qquad \text{(i)}$$

$$[\mathrm{Sens}]^* + \mathrm{D}{:} \xrightarrow{\mathrm{SET}} \mathrm{D}^{\cdot+} + \mathrm{Sens}^{\cdot-} \xrightarrow[R_2\overset{+}{N}{=}CR_2]{} \mathrm{Sens} + R_2\ddot{N}{-}\dot{C}R_2 \qquad \text{(ii)}$$

[9] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

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Table I. Arene Quenching of 2-Phenyl-1-pyrrolinium Perchlorate (**1**) Fluorescence

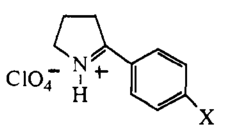
arene quencher	arene $E^{\mathrm{S}}_{1/2}(+)$,[a] V vs. SCE	calcd $\Delta G°_{\mathrm{SET}}$,[b] kcal/mol	$k_q \times 10^{-9}$,[c] $M^{-1}\cdot s^{-1}$
p-$MeOC_6H_4Me$	+1.24	−40	7.81
p-MeC_6H_4Me	+1.71	−29	5.93
p-BrC_6H_4Me	+1.71	−29	5.50
p-ClC_6H_4Me	+1.88	−26	4.75
p-FC_6H_4Me	+1.97	−23	4.44
p-$CF_3C_6H_4Me$	+2.33	−14	1.08
C_6H_5Me	+1.88	−26	4.88
$C_6H_5CH_2SiMe_3$	+1.78	−27	6.80
$C_6H_5CH_2SnMe3$			9.30
$C_6H_5OCH_3$	+1.56	−33	6.63
C_6H_5Cl	+2.25	−17	6.56
C_6H_6	+2.33	−15	3.84
$C_6H_5CF_3$	+2.77	−5	0.69

[a] Oxidation potentials are calculated from known ionization potentials (ref 12) by the method of Miller (ref 13). [b] Calculated by use of the Rehm–Weller method (ref 9) based upon the known singlet energy and reduction potential of 2-phenyl-1-pyrrolinium perchlorate (ref 2a). [c] Measured in MeCN (nondegassed at 25 °C).

pathways available to the arene cation radical intermediates. We expected that the presence and nature of electrofugal groups at benzylic positions of the arene donors would significantly influence this selectivity. Thus, arene cation radicals can be transformed to benzylic radicals by loss of electrofugal groups (H, SiR_3, or SnR_3) from this position[10] or to cationic adducts via coupling to α-amino radicals arising by one-electron reduction of the iminium salts (Scheme II). The operation of electron-transfer pathways, initiated by irradiation of either the arene or iminium salt chromophores, has been tested initially through investigations of fluorescence quenching. This has been followed by an exploration of photoaddition reactions. Product distributions suggest that the chemical selectivities of these processes are dependent upon the nature of benzylic, electrofugal groups in the arene donors. The results of these efforts are detailed below and discussed within the context of reaction mechanisms.

Results

Fluorescence Quenching Studies. Preliminary information about the potential for the operation of electron-transfer pathways in the excited-state chemistry of arene–iminium salt systems has derived from fluorescence quenching studies. The efficiency of electron transfer from arene donors to singlet excited states of iminium salts should be reflected in the rate constants for fluorescence quenching. The fluorescing 2-aryl-1-pyrrolinium perchlorates **1**–**4**, prepared by in situ (MeCN) protonation of the known 1-pyrrolines[2a,11] with 70% aqueous $HClO_4$, were selected for these investigations. Reduction potentials and singlet energies of these substances (Table II) were determined by standard techniques (Experimental Section) or, in the case of **1**, are known.[2a]

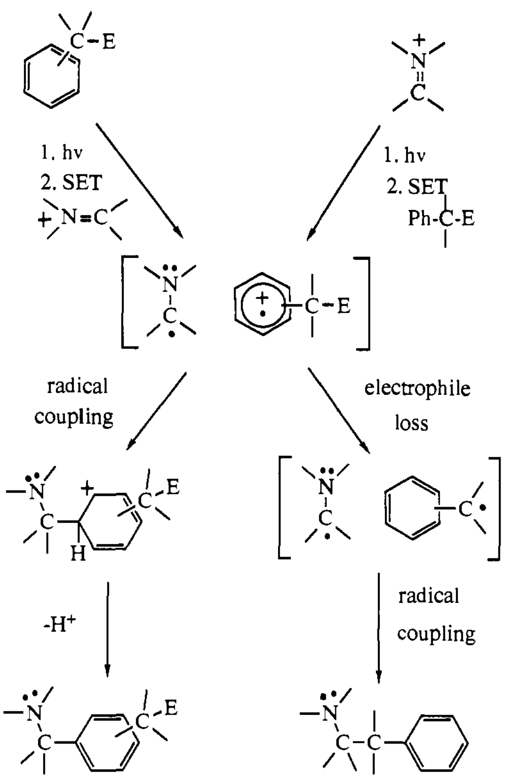


1 (X=H) **3** (X=Cl)

2 (X=CF_3) **4** (X=OCH_3)

The arene quenchers constitute a series of commercially available substituted toluenes and benzenes with known ionization potentials from which the oxidation potentials recorded in Table I were obtained by use of the relationship suggested by Miller.[13]

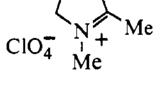
Scheme II



Fluorescence quenching constants (Table II) ($k_q\tau$) were determined by use of the familiar Stern–Volmer analytical technique. In the case of 2-phenyl-1-pyrrolinium perchlorate (**1**), the quenching constants were converted to rate constants for fluorescence quenching (k_q) (Table I) since the singlet lifetime of this substance in MeCN has been accurately measured.[2a] Finally, the wavelengths used for excitation of the 2-arylpyrrolinium salts were sufficiently long (300–310) nm) to ensure that the arene quenchers are not competitively absorbing light.

The k_q values for arene quenching of the fluorescence of **1** clearly support the operation of electron-transfer pathways in the singlet manifold. Indeed, the lower singlet-state energies of the pyrrolinium salts **1**–**4** compared to those of the toluenes and benzenes rule out exchange energy transfer as a mechanism for fluorescence quenching. Moreover, the quenching rate constants correlate well with the estimated[9] free energies for electron transfer (ΔG_{SET}). Thus, as expected for electron-transfer processes, rates of fluorescence quenching and the quenching constants are dependent upon the electron-donating ability of the arenes.

In order to determine if electron transfer occurs between singlet excited states of arene donors and ground states of nonconjugated iminium salts, fluorescence studies were conducted with the quenchers, 1,2-dimethyl-1-pyrrolinium perchlorate (**5**) and N-isopropylidenepyrrolidinium perchlorate (**6**). A series of fluor-



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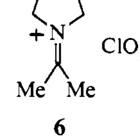

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escing arenes covering a range of ground-state oxidation potentials

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(10) (a) The electron-transfer photochemistry of benzylstannane has been probed in detail by Eaton:[10b] (b) Eaton, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 7235.

(11) Mariano, P. S.; Leone-Bay, A. *Tetrahedron Lett.* **1980**, 4581.

(12) Turner, D. W.; Baker, A. D.; May, D. P. *J. Chem. Soc. B* **1968**, 22. Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2563. Pitt, C.; Bock, H. *J. Chem. Soc., Chem. Commun.* **1972**, 28.

(13) Miller, L.; Nordblom, G.; Mayeda, E. *J. Org. Chem.* **1972**, *37*, 916.

(14) (a) The singlet lifetimes of **2**, **3**, and **4** are estimated to be 10, 14, and 0.4 ns, respectively, based upon absorption spectroscopic data determined by the method outlined in ref 14b. (b) Turro, N. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, CA, 1978, p 88.

(15) Marcondes, M. E.; Toscano, V. G.; Weiss, R. G. *J. Photochem.* **1979**, *10*, 425. Marcondes, M. E.; Toscano, V. G.; Weiss, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 4485.

(16) The singlet energies of 2-methoxynaphthalene and naphthalene are reported in ref 9.

(17) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(18) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535.

Table II. Arene Quenching of 2-Aryl-1-pyrrolinium Perchlorate **1–4** Fluorescence

arylpyrrolinium perchlorate[a]			$k_q\tau$,[d] M^{-1}					
compd	$E^{S_1}_{0,0}$,[b] kcal/mol	$E^{S_0}_{1/2}(-)$,[c] V vs. SCE	p-MeC_6H_4OMe	p-MeC_6H_4Me	p-MeC_6H_4Br	p-MeC_6H_4Cl	C_6H_5Me	p-MeC_6H_4F
1	90.3	−0.93	125	95	88	76	78	71
2	90.3	−0.73	106	92	95	78	70	63
3	91.7	−0.88	8.3	5.6	4.5	4.1	4.0	3.4
4	84.1	−1.08	0.98	0.88	0.68	0.43	0.41	0.38

[a] Salts were prepared in situ by addition of 70% $HClO_4$ to CH_3CN solutions of the corresponding pyrrolines. [b] Determined by intersection of fluorescence emission and excitation spectral curves. [c] Measured in 5% aqueous CH_3CN with $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte vs. SCE. [d] Measured in CH_3CN at 25 °C on nondegassed solutions by use of Stern–Volmer analyses.

Table III. Dimethylpyrrolinium **5** and Pyrrolidinium **6** Perchlorate Quenching of Arene Fluorescence

fluorescing arene		$k_q \times 10^{-9}$,[c,d] $M^{-1}\cdot s^{-1}$	
compd	$E^{S_1}_{1/2}(+)$,[a,b] V vs. Ag/Ag+	**5**	**6**
toluene	−2.62	2.56	
$PhCH_2SiMe_3$	−2.59	1.25	
2-methoxynaphthalene	−2.28	4.32	5.43
naphthalene	−2.34	0.73	1.07
1-cyanonaphthalene	−1.66		0.84

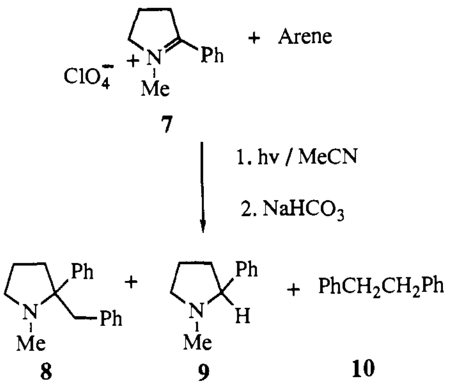
[a] Calculated based upon the knonw [toluene (ref 15), 2-methoxynaphthalene, and naphthalene (ref 16)] or determined singlet energies ($\Delta E^{S_1}_{0,0}$) and estimated [toluene, $PhCH_2SiMe_3$, and 1-cyanonaphthalene (ref 13)] or known [2-methoxynaphthalene and naphthalene (ref 16)] oxidation potentials ($E^{S_1}_{1/2}(+)$). The relationship is $E^{S_1}_{1/2}(+) = E^{S_0}_{1/2}(+) - \Delta E^{S_1}_{0,0}$. [b] The reduction potentials for **5** and **6** are −2.2 and −1.94 V (vs. SCE), respectively. [c] Measured at 25 °C in MeCN. [d] The singlet lifetimes used for determining k_q are either known [toluene (ref 17), naphthalene, 2-methoxynaphthalene (ref 16), and 1-cyanonaphthalene (ref 18)] or calculated [$PhCH_2SiMe_3$ (ref 14b)].

and excited singlet-state energies were used. These include toluene, benzyltrimethylsilane, 2-methoxynaphthalene, naphthalene, and 1-cyanonaphthalene. As can be seen by inspection of the results presented in Table III the quenching rate constants derived by Stern–Volmer analysis display a rough correlation with the singlet-state oxidation potentials ($E^{S_1}_{1/2}(+)$) of the arenes. The absence of a more precise correlation can be attributed to the varying sources for singlet lifetimes used to calculate k_q and for singlet energies and ground-state oxidation potentials employed to determine $E^{S_1}_{1/2}(+)$. In spite of this, these observations collectively indicate that singlet quenching in arene–iminium salt systems follows electron-transfer pathways.

Exploratory Photochemistry. The fluorescence quenching data summarized above suggest that photoinitiated electron transfer is possible between arene donor and iminium salt acceptor pairs. Thus, irradiation of these systems should serve as a method for generating radical cation pairs in pathways leading to the production of photoaddition products as outlined in Scheme II. Our study of these systems has confirmed this expectation and has provided useful information about factors controlling the chemical selectivities displayed in the reaction pathways followed.

Photoaddition Reactions Promoted by Excitation of the Iminium Salt Chromophore. In order to probe the excited-state reactivity of iminium salt systems promoted by excitation of the acceptor component, the photochemistry of 2-phenyl-1-pyrrolinium perchlorate (**1**) and its *N*-methyl analogue **7** was explored with toluene, benzyltrimethylsilane, and benzyltrimethylstannane as arene donors. Owing to the UV absorption characteristics of these donor acceptor pairs, it is possible to selectively excite the conjugated pyrrolinium salt chromophores by irradiation at wavelengths longer than 260 nm, which is provided in a preparative apparatus by Corex glass-filtered light. In addition, the arene concentrations can be adjusted on the basis of fluorescence quenching rate data to insure that >90% of the pyrrolinium salt singlet states are intercepted.

Scheme III



Arene	Percent Yield		
	8	**9**	**10**
$PhCH_3$	28	15	4
$PhCH_2SiMe_3$	37	18	10
$PhCH_2SnMe_3$	32	trace	1

Irradiation of an acetonitrile solution of the *N*-methyl perchlorate salt **7** containing toluene, followed by basic workup of the photolysate and chromatographic separation, provided the photoaddition product, 1-methyl-2-phenyl-2-benzylpyrrolidine (**8**; 28%), along with 1-methyl-2-phenylpyrrolidine (**9**; 15%) and bibenzyl (**10**; 4%) (Scheme III). The structure of the photoreduction product **9** was confirmed by its independent synthesis through $NaBH_4$ reduction of the pyrrolinium salt **7**.[19] Identification of the major photoadduct **8** was based firmly upon the spectroscopic evidence provided in the Experimental Section. Finally, similar products (but in different relative yields) were produced when acetonitrile solutions of **7** containing either benzyltrimethylsilane or benzyltrimethylstannane were irradiated (Scheme III).

The nature of products obtained from irradiation of the *N*-methylpyrrolinium salt **7** and arene systems changes when methanol is employed as solvent. Thus, while similar addition and reduction products (e.g., **8–10**) were produced in reactions of **7** in methanol with benzyltrimethylsilane and the corresponding tin compound, only trace quantities of the benzylpyrrolidine **8** and no bibenzyl were formed when **7** was irradiated in methanol solutions containing toluene (Scheme IV). In the latter case, the major photoproducts were the known[20] hydroxymethylpyrrolidine **11** and pyrrolidine **9**. Interestingly, a mixture of ortho and para arylation products **12** and **13** was also formed in low yields (5%) and in a 2:1 ratio[21] in the photoreaction of **7** with toluene in methanol. It is important to note that **12** and **13** or related substances could not be detected in reaction mixtures arising from photoreaction of the pyrrolinium salt **7** with toluene in acetonitrile or with benzyltrimethylsilane or -stannane in either acetonitrile or methanol.[22]

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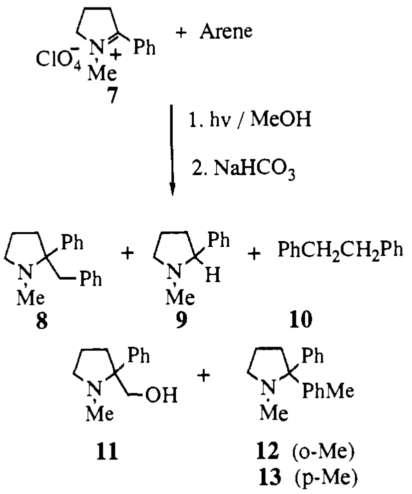
(19) Burckhalter, J. H.; Short, J. H. *J. Org. Chem.* **1958**, *23*, 1281. Craig, L. *J. Am. Chem. Soc.* **1933**, *55*, 2543.

(20) Mariano, P. S.; Stavinoha, J. L.; Bay, E. *Tetrahedron* **1981**, *37*, 3385.

(21) Separations to obtain pure samples of the para adduct **13** were unsuccessful.

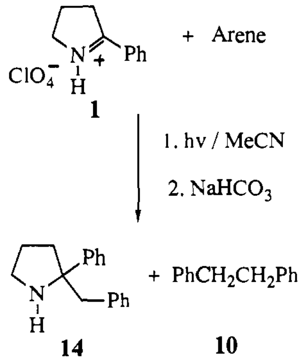
(22) The yields of products reported in the preliminary communication (ref 6) were found to be in error.

Scheme IV



Arene	Percent Yield 8	9	10	11	12+13
$PhCH_3$	1	6	--	14	5 (2:1)
$PhCH_2SiMe_3$	20	17	10	--	------
$PhCH_2SnMe_3$	28	trace	1	--	------

Scheme V

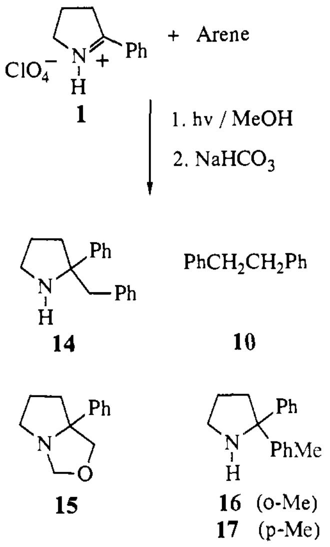


Arene	Percent Yield 14	10
$PhCH_3$	21	trace
$PhCH_2SiMe_3$	49	16
$PhCH_2SnMe_3$	48	18

The structural and regiochemical assignments for the ortho and para arylation products **12** and **13** were based upon spectroscopic data. The difficulty in obtaining pure samples of **13** uncontaminated with its regioisomer **12** limited the amount of data which could be accumulated for this substance. Both the ^{1}H NMR and ^{13}C NMR spectra of **12** and **13** contain resonances characteristic of both mono- and disubstituted aromatic rings and benzylic methyl groups. Infrared spectra, discussed below, provided data needed to make regiochemical assignments to the methyl-substituted aromatic moieties in these isomers.

The product distributions in photoreactions of **7** are mimicked by the corresponding N–H pyrrolinium salt **1**. Accordingly, irradiation of acetonitrile solutions of **1** containing the arenes shown in Scheme V, after workup and separation, gave the benzyl adduct **14** and bibenzyl. These reactions are generally cleaner than those occurring with the *N*-methyl analogue and proceed in higher yields. It should be noted that the photoreduction product, 2-phenylpyrrolidine, could be detected in trace quantities by GLC analysis of the photolysates but was not isolated in the chromatographic separation procedure.

Scheme VI

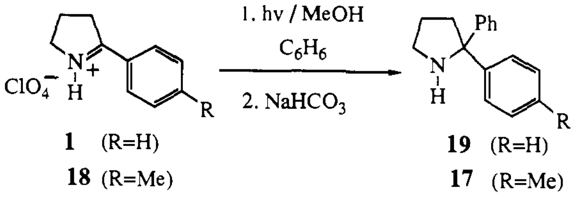


Arene	Product Yield 14	10	15	16+17
$PhCH_3$	trace	--	trace	6(3:1)
$PhCH_2SiMe_3$	67	12	--	--
$PhCH_2SnMe_3$	63	18	--	--

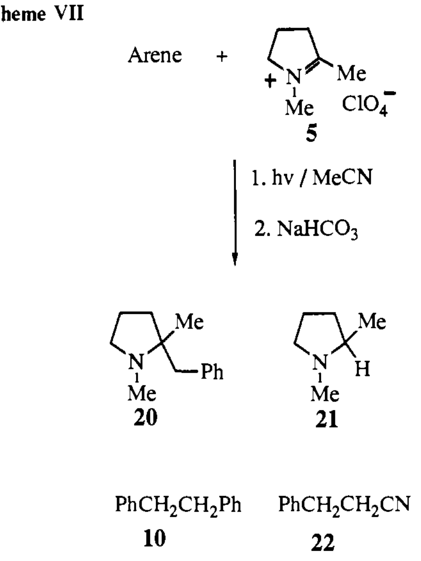
As in the case of the *N*-methyl salt, divergent behavior was displayed in photoreactions of **1** with the arenes conducted in methanol. While the yields of adduct **14** are high in the case of the benzyltrimethylsilane and -stannane, only trace quantities of this substance are generated when toluene is the arene substrate (Scheme VI).[22] In the toluene reaction, the ortho and para arylation products **16** and **17** are formed in a 3:1 ratio along with trace quantities of **14** and the known[20] oxazolidine 15.

Spectroscopic data again serve as the basis for the assignments of structures to the arylation products **16** and **17**. Infrared spectral measurements at resolutions provided by an FT instrument provided useful information needed to assess aryl ring substitution regiochemistry in **16** and **17** as well as in the related *N*-methyl analogues **12** and **13**. Analysis focused on the 600–900-cm^{-1} region where bands associated with out-of-plane aryl ring C–H bending vibrations occur. All four substances exhibit bands at ca. 750 and 700 cm^{-1}, characteristic of the mono-substituted benzene ring in each. However, the adducts **12** and **16** possess additional bands at 786 cm^{-1} typical of ortho-disubstituted benzenes while the para adduct **17** shows an additional band at 816 cm^{-1} for the 1,4-disubstituted benzene moiety. Importantly, the absence of a set of four bands (two for a monosubstituted and two for meta disubstituted benzene rings between 810–750 and 725–680 cm^{-1}) in the aromatic C–H bending region of the infrared suggests that none of these adducts have the meta regiochemistry.

In an effort to provide further examples of this novel photoarylation process, and to develop an independent synthesis of one of these adducts (i.e., **17**), photoaddition reactions of benzene, 2-phenyl-1-pyrrolinium perchlorate (**1**), and its *p*-methyl analogue **18** were explored. Prolonged irradiation of **1** in methanol solutions



Scheme VII



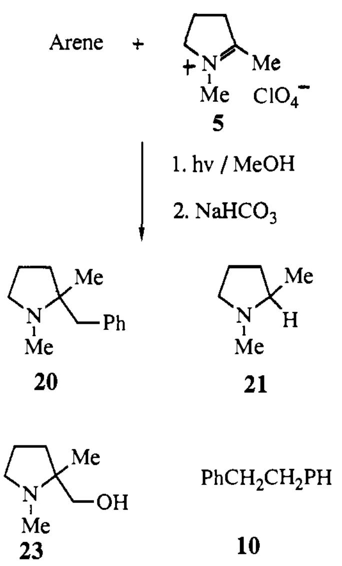
Arene	Product Yield			
	20	21	10	22
PhCH$_3$	--	7	4	trace
PhCH$_2$SiMe$_3$	23	--	13	--

containing benzene resulted in low-yielding production of 2,2-diphenylpyrrolidine (**19**), a substance previously described in the literature.[23] In an analogous fashion, photoaddition of benzene to the *p*-tolylpyrrolinium perchlorate **18** in methanol gave the adduct **17** (ca. 10%), identical in all respects with the substance arising by toluene addition to phenylpyrrolinium salt **1**.

Photoreactions Promoted by Excitation of the Arene Chromophore. In order to determine if electron-transfer-initiated reaction pathways would be followed in arene–iminium salt systems when the arene donor excited state is populated, the photochemistry of toluene, benzyltrimethylsilane, and benzyltrimethylstannane in the presence of 1,2-dimethyl-1-pyrrolinium perchlorate (**5**) was explored. The conditions employed were designed to ensure that the arene chromophore is the light acceptor and that the pyrrolinium salt quenches nearly all of the arene singlet excited states. Selective light absorption was easily accomplished since the nonconjugated iminium salt does not absorb at wavelengths greater than 230 nm. Also, fluorescence quenching rate constants in the case of toluene and benzyltrimethylsilane were used to determine the iminium salt concentration needed for maximization of singlet quenching. However, the lack of fluorescence of the corresponding tin substrate prohibits quenching studies. Moreover, the results presented below suggest that the singlet-excited-state lifetime of benzyltrimethylstannane must be exceedingly short and, thus, difficult to quench by iminium salt acceptors.

Irradiation of toluene in acetonitrile solutions containing the pyrrolinium salt **5**, followed by basic workup and chromatographic separation, led to isolation of 1,2-dimethylpyrrolidine (**21**; 7%) and bibenzyl (4%) along with trace quantities of hydrocinnamonitrile (**22**) (Scheme VII). None of the corresponding benzyl addition product **20** could be detected in this reaction mixture. However, photolysis of benzyltrimethylsilane with the pyrrolinium salt **5** in acetonitrile furnishes the benzylpyrrolidine **20** in a 23% yield along with bibenzyl (13%). The structure of this adduct was deduced on the basis of spectroscopic data and

Scheme VIII



Arene	Product Yield			
	20	21	10	23
PhCH$_3$	2	23	1	35
PhCH$_2$SiMe$_3$	40	26	16	10

unambiguously proven by its independent synthesis through benzylmagnesium bromide addition to **5**. Finally, none of the pyrrolidine **21** was generated in the silane irradiation process.

The photochemical behavior of benzyltrimethylstannane is both unusual and interesting in light of the results obtained from studies of both the toluene and benzylsilane systems. Thus, when this substance is irradiated in the presence or absence of the pyrrolinium salt **5** in acetonitrile, only bibenzyl is produced. No products resulting from addition to or reduction of the pyrrolinium salt can be detected in the product mixture. When this same reaction is carried out in methanol, only bibenzyl and toluene are produced. Again, no substances resulting from reaction of the pyrrolinium salt are observed.

The results arising from studies of toluene and benzyltrimethylsilane photoreactions with 1,2-dimethylpyrrolinium perchlorate (**5**) in methanol are summarized in Scheme VIII. The interesting finding here is that the hydroxymethylpyrrolidine **23** is the major substance produced in the toluene reaction while the benzyl adduct **20** dominates the product mixture arising by irradiation of the silicon-substituted arene.

The quantum yields for product formation in photoreactions of toluene and benzyltrimethylsilane with 1,2-dimethyl-1-pyrrolinium perchlorate (**5**) were measured in order to gain additional insight into the factors controlling these electron-transfer-induced, excited-state processes. Quantum efficiencies were determined for reactions in methanol and acetonitrile at fixed arene (0.099 M) and pyrrolinium salt (0.018 M) concentrations. The results are listed in Table IV. While the overall quantum yields for formation of the benzylpyrrolidine **20** and other products are low, they demonstrate a dramatic difference between the arene donors. Accordingly, the benzyltrimethylsilane photoreaction products are produced with quantum efficiencies that are ca. 10-fold larger than those for corresponding processes starting with toluene.

Quantum yields for selected product formation have been measured as a function of pyrrolinium perchlorate **5** concentration in reactions of the toluene and benzyltrimethylsilane systems. The double reciprocal plots of quantum yields for product formation vs. concentration of **5** (ϕ^{-1} vs. $[5]^{-1}$) were found to be linear in

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(23) Axiotis, G. P.; Gauthier, R.; Chastrette, M. *J. Organomet. Chem.* **1979**, *166*, 87.

Table IV. Quantum Yields for Product Formation by Irradiation of Toluene and Benzyltrimethylsilane in the Presence of 1,2-Dimethyl-1-pyrrolinium Perchlorate

		product formation efficiencies ($\times 10^{-3}$)^a				
arene	solvent	**10**	**20**	**21**	**22**	**23**
toluene	MeCN	0.5		0.9	0.1	
toluene	MeOH		0.9	10.0		13.0
benzyltrimethylsilane	MeCN	1.7	3.0		0.1	
benzyltrimethylsilane	MeOH	5.0	12.0	8.0		3.0

^{a}Concentrations of the arenes were 9.85×10^{-2} M and of the pyrrolinium salt were 1.80×10^{-2} M.

Table V. Summary of Concentration Dependencies of Quantum Yields for Selected Product Formation in the Dimethylpyrrolinium Perchlorate **5**–Toluene and –Benzyltrimethylsilane Systems

arene	solvent	photoproduct	intercept/slope^a	quenching constants $k_q\tau$
$PhCH_3$	MeCN	**10**	89.5	87.3
$PhCH_3$	MeOH	**23**	27.0	77.0
$PhCH_2SiMe_3$	MeCN	**20**	27.4	100
$PhCH_2SiMe_3$	MeCN	**10**	26.1	
$PhCH_2SiMe_3$	MeOH	**20**	69	100

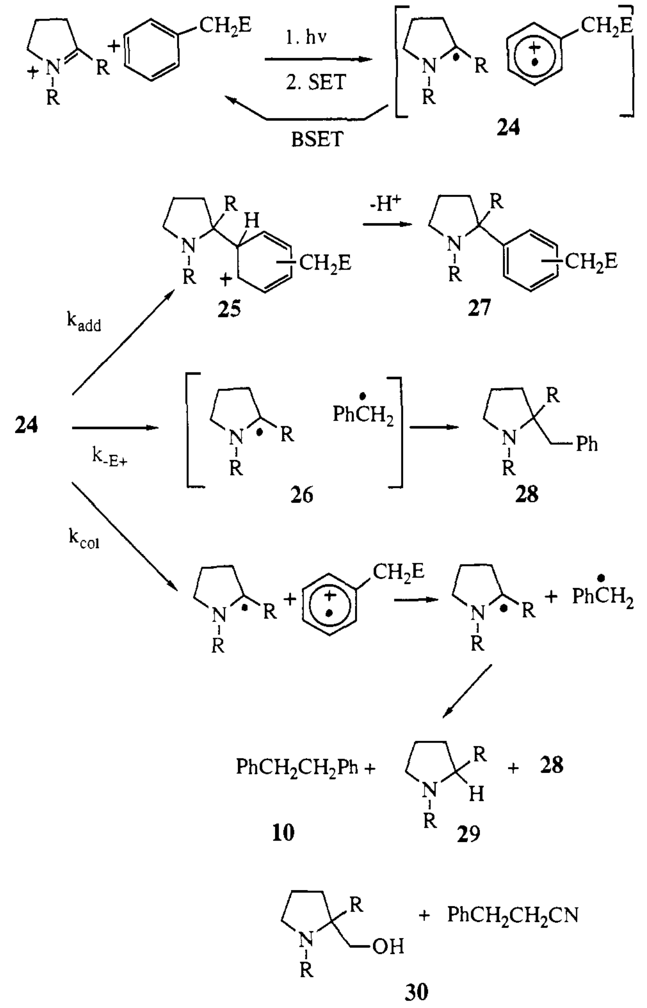
^{a}Obtained from plots of ϕ^{-1} vs. $[\mathbf{5}]^{-1}$.

the concentration region (1.8–9.0×10^{-3} M) employed. The intercept to slope ratios obtained from these plots are summarized in Table V and correspond to the quenching constants ($k_q\tau$) for the pathways leading to product formation. The modestly close correspondence between these values, obtained for selected photoproduct formation, and those obtained by Stern–Volmer analysis of fluorescence quenching data suggests that the photoreaction pathways emanate from the arene singlet excited states.

Discussion

Mechanistic Aspects of the Arene–Iminium Salt Photoreactions. The nature of photoproducts generated by irradiations of the arene–iminium salt systems discussed above suggest the operation of electron-transfer pathways. The adducts produced in these reactions appear to arise by a variety of processes available to intermediate radical cation and neutral radical pairs. Reasonable routes for product formation are included in Scheme IX. Accordingly, excitation of either the arene donors or the iminium salt acceptors leads to thermodynamically driven electron transfer resulting in formation of the radical cation pairs **24**. On the basis of the fluorescence quenching results and the concentration dependencies of photoreaction quantum yields, electron-transfer processes in these cases are promoted in the singlet-excited-state manifolds and perhaps via singlet exciplexes. Reverse electron transfer from **24** along with exciplex decay serves as a route for singlet-state quenching. The photochemistry of these systems derives from alternate decay pathways open to the radical cation pairs. Thus, radical coupling between the components of **24** serves as the route for formation of the arylation products **27**. Also, fragmentation, involving base- or nucleophile-induced loss of electrofugal group (H, $SiMe_3$, or $SnMe_3$) from benzylic positions, can occur to produce the neutral radical pairs **26**, which are precursors of the benzylation products **28**. Cage collapse is possible at either the cation or neutral radical pair stage. The 2-pyrrolidinyl and benzylic free radicals produced by these routes undergo typical processes including radical coupling and hydrogen atom abstraction resulting in eventual formation of **28** and bibenzyl along with the methanol or acetonitrile adducts **30** and pyrrolidines **29**.

Scheme IX



Factors Influencing Product Distributions. Several general trends can be seen through inspection of the relative yields and quantum efficiencies for product formation in these arene–iminium salt photoreactions. Firstly, the yields of benzylpyrrolidine **28** production from reactions of either the conjugated **1** and **7** or the nonconjugated **5** pyrrolinium salts appear to be significantly higher when the potential electrofugal groups at the benzylic positions of the arene donors are either $SiMe_3$ or $SnMe_3$. A representative example of this feature is found in photoreactions of the phenylpyrrolinium perchlorate **1** in methanol. The yields of benzylpyrrolidine **14** production range from 63% to 67% when the tin- or silicon-substituted arenes serve as donors, while none of this adduct is found when toluene is used as the donor. Similarly, the yields for generation of benzylpyrrolidine **20** from reactions of 1,2-dimethyl-1-pyrrolinium perchlorate (**5**) are significantly higher when benzyltrimethylsilane rather than toluene serves as the arene donor. Secondly, the yields for photoadditions of benzyltrimethylsilane or -stannane to the N–H-substituted pyrrolinium salt **1** leading to production of the benzyl adduct **14** are higher than those for the analogous process of the corresponding *N*-methyl salt **7**. Thirdly, photoadditions leading to generation of the arylation products **12**, **13**, **16**, and **17** occur in reactions of the pyrrolinium salts **1** and **7** only when toluene (or benzene) serves as the arene donor and when the solvent used is methanol rather than acetonitrile. Finally, photoaddition reactions involving the 1,2-dimethylpyrrolinium salt **5** and benzyltrimethylsilane proceed with quantum efficiencies which are approximately 1 order of magnitude greater than when toluene is the arene donor.

The mechanistic sequence outlined in Scheme IX provides a useful framework for rationalizing (perhaps understanding) the observations summarized above. Also, a consideration of reaction pathways available to arene-derived cation radical intermediates and of how the relative rates of these processes are influenced by electrofugal groups at benzylic positions and solvent appears relevant to this discussion. Numerous observations suggest that β-silyl and β-stannyl cationic systems are rapidly transformed to unsaturated products via nucleophile-induced demetalation pathways.[24] The facility of these processes is due to the elec-

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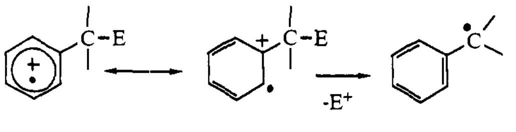
[24] Colvin, E. *Silicon in Organic Synthesis*, Butterworth: Boston, 1981; pp 4–5.

tropositive nature of the metals and the stabilization (in a thermodynamic and not kinetic sense) resulting from overlap of the high-energy, filled $\sigma_{\text{metal-carbon}}$- and vacant p-orbitals. Moreover, demetalations occur to the complete exclusion of competitive deprotonations in these systems despite the fact that the triallylsilyl and -stannyl groups render the adjacent hydrogens more acidic. The same factors appear to influence the reactivity of the closely related silicon- and tin-substituted cation radicals like those arising by electron transfer from benzylsilanes and -stannanes. In this regard, we expect that transformations of arene cation radicals **31** to neutral benzyl radicals **32** would have rates which are a sensitive function of the nature of the electrofugal groups at the benzylic positions. Specifically, by analogy with closed-shell cation counterparts, demetalation in the silicon- and tin-substituted systems should be fast compared to deprotonation in these as well as the toluene-derived systems.[25]

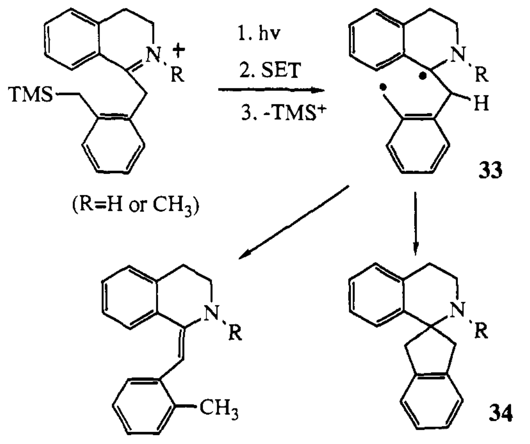


31 **32**

The relative rates of electrofugal group loss (k_{-E^+}) vs. those of other pathways (e.g., k_{BSET}, k_{add}, and k_{col}) available to cation radical pairs **24** (Scheme IX) will govern the nature, yields, and quantum efficiencies of arene–iminium salt photoaddition reactions. For example, the competition reflected by the rate constant ratio k_{-E^+}/k_{BSET} directly influences reaction quantum yields since the back-electron-transfer pathway serves as an energy-wasting process. Indeed, the higher quantum yields measured for reaction of benzyltrimethylsilane as compared to toluene with the pyrrolinium salt **5** can be directly attributed to this effect. Also, collapse of the initially formed radical cation pair cage **24** (k_{col}) will result in ultimate generation of free pyrrolidinyl and benzyl radical species. Depending upon when and to the extent that this occurs, the yields for benzylpyrrolidine formation should decrease while those for substances arising by an out-of-cage radical process (H atom abstraction and coupling) should increase. Electrofugal group loss in the cation radical pair **24** involving deprotonation or demetalation by a solvent molecule as part of the cage serves as a route for in-cage production of the radical pair **26**. Thus when the rate constant ratio k_{-E^+}/k_{col} is large (e.g., when E = $SiMe_3$ or $SnMe_3$), the yield of benzylpyrrolidine **28** formation should be large. Indeed, this is observed in reactions of the arene–pyrrolinium salt systems.

The higher yields for benzyl adduct production in the reaction of the N–H (**1**) vs. N–CH_3 (**7**) pyrrolinium salts with either the silicon- or the tin-substituted arenes appear to reflect steric effects on the rates of radical pair **26** coupling vs. cage collapse. The rates of radical coupling leading to formation of a quaternary center adjacent to nitrogen in the pyrrolidine ring should be retarded when alkyl substituents are present on nitrogen. We have observed results consistent with this effect in studies of photocyclization reactions of arene–iminium salt systems.[7] In that case, partitioning of the diradical intermediate **33**, arising by sequential electron-transfer pathways, occurs by radical coupling and hydrogen shift routes (Scheme X). Significantly higher yields (30% vs. 50%) of spirocyclic products **34** are obtained when the nitrogen substituent is hydrogen rather than methyl.

Scheme X



Photoarylation Reactions. Detection of ring-arylation products **27** in photoreaction mixtures arising by irradiation of the 2-phenylpyrrolinium salts **1**, **7**, and **18** with toluene and benzene in methanol suggests that yet another process is available in the excited-state electron-transfer chemistry of arene–iminium salt systems. The reaction leading to these products stands as an excited-state version of a "Friedel–Crafts-like" electrophilic aromatic substitution process. A likely mechanism is shown in Scheme IX and involves partitioning of the radical cation pair **24** by radical coupling. This generates the cation percursor **25** of the adducts **27**.[27] A mechanism for photoarylation in the toluene–iminium salt systems which involves para and ortho coupling in the radical pair **26** (Scheme IX) appears unlikely based upon the fact that benzene, which lacks this mechanistic option, participates in these processes. In addition, photoreactions of the silicon- and tin-substituted systems do not lead to generation of the arylation products despite the fact that radical pairs are efficiently produced in these cases. Indeed, it appears that cation radical pair coupling to produce adducts **27** is seen only in those systems where the electrofugal group loss pathway is absent (benzene) or slow (toluene). In the following paper[29] we describe results which demonstrate that the relative rates of diradical cation coupling vs. fragmentation to produce diradical species can have a pronounced effect on the nature of photocyclization products produced in intramolecular photoreactions, of arene–iminium salt systems.

Two additional features of the arylation reactions are worthy of further comment. Toluene photoadditions to pyrrolinium salts **1** and **7** generate only ortho and para adducts where the more sterically encumbered ortho adducts predominate. This regioselectivity is reminiscent of that observed by Ledwith[30] for the sodium peroxydisulfate initiated chlorinations of toluene in the presence of copper(II) chloride. Production of ortho (major) and para (minor) chlorination products in this case could be rationalized by the intermediacy of the toluene radical cation which undergoes reaction with copper chloride at the arene ring positions of highest odd electron density (i.e., ortho and para).[31] This same factor should operate in governing the regiochemistry of cation radical pair **24** coupling processes.

It is also interesting that the arylation products are formed only when photoreactions of the arylpyrrolinium salts and toluene or benzene are conducted in methanol and not acetonitrile. We have tentatively attributed this effect to solvent polarity and its influence on the rates of cation radical pair coupling processes. Thus, cation radical pair **24** coupling leads to generation of the cation **25** (Scheme IX); the rates of this process could very well be enhanced

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(25) (a) The effects of fast cation demetalation on the nature and yields of electron-transfer-induced photoreactions have been alluded to before (ref 5 and 26). The issue of deprotonation of methylbenzene cation radicals has been addressed by others (ref 25b). The nature of the base involved in the above processes is unknown. Candidates are solvent (MeOH or MeCN) or the 2-pyrrolidinyl radical. In addition, whether or not desilylation of the benzylsilane-derived cation radical involves an S_N1- or S_N2-type process is unknown at this time. (b) For example: Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472. Meot-Ner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5.

(26) Borg, R. M.; Mariano, P. S. *Tetrahedron Lett.* **1986**, 2821.

(27) Radical cation pair or diradical cation coupling processes have been observed or suggested in other iminium salt electron-transfer-induced photoreactions (ref 3, 28, and 29).

(28) Unpublished results of L. Tu and P. S. Mariano on the photochemistry of *N*-allylpyrrolinium salts indicate that solvent polarity might have an effect upon the rates of diradical cation coupling.

(29) Lan, A. J. Y.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.*, following paper in this issue.

(30) Ledwith, A.; Russell, P. J. *J. Chem. Soc., Chem. Commun.* **1974**, 959; *J. Chem. Soc., Perkin Trans. 2* **1975**, 1503.

(31) Komatsu, T.; Lund, A.; Kinell, P. *J. Phys. Chem.* **1972**, *76*, 1721.

when the medium polarity is high.[28] While the solvent effect observed here appears interesting, information required to draw definite conclusions about its source is currently not available. Furthermore, the reasons why no arylation products are formed in photoreaction of toluene with the dimethylpyrrolinium salt **5** in methanol remain unclear at this time. These questions are intriguing in light of results obtained from studies of intramolecular arene-iminium salt systems, which serve as the subject of the following paper.[29]

Benzyltrimethylstannane Photochemistry. Our results from studies of benzyltrimethylstannane photochemistry indicate that this substance undergoes excited-state homolysis leading to formation of benzyl and, presumably, trimethyltin radicals. This process is not quenched by the addition of the electron acceptor, dimethylpyrrolinium perchlorate **5**. In addition, no products arising through radical cation or neutral radical pair intermediates related to **24** and **26** in Scheme IX are observed in photolysates generated by irradiations in the presence of **5**. Electron transfer between the singlet state of benzyltrimethylstannane and iminium salt **5** is expected to be a thermodynamically favorable process. Thus, the absence of products resulting from electron-transfer pathways suggests that the benzyl–tin singlet is a short-lived species owing to either fast homolysis or intersystem crossing modes for deactivation. Furthermore, the results also suggest that the benzyl–tin triplet, if formed by intersystem crossing, is also unreactive with iminium salts.

It is worth noting that, to our knowledge, no reports have appeared previously describing the photohomolysis reaction of benzyltrimethylstannane. On the other hand, the analogous process has been observed for benzylsilanes.[32] However, in the silicon-substituted system, photohomolysis is exceptionally inefficient.

Conclusions. The results obtained from our studies of arene–iminium salt, electron-transfer photochemistry demonstrate that the process can be initiated by excitation of either the arene donor or the iminium salt acceptor groups. In addition, reactions occurring in these systems can be understood in terms of mechanisms involving the intermediacy of cation radical pairs which partition to products through radical coupling, electrofugal group loss, and cage collapse pathways. The effects of electrofugal groups, nitrogen substituents, and solvent on product distributions can be rationalized on the base of this mechanistic sequence and the control of rate constants for cation radical pair reactions. Finally, in some cases, these intermolecular processes proceed with chemical efficiencies needed for synthetic utility. Further studies of intramolecular analogues of these excited-state processes confirm this view.[29]

Experimental Section

General. NMR spectra were recorded with $CDCl_3$ solutions by using Varian XL-200, XL-100, and EM-360 or Bruker AM-400 instruments. Proton chemical shifts are reported in ppm downfield from Me_4Si as internal standard. Carbon chemical shifts are reported in ppm vs. $CDCl_3$. UV spectra were recorded on GCA-McPherson Model EV-700-56 or Perkin-Elmer Lambda 5 instruments. IR-spectra were measured on a Perkin-Elmer 281 or FT-1800 instrument. Mass spectrometric data were obtained by use of Dupont 21-390, Hitachi RMU-6E, or VG-7070 instruments. Elemental analyses were performed by F. Kasler at the University of Maryland. Gas chromatographic analyses were performed on a Varian 940 chromatograph with flame-ionization detection. Preparative gas chromatography was carried out on a Varian 2700 instrument. The columns used were 6 ft × $^1/_4$ in. (analytical) or 6 ft × $^3/_8$ in. (preparative), packed with Chromosorb W (60–80 mesh) loaded with 10% SE-30. The carrier gas in all cases was helium.

Melting points are reported uncorrected. Column chromatography was performed on Merck Silica Gel, 230–400 mesh, by using the flash technique. Preparative thin-layer chromatography (TLC) was performed on 20- × 20-cm plates coated with Merck Silica Gel 60 GF-254. Molecular distillations were performed at reduced pressure on a Kugelrohr apparatus.

Acetonitrile, methanol, benzene, and toluene were of spectral grade (Aldrich Chemical Company) and were used without further purification. Benzyltrimethylsilane was purchased from Petrarch and was distilled before use. Benzyltrimethylstannane was prepared by the in situ Grignard reaction between chlorotrimethylstannane and benzyl chloride. The pyrrolinium perchlorates **1**[2a] and **7**[5] were prepared as described previously. The 2-(4-chlorophenyl)- (**3**), 2-(4-methoxyphenyl)- (**4**), and 2-(4-(trifluoromethyl)phenyl)-1-pyrrolinium perchlorate (**2**) were prepared in situ by treatment of CH_3CN solutions of the parent pyrrolines with 70% aqueous $HClO_4$. *N*-Isopropylidenepyrrolidinium perchlorate **6** was prepared by the method of Leonard.[33]

Preparative photolyses were conducted by means of an apparatus consisting of a 450-W Hanovia medium-pressure mercury vapor lamp surrounded by a glass filter in a quartz immersion well under an inert atmosphere of nitrogen. Typically, the course of the irradiation was followed by NMR, UV, or GLC. When ca. 75% of the starting material (iminium salt or arene) had been consumed, the photolysis was terminated and the solvent concentrated in vacuo. The residue was then dissolved in chloroform and shaken with saturated sodium bicarbonate solution. The chloroform extracts were washed with saturated sodium chloride and dried over anhydrous sodium sulphate. After concentration in vacuo, the mixtures were chromatographed as described below. Except where otherwise noted, yields are quoted for pure compounds isolated in this manner. Further purification was carried out by column chromatography or by preparative gas chromatography to obtain materials for spectroscopic analyses.

Measurements of Reduction Potentials. Reduction potential measurements were made by using an EG&E Princeton Applied Research Model 174A polarographic analyzer and a Houston Instrument Omnigraphic 2000 recorder. The scan rate was 20 mV/s, current 0.1 mA, scan range 0 to −1.5 V in the case of 2-aryl-substituted pyrrolinium perchlorates.

The electrodes were mercury (working), standard calomel (reference), and Pt wire (auxiliary). Solutions were made in 5% H_2O-CH_3CN containing the iminium salt (2×10^{-3} M) and tetra-*n*-butylammonium perchlorate (0.1 M) as supporting electrolyte.

Fluorescence Measurements. Fluorescence spectra were recorded by using a Perkin-Elmer MPF 44B fluorescence spectrophotometer equipped with a differential corrected spectra unit. The wavelength of excitation corresponded to the wavelength of maximum absorption in the UV absorption spectrum. Emission scans were run in the range of emission with appropriate excitation band-pass and emission band-pass slits. The scan rate is 120 nm/min. Solutions of the fluorescing species (1×10^{-4} M) and varying concentrations of the quenchers in the range 2.0×10^{-3} to 8.0×10^{-2} M were used. The fluorescence spectra were recorded at 25 °C on nondegassed acetonitrile solutions. Stern–Volmer plots of the data yielded straight lines with slopes $k_q\tau$.

Quantum Yield Measurements. Quantum yields were measured by using a "linear optical bench" system equipped with a high-pressure 500-W mercury lamp (Illumination Industries Model CA-200-8003), the output of which was focused with a quartz collimator and passed through a quartz-faced water-cooled filter solution cell with three compartments. The three 1-cm compartments contained separately 1.0 M (260 g/L) nickel sulfate hexahydrate in distilled water, 0.85 M (240 g/L) cobalt sulfate heptahydrate in distilled water, and 0.9 mM (0.200 g/L) 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate in distilled water. The UV transmission of this filter system is 230–285 nm with a maximum at 255 mn. The filtered light, monitored by electronic actinometry, was then passed through a solution containing the arene, toluene, or benzyltrimethylsilane, and 1,2-dimethylpyrrolinium perchlorate (**5**). Product analysis was performed by GLC with 2,6-dimethoxynaphthalene and biphenyl as internal standards. Conversion to product did not exceed 5% in these measurements. The results of these measurements are recorded in Table V.

Irradiation of 1-Methyl-2-phenyl-1-pyrrolinium Perchlorate (7) with Toluene in CH_3CN. A solution of **7** (0.50 g) in 120 mL of CH_3CN containing 0.60 g of toluene was irradiated (Corex) for 4 h. The materials obtained after workup and chromatographic separation were bibenzyl (**10**; 4%), 1-methyl-2-phenylpyrrolidine (**9**; 15%), and 1-methyl-2-benzyl-2-phenylpyrrolidine (**8**; 28%). Pyrrolidine **9** was identified by comparison of the spectral data to that of an authentic sample prepared by the reduction of **7**, as described previously.[34]

Spectroscoic Data for 1-Methyl-2-benzyl-2-phenylpyrrolidine (8): ^{1}H NMR δ 1.68–1.91 (m, 2 H, CH_2), 2.09–2.18 (m, 2 H, CH_2), 2.25 (s, 3 H, NCH_3), 2.43–2.55 (m, 1 H, CH_2), 2.88–2.97 (m, 1 H, CH_2), 2.96, 3.03 (d, 1 H, wing of AB quartet, J = 13.7 Hz, benzylic CH_2), 3.46, 3.53 (d, 1 H, other wing of AB quartet, J = 13.7 Hz), 6.95–7.16 (m, 2 H, aromatic), 7.21–7.38 (m, 8 H, aromatic); ^{13}C NMR δ 141.5 (C-1, aro-

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[32] Kira, M.; Yoshida, H.; Sakurai, H. *J. Am. Chem. Soc.* **1985**, *107*, 7767.

[33] Leonard, N. J.; Paukstelis, J. V. *J. Org. Chem.* **1963**, *28*, 3021.

[34] Blake, K.; Gilles, Denny, R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 700.

matic ring), 138.9 (C′-1, aromatic ring), 130.4, 127.7, 127.6, 126.4, 125.8 (remainder aromatic, some coincident), 68.7 (C-2, ring), 53.6 (benzylic CH_2), 42.6 (CH_2), 35.9, 35.7 (N–CH_3, CH_2), 21.8 (CH_2); IR (neat) 3040, 2960, 2800, 1610, 1500, 1450, 1250, 1100, 910, 730, and 700 cm^{-1}; mass spectrum, *m/e* (relative intensity) 250 (1, M – 1), 160 (100, M – CH_2Ph), 145 (17), 117 (28), 91 (33), 77 (19), 65 (8); high-resolution mass spectrum, *m/e* 251.1653 ($C_{18}H_{21}N$ requires 251.1645).

Irradiation of Pyrrolinium Salt 7 with Benzyltrimethylsilane and Benzyltrimethylstannane in CH_3CN and CH_3OH. Solutions of **7** (0.50 g) in 120 mL of either CH_3CN or CH_3OH with benzyltrimethylsilane (1.00 g) or benzyltrimethylstannane (1.55 g) were irradiated (Corex) for 1 h. Products and yields obtained after separation are as follows. Benzyltrimethylsilane/CH_3CN:bibenzyl (10%), 1-methyl-2-phenylpyrrolidine (8%), and 1-methyl-2-benzyl-2-phenylpyrrolidine (37%); in methanol, the yields were 5%, 17%, and 20%, respectively. Benzyltrimethylstannane-/CH_3CN: bibenzyl (1%), 1-methyl-2-phenylpyrrolidine (trace), and 1-methyl-2-benzyl-2-phenylpyrrolidine (32%); in methanol, yields were 7%, trace, and 28%, respectively.

Irradiation of Pyrrolinium Salt 7 with Toluene in CH_3OH. A solution of **7** (0.50 g) in 120 mL of CH_3OH and 0.60 g of toluene was irradiated (Corex) for 6 h. Separation provided the following substances: 1-methyl-2-phenylpyrrolidine (**9**; 6%), 1-methyl-2-benzyl-2-phenylpyrrolidine (**8**; trace), 1-methyl-2-(hydroxymethyl)-2-phenylpyrrolidine (**11**; 14%), 1-methyl-2-(2-methylphenyl)-2-phenylpyrrolidine (**12**), and 1-methyl-2-(4-methylphenyl)-2-phenylpyrrolidine (**13**) (a mixture 2:1 totalling 5%). Compound **8** has previously been described.[35]

Spectroscopic data for 1-methyl-2-(2-methylphenyl)-2-phenylpyrrolidine (**12**): ^1H NMR δ 1.92–2.07 (m, 2 H, CH_2), 2.01 (s, 3 H, NCH_3), 2.26–2.42 (m, 2 H, CH_2), 2.33 (s, 3 H, aromatic CH_3), 2.62–2.83 (m, 2 H, CH_2), 6.97–7.34 (m, 9 H); ^{13}C NMR δ 144.0 (C-1, aromatic), 143.6 (C′-1, aromatic), 136.7 (C-2, aromatic, methyl substituted), 128.6, 128.2, 127.3, 126.9, 126.1, 125.3 (aromatic), 73.0 (C-2 ring), 53.3 (CH_2), 41.8 (CH_2), 36.5 (CH_3–N), 22.1 (CH_2), 21.6 (aromatic CH_3); IR (FT, neat) 3010, 3025, 2970, 2930, 2840, 2790, 1605, 1485, 1465, 1445, 786, 759, 705 cm^{-1}; mass spectrum, *m/e* (relative intensity) 251 (5, M^+), 250 (24, M – 1), 235 (2), 222 (6), 221 (27), 174 (20), 173 (74), 160 (22), 159 (100); high-resolution mass spectrum, *m/e* 251.1639 ($C_{18}H_{21}N$ requires 251.1645).

Spectroscopic data for 1-methyl-2-(4-methylphenyl)-2-phenylpyrrolidine (**13**): We were unable to separate mixtures of **12** and **13** so as to obtain pure **13**. However, ^1H NMR spectra of the mixture are consistent with the presence of **13**. The only peaks resolvable in the mixture are the aromatic methyl resonances, which for **13** occur at 2.34 ppm (2.33 ppm for **12**). Our structural assignment is therefore based on the similarity of the spectra and also on the data obtained for related compounds (see below).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate (1) with Toluene in CH_3CN. The pyrrolinium salt **1** was prepared in situ by the addition of 0.32 g of $HClO_4$ to 0.31 g of 2-phenylpyrroline[37] in 120 mL of CH_3CN containing 0.60 g of toluene. This mixture was irradiated (Corex) for 1.5 h. Separation provided the following substances: bibenzyl (**10**; trace) and 2-benzyl-2-phenylpyrrolidine (**14**; 21%). The presence of 2-phenylpyrrolidine was also detected in the reaction mixture by GLC prior to workup, but it was not isolated quantitatively.

Spectroscopic data for 2-benzyl-2-phenylpyrrolidine (**14**): ^1H NMR δ 1.68–1.78 (m, 1 H), 1.81–1.91 (m, 1 H), 1.86 (s, 3 H, NCH_3), 2.01–2.13 (m, 2 H, CH_2 ring), 2.94–3.02 (m, 1 H), 2.99 (d, center position of AB quartet, outer lines not visible, 2 H, benzylic CH_2), 3.08–3.14 (m, 1 H), 6.74–6.78 (m, 2 H, aromatic), 7.11–7.29 (m, 8 H); ^{13}C NMR δ 146.8 (C-1 aromatic), 137.7 (C′-1, methylene substituted), 130.2, 127.8, 127.7, 126.4, 126.2, 126.1 (remainder aromatic, some coincident), 68.7 (C-2), 48.0 (benzylic CH_2), 45.0, 37.5, 24.4; IR (neat) 3300, 3020, 2970, 2940, 2880, 1610, 1500, 1450, 1030, 910, 750, 700 cm^{-1}; mass spectrum, *m/e* (relative intensity) 237 (1, M^+), 236 (2.7), 160 (18), 146 (100); high-resolution mass spectrum, *m/e* 237.1500 ($C_{17}H_{19}N$ requires 237.1517).

Irradiation of Pyrrolinium Salt 1 with Benzyltrimethylsilane and Benzyltrimethylstannane in CH_3CN and CH_3OH. Solutions of **1** prepared in the manner described above, containing either 1.00 g of benzyltrimethylsilane or 1.55 g of benzyltrimethylstannane, were irradiated (Corex) for 1.5 h. The products obtained by chromatographic separation are as follows. Benzyltrimethylsilane/CH_3CN: bibenzyl (16%) and 2-benzyl-2-phenylpyrrolidine (49%); CH_3OH the yields were 12% and 67%, respectively. Benzyltrimethylstannane/CH_3CN: bibenzyl (18%) and 2-benzyl-2-phenylpyrrolidine (48%) (in methanol, 23% and 63%, respectively). 2-Phenylpyrrolidine was detected by GLC analysis of the photolysate but was not isolated.

Irradiation of Pyrrolinium Salt 1 with Toluene in CH_3OH. A solution of **1**, prepared in the manner described above, in 120 mL of CH_3OH containing 0.60 g of toluene was irradiated (Corex) for 6 h. Chromatographic separation gave the following substances: 2-benzyl-2-phenylpyrrolidine (**14**; trace), 5-phenyl-1-aza-3-oxabicyclo[3.3.0]octane (**15**; trace), 2-(2-methylphenyl)-2-phenylpyrrolidine (**16**), and 2-(4-methylphenyl)-2-phenylpyrrolidine (**17**) (a mixture 3:1 totalling 6%). The oxazolidine **15** has been described previously.[35]

Spectroscopic data for 2-(2-methylphenyl)-2-phenyl-pyrrolidine (**16**): ^1H NMR δ 1.72–1.86 (m, 3 H, CH_2 + NH), 2.30 (s, 3 H, CH_3), 2.42 (t, 2 H, J = 7.4 Hz, CH_2), 3.07 (t, 2 H, J = 7.3 Hz, CH_2), 6.96–7.48 (m, 9 H); ^{13}C NMR δ 147.9 (2 aromatic C-1), 138.0 (C-2, aromatic, methyl substituted), 129.3, 128.8, 128.5, 128.4, 128.0, 127.4, 126.7, 126.5, 123.8 (remaining aromatic), 71.9 (C-2 ring), 45.8 (CH_2), 39.5 (CH_2), 25.3 (CH_2), 22.0 (CH_3); IR (FT, neat) 3335, 3060, 3025, 2960, 2880, 1605, 1490, 1445, 1415, 786, 755, 708, 700 cm^{-1}; mass spectrum, *m/e* (relative intensity) 237 (24, M^+), 209 (16), 208 (57), 194 (13), 161 (13), 160 (100), 147 (13), 146 (100); high-resolution mass spectrum, *m/e* 237.1495 ($C_{17}H_{19}N$ requires 237.1517).

Spectroscopic data for 2-(4-methylphenyl)-2-phenylpyrrolidine (**17**): ^1H NMR δ 1.72–1.90 (m, 3 H, CH_2 + NH), 2.29 (s, 3 H, CH_3), 2.42 (t, 2 H, J = 7.5 Hz, CH_2), 3.06 (t, J = 7.3 Hz, CH_2), 7.06–7.47 (m, 9 H); ^{13}C NMR δ 147.8 (C-1, aromatic), 144.7 (C′-1, aromatic), 135.7 (C-4, methyl substituted), 128.8, 128.1, 126.3, 126.2, 126.1 (remaining aromatic), 71.3 (C-2 ring), 45.5 (CH_2), 39.1 (CH_2), 24.9 (CH_2), 20.9 (CH_3); IR (FT, neat) 3330, 3060, 3025, 2970, 2880, 1600, 1515, 1490, 1450, 1420, 816, 758, 721, 699 cm^{-1}; mass spectrum, *m/e* (relative intensity) 237 (22, M^+), 209 (19), 208 (69), 161 (15), 160 (100), 146 (75), 91 (15); high-resolution mass spectrum, *m/e* 237.1509 ($C_{17}H_{19}N$ requires 237.1517).

Irradiation of the Pyrrolinium Salt 1 with Benzene in CH_3OH. A solution of 1, prepared from 2-phenyl-1-pyrroline (0.31 g) and 0.31 g of $HClO_4$, in 120 mL of CH_3OH with 0.87 g of benzene was irradiated (Corex) for 5.5 h. Chromatographic separation gave a substance (2%) identified as 2,2-diphenylpyrrolidine (**19**). The ^1H NMR spectrum of this substance [1.62–1.88 (m, 3 H, CH_2 and NH), 2.44 (t, 2 H, CH_2), 3.06 (t, 2 H), 7.11–7.54 (m, 10 H)] matched that previously reported for **19**.[23]

Preparation of 2-(4-Methylphenyl)-1-pyrrolinium Perchlorate (18). This substance was prepared starting with the addition of *p*-tolyllithium to *N*-vinylpyrrolidone according to the method of Bielawski.[37] Protonation of 2-(4-methylphenyl)-1-pyrroline generated in this way by treatment with 70% aqueous $HClO_4$ provided the corresponding pyrrolinium perchlorate 18.

Spectroscopic data for 2-(4-methylphenyl)-1-pyrroline (mp 47–49 °C) is as follows: ^1H NMR δ 1.75 (m, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 2.75 (t, 2 H, CH_2), 3.95 (t, 2 H, CH_2), 7.05, 7.65 (dd, 4 H, aromatic); IR ($CHCl_3$) 3020, 2980, 1615, 1520, 1340, 1170, 1050, 820 cm^{-1}. mass spectrum, *m/e* (relative intensity) 159 (54, M^+), 131 (100), 117 (22), 91 (21).

Anal. Calcd for $C_{11}H_{13}N$: C, 82.98; H, 8.23; N, 8.80. Found: C, 82.63; H, 8.50; N, 8.65.

Irradiation of 2-(4-Methylphenyl)-1-pyrrolinium Perchlorate 18 with Benzene in CH_3OH. A solution of **18** (0.34 g) in 120 mL of CH_3OH and 0.87 g of benzene was irradiated for 6 h. Analysis of the crude photolysate after workup by GLC indicated the presence of a substance with an identical retention time as that of the arylation product **17** obtained from the photoreaction of toluene **7**. Isolation by preparative GLC gave 10% of **17** with spectroscopic properties identical with those described above.

Preparation of 1,2-Dimethyl-1-pyrrolinium Perchlorate 5.[37] To a solution of 2-methyl-1-pyrroline[36] (15 g in CH_3CN (200 mL)) was slowly added CH_3I (26.0 g). The resulting solution was stirred at 25 °C for 1 h an concentrated in vacuo giving the corresponding iodide salt (88%) mp 230 °C dec): ^1H NMR δ 2.26–2.72 (q, 2 H, CH_2), 2.66 (s, 3 H, CH_3), 3.30–3.72 (t, 2 H, CH_2), 3.62 (s, 3 H, NCH_3), 4.15–4.61 (t, 2 H, CH_2). The iodide salt was eluted through a perchlorate anion-exchange column (Dowex-1, 50-100 mesh) with methanol. The eluant was concentrated under reduced pressure and recrystallized from absolute ethanol to give the known[37] perchlorate salt **18** (75%) (mp 230 °C dec). Spectral data for 1,2-dimethyl-1-pyrrolinium perchlorate (**5**): ^1H NMR δ 1.91–2.63 (q, 2 H, CH_2), 2.44 (s, 3 H, CH_3), 2.99–3.58 (t, 2 H, CH_2), 3.44 (s, 3 H, NCH_3), 3.98–4.42 (t, 2 H, CH_2).

Irradiation of Toluene and Benzyltrimethylsilane with 1,2-Dimethyl-1-pyrrolinium Perchlorate (5) in CH_3CN or CH_3OH. Solutions of 1,2-dimethyl-1-pyrrolinium perchlorate (**5**) (0.8 g) in CH_3CN or CH_3OH

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(125 mL) containing toluene (12 g) or benzyltrimethylsilane (**6**, 2 g) were irradiated (Vycor) for 4 and 2 h, respectively. The usual workup, followed by column chromatography, gave the following compounds. Toluene/CH_3CN: 1,2-dimethylpyrrolidine (**21**; 7%), bibenzyl (**10**, 4%), hydrocinnamonitrile (**22**; 1%). Toluene/CH_3OH: (**21**; 23%), (**10**; 1%), 1,2-dimethyl-2-benzylpyrrolidine (**20**; 2%), 1,2-dimethyl-2-(hydroxymethyl)pyrrolidine (**23**; 35%). Benzyltrimethylsilane/CH_3CN: **10** (13%), **20** (23%). Benzyltrimethylsilane/CH_3OH: **21** (26%), **20** (40%), **23** (10%), **10** (16%).

Spectral data for 1,2-dimethyl-2-benzylpyrrolidine (**20**): ^1H NMR δ 1.97 (s, 3 H, CH_3), 1.27–2.21 (m, 4 H, 2 × CH_2), 2.39 (s, 3 H, NCH_3), 2.71 (s, 2 H, benzylic CH_2), 2.57–3.32 (m, 2 H, CH_2), 7.30 (s, 5 H); ^{13}C NMR δ 134.7, 130.3, 128.7, (aromatic, some coincident), 71.8 (C-2, ring), 54.7 (CH_2), 41.8 (benzylic CH_2), 35.5 (CH_2), 34.8 (NCH_3), 19.7 (CH_2), 18.4 (CH_3); mass spectrum, *m/e* (relative intensity) 189 (1, M^+), 188 (1), 174 (2, M – CH_3), 98 (100, M – $PhCH_2$); high-resolution mass spectrum, *m/e* 189.1500 ($C_{13}H_{17}N$ requires 189.1517).

Spectral data for 1,2-dimethyl-2-hydroxymethylpyrrolidine (**23**): ^1H NMR δ 0.83 (s, 3 H, CH_3), 1.47–2.06 (m, 4 H, 2 × CH_2), 2.22 (s, 3 H, NCH_3), 2.87–3.16 (m, 2 H, CH_2), 3.25 (q, 2 H, CH_2OH); ^{13}C NMR 65.1 (CH_2OH), 62.9 (C-2), 54.3 (CH_2), 35.0 (CH_2), 33.7 (CH_3-N), 21.7 (CH_2), 17.4 (CH_3); IR ($CHCl_3$) 3382 cm^{-1}; mass spectrum, *m/e* (relative intensity) 128 (20, M – 1), 114 (3), 112 (1), 98 (100, M – CH_2OH), 84 (13), 71 (4); high-resolution mass spectrum, *m/e* 128.1074 ($C_7H_{14}NO$, M – 1, requires 128.1075).

Independent Synthesis of 1,2-Dimethyl-2-benzylpyrrolidine (20). To a solution of benzylmagnesium bromide (8.86 mmol, prepared by the reaction of toluene with *n*-butyllithium followed by metal exchange with $MgBr_2$) in 25 mL THF was added 1,2-dimethyl-1-pyrrolinium perchlorate (**5**) (0.35 g, 1.77 mmol). After stirring at reflux for 14 h, the mixture was cooled to 0 °C, and 10% HCl was added. The solution was then washed with ether, made basic (pH 11) by the addition of aqueous NaOH, and extracted with $CHCl_3$. The extracts were dried and concentrated in vacuo to yield 0.28 g (84%) of 2-benzyl-1,2-dimethylpyrrolidine (**2**). A sample of this, purified by column chromatography on Silica gel, had spectroscopic properties identical with those of the material obtained in the photochemical process.

Irradiation of Benzyltrimethylstannane and 1,2-Dimethylpyrrolinium Salt (5) in CH_3CN or CH_3OH. A solution of 1.50 g of benzyltrimethylstannane in 125 mL of CH_3CN or CH_3OH containing 0.8 g of the perchlorate salt **5** was irradiated (Vycor) for 1 h. Workup followed by chromatography afforded the following products. CH_3CN: bibenzyl (**10**; 6%), 1,2-dimethyl-2-benzylpyrrolidine (**20**; trace). CH_3OH: (**10**; trace), (**20**; trace).

In the above irradiations, the presence of toluene was detected by GC in varying yields, which were higher in methanol irradiations.

Irradiation of Benzyltrimethylstannane in CH_3CN or CH_3OH. Solutions of benzyltrimethylstannane (1.0 g) in 120 mL of CH_3CN or CH_3OH were irradiated (Vycor) for 1 h. Evaporation of solvent, followed by column chromatography on silica gel, afforded the following yields of bibenzyl (**10**): CH_3CN, 49%; CH_3OH, 7%. Considerable quantities of toluene were also detected by GLC analysis.

Concentration Dependence of Quantum Yields for Product Formation in the 1,2-Dimethyl-1-pyrrolinium Perchlorate Arene Systems. Irradiations were conducted in 3- × 20-cm quartz tubes by using Vycor filtered light. The concentrations of the aromatic species, toluene or benzyltrimethylsilane, in CH_3OH or CH_3CN were 9.90 × 10^{-2} M in all tubes, and the concentrations of 1,2-dimethyl-1-pyrrolinium perchlorate varied from 18 to 80 mM. The photolysates were individually concentrated in vacuo, diluted with saturated aqueous $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried, concentrated in vacuo, and analyzed by GLC under the same conditions as employed in the preparative runs. Summaries of the results obtained are given below as follows: arene; solvent; product analyzed; quantum yield (concentration of pyrrolinium salt).

Toluene; CH_3CN; bibenzyl; 0.0005 (0.018 M), 0.0006 (0.023 M), 0.0006 (0.030 M), 0.0007 (0.045 M), 0.0007 (0.090 M).

Toluene; CH_3OH; 1,2-dimethyl-2-(hydroxymethyl)pyrrolidine (**23**); 0.013 (0.018 M), 0.015 (0.023 M), 0.019 (0.030 M), 0.022 (0.045 M), 0.027 (0.090 M).

Benzyltrimethylsilane; CH_3CN; 2-benzyl-1,2-dimethylpyrrolidine (**20**) and bibenzyl (**10**), respectively; 0.003, 0.002 (0.018 M), 0.003, 0.002 (0.022 M), 0.005, 0.003 (0.054 M), 0.007, 0.004 (0.090 M).

Benzyltrimethylsilane; CH_3OH; 2-benzyl-1,2-dimethylpyrrolidine (**20**); 0.012 (0.018 M), 0.015 (0.023 M), 0.015 (0.027 M), 0.019 (0.036 M), 0.019 (0.045 M), 0.018 (0.054 M), 0.021 (0.090 M).

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