Electron-Transfer-Induced Photocyclization Reactions of Arene–Iminium Salt Systems. Effects of Cation Diradical Deprotonation and Desilylation on the Nature and Efficiencies of Reaction Pathways Followed

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Abstract: Photocyclization reactions of the *N*-xylyl-1-pyrrolinium perchlorates **3–6**, induced by excited-state electron transfer, have been explored with the intent of uncovering mechanistic details and developing synthetic applications. Both of the silicon-substituted salts **4** and **6** undergo photocyclization to produce the respective benzoindolizidine products, **30** and **13**, exclusively via mechanisms involving sequential electron transfer–desilylation. On the other hand, the non-silicon-containing 2-phenyl-1-pyrrolinium perchlorate **5** undergoes conversion to both the indolizidine **13** and 2-phenyl-1-pyrroline (**10**) upon irradiation. Photofragmentation generating **10** is proposed to arise by cleavage of the intermediate diradical cation **14**, which occurs in competition with deprotonation and 1,6-diradical coupling to form **13**. Finally, the benzopyrrolizidines **22** and **23** are produced when the 2-methyl-*N*-xylyl- and 2-methyl-*N*-benzylpyrrolinium perchlorates **3** and **21** are irradiated. Deuterium labeling studies have shown that these photocyclization reactions proceed through diradical cation coupling processes. The features of these photochemical processes whose chemical outcomes are dependent upon the nature of reaction pathways available to cation diradical intermediates are discussed. Finally, the photoinduced, diradical cyclization methodology for transformation of the silicon-containing *N*-xylylpyrrolinium perchlorates **4** and **6** has been compared to the alternative dipolar pathway promoted by fluoride-induced desilylation. The indolizidines **30** and **13** are formed when these salts are treated with cesium fluoride at high temperature. However, the yields are much lower than those observed for the photocyclization processes.

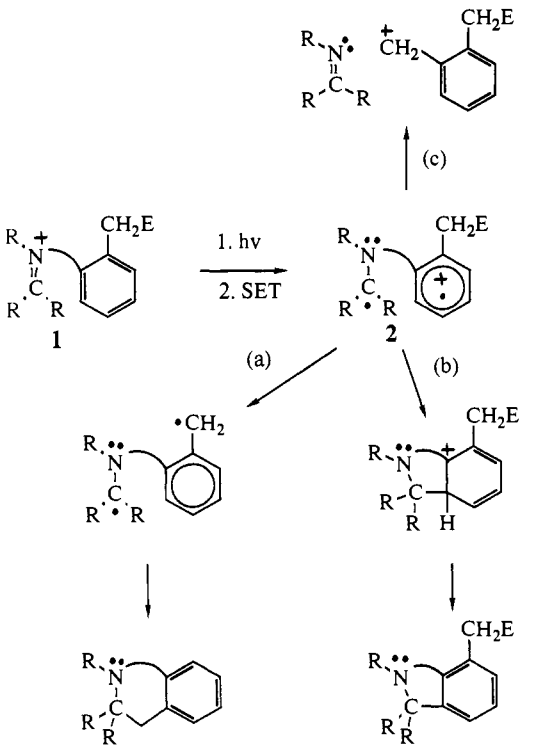
In the preceding paper[1] we have described the results of studies probing the electron-transfer-initiated, photoaddition reactions of 1-pyrrolinium salts and arene systems. The results of that effort suggested that photoreactions in these systems could be promoted by excitation of either the arene donors or iminium salt acceptors and that the intermediate cation radical pairs generated by excited-state electron transfer are transformed to products by a number of pathways including electrofugal group loss from benzylic positions, radical coupling, and cage collapse. The important conclusion drawn from this study is that product distributions in these photoreactions are governed by the nature of benzylic electrofugal groups which influence the rates of cation radical pair conversion to radical pair precursors of the photoproducts.

Investigations of arene–iminium salt electron-transfer photochemistry have been extended to intramolecular systems with the intent of probing further the effects of benzylic electrofugal groups on the nature and efficiencies of photocyclization processes available to these systems. In addition, we felt that an exploratory study of this type would provide preliminary information about the synthetic application of arene–iminium salt photocyclization processes in the area of N-heterocycle synthesis.

At the outset, we envisaged that diradical cation intermediates **2** (Scheme I) would be formed by intramolecular electron transfer in the excited state of the linked arene–iminium salt **1**. Ensuing reactions of these intermediates could occur via electrofugal group loss (path a), radical coupling (path b), or heterolytic fragmentation (path c) pathways and lead to generation of cyclization or cleavage products. In the intramolecular systems, cage escape resulting in intermolecular processes should be highly improbable. Therefore, photoreactions of linked arene–iminium salts have the potential of displaying high degrees of chemoselectivity, controlled by the nature of benzylic electrofugal groups.

Our preliminary investigations in this area have focused on several *N*-xylylpyrrolinium perchlorates, **3–6**, whose structural and electronic characteristics have the potential of revealing information about the mechanisms, scope, and synthetic utility of photocyclization processes initiated by intramolecular electron transfer. Owing to the electronic differences between the 2-

Scheme I



3 (E=H) **5** (E=H)
4 (E=TMS) **6** (E=TMS)

(1) Borg, R. M.; Heuckeroth, R. O.; Lan, A. J. Y.; Quillen, S. L.; Mariano, P. S. *J. Am. Chem. Soc.*, preceding paper in this issue. Lan, A. S. Y.; Quillen, S. L.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6439.

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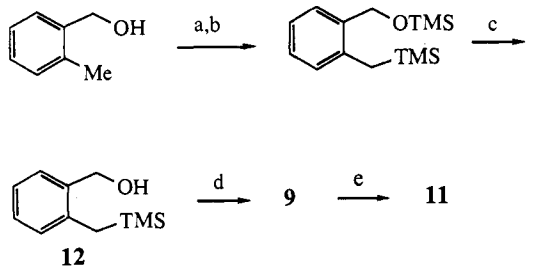
Scheme II[a]

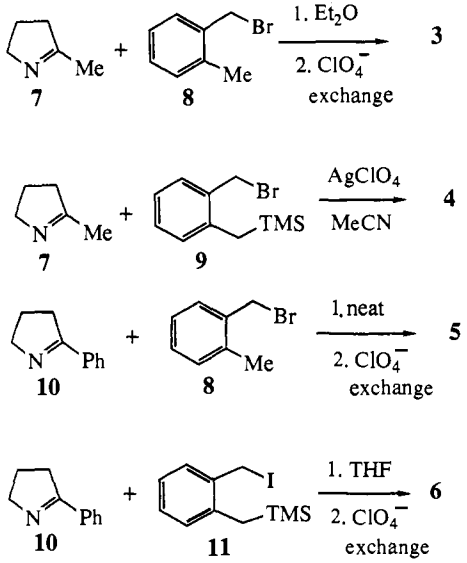


[a](a) *n*-BuLi, TMEDA, THF; (b) Me_3SiCl; (c) H_2SO_4, THF; (d) Ph_3P, CBr_4, Et_2O; (e) NaI, acetone.

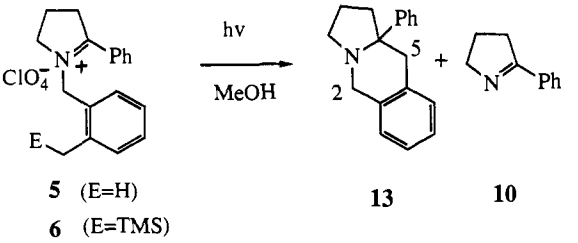
phenyl- and 2-methyl-1-pyrrolinium cation function in these salts, activation of electron transfer can occur via selective excitation of either the arene donor groupings (in **3** and **4**) or the conjugated iminium salt moieties (in **5** and **6**). The presence of both hydrogen and trimethylsilyl substituents at benzylic positions of the arene groupings in these salts should provide an opportunity to probe the chemistry of cation diradical intermediates under conditions in which both fast (in the case of $SiMe_3$) and slow (in the case of H) pathways for electrofugal group loss are available.

Preparation of the *N*-Xylylpyrrolinium Perchlorates. The *N*-xylylpyrrolinium perchlorates **3–6** were prepared by benzylation of the corresponding 1-pyrrolines,[2] **7** and **10**, with either *o*-methylbenzyl bromide (**8**) or the corresponding trimethylsilyl-substituted benzyl bromide or iodide, **9** and **11**. In the case of the silicon-substituted pyrrolinium salt, **4**, benzylation was promoted by use of silver perchlorate, which furnished the perchlorate salt directly. In all other cases the pyrrolinium halide salts were subjected to perchlorate ion exchange on Dowex-1 in order to produce substances having a non-electron-donating counteranion.

o-((Trimethylsilyl)methyl)benzyl bromide and iodide, **9** and **11**, were prepared by standard procedures from the corresponding benzyl alcohol **12**, which itself was generated by an O,C-bistrimethylsilylation, O-desilylation sequence (Scheme II) analogous to that described by Trost[3] for (trimethylsilyl)methallyl alcohol synthesis. It should be noted that the silylbenzyl alcohol **12** has been prepared previously by use of a different methodology.[4]



Photochemistry of the 2-Phenyl-1-pyrrolinium Perchlorates 5 and 6. Irradiation (Corex) of a methanol solution of the non-silicon-containing *N*-xylyl-2-phenylpyrrolinium perchlorate **5** followed by basic workup of the crude photolysate and chromatographic separation led to isolation of two major photoproducts. These substances were characterized as the known 2-phenyl-1-pyrroline (**10**)[2] (15%) and the phenylbenzoindolizidine **13** (18%).



Spectroscopic data for the latter material were in full accord with the assigned structure. Especially characteristic in this regard was the mass spectrum which contained intense signals at *m/e* 144 and 104 corresponding to retro [4 + 2] fragmentation of the benzoindolizidine nucleus. In addition, two AB quartets in the ^1H NMR spectra at ca. 3.0 and 3.7 ppm are fully consistent with expected resonances corresponding to the protons at C-5 and C-2 in **13**.

In contrast, irradiation (Corex) of methanol or acetonitrile solutions of the trimethylsilyl-substituted *N*-xylylpyrrolinium perchlorate **6** followed by basic workup and chromatography afforded exclusively the benzoindolizidine **13** in yields which vary between 40% and 60%. Careful inspection of the crude photolysate failed to reveal the presence of pyrroline **10** in the reaction mixture.

Generation of both the indolizidine **13** and pyrroline **10** can be understood by consideration of the nature and reactivity of intermediates formed following intramolecular electron transfer in the excited state of the xylylpyrrolinium salt **5**. The UV spectroscopic properties of the 2-phenyl- and 2-methylpyrrolinium perchlorates demonstrate that irradiation of **5** at wavelengths greater than 280 nm leads to excitation of the more strongly absorbing conjugated iminium cation chromophore. In addition, considerations of electrochemical potentials and fluorescence quenching information, gained from our studies with iminium salt–arene systems,[1] suggest that singlet electron transfer from the arene to the excited singlet state of pyrrolinium salt grouping in **5** should be rapid. Indeed, the availability of a reversible electron-transfer pathway must be the reason why the fluorescence efficiency of **5** is negligibly small as compared to that of 1-methyl-2-phenyl-1-pyrrolinium perchlorate.

The cation diradical **14** (E = H) produced by electron transfer in the singlet state of **5** can transform to the singlet biradical **15** through deprotonation at the unsubstituted benzylic position. Homolytic fragmentation of cation diradicals related to **14** (E = H) is also known to be a facile process based upon our earlier studies of N-allylquinolinium salt photochemistry.[5] Thus, fragmentation of **14** (E = H) by C–N bond cleavage would give 2-phenyl-1-pyrroline (**10**). In this sequence (Scheme III), generation of photocyclization and photofragmentation products occurs by partitioning at near equal rates of the initially formed cation diradical **14** (E = H) through deprotonation and C–N bond cleavage pathways.

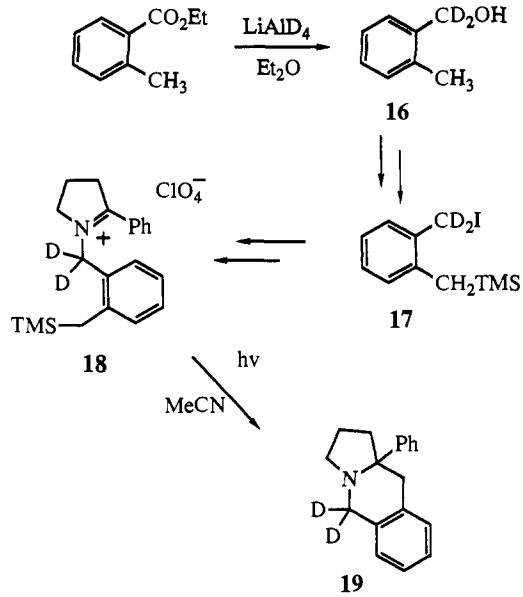
The exclusive production of benzoindolizidine **13** from photoreaction of the trimethylsilyl-substituted pyrrolinium salt **6** can be understood in terms of this same mechanistic scheme. The enhanced chemoselectivity occurring upon replacement of hydrogen by the $SiMe_3$ substituent at benzylic centers in these systems appears to be related to the relative rates of electrofugal group loss, converting cation diradicals **14** (E = $SiMe_3$) to the neutral diradical **15** and other processes such as C–N bond cleavage available to **14**. Thus, exclusive production of **13** from **6** is in accord with the greater rate for arene cation radical desilylation vs. deprotonation noted in studies with intermolecular systems.[1,6] Rapid desilylation of **14** (E = $SiMe_3$) results in its selective transformation to diradical **15** and onward to benzoindolizidine **13**.

(2) Bielawski, J.; Brandage, S.; Lindblom, L. *J. Heterocycl. Chem.* **1978**, *15*, 97.
(3) Trost, B. M.; Chen, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315.
(4) Swenton, J. S.; Shih, C. *J. Org. Chem.* **1982**, *47*, 2668.
(5) Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinoha, J. L.; Bay, E.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 1204.
(6) Farid, S.; Mattes, S., unpublished results from studies probing the photoaddition reactions of benzyltrimethylsilane and 9,10-dicyanoanthracene.

The facility of desilylation of the cation diradical **14** is also reflected in the quantum yield for benzoindolizidine formation. Electrofugal group loss from **14** should be competitive with energy-wasting, back electron transfer that transforms **14** to the starting xylylpyrrolinium salt. The rate constants for electrofugal loss, k_{-E}, and back electron transfer, k_{BSET}, will be reflected in photocyclization quantum efficiencies, ϕ_r, according to the following proportionality [$\phi \propto k_{-E^+}/(k_{-E^+} + k_{BSET})$]. Indeed, the quantum yield for benzoindolizidine **13** formation from the silicon-containing pyrrolinium salt **6** ($\phi_r = 0.12 \pm 0.02$) is ca. 12 times larger than that for the protio analogue **5** ($\phi_r = 0.010 \pm 0.002$). Thus, the more rapid rate of desilylation vs. deprotonation of **14** has a pronounced effect not only on the reaction chemoselectivity but also on the quantum efficiencies for photocyclization.

As indicated above, the singlet diradical **15** is most likely the direct precursor of benzoindolizidine **13**. An alternative and more complex route for transforming **15** to **13** is possible. This involves fragmentation of the diradical **15** to produce the *o*-xylylene–pyrroline pair followed by Diels–Alder cycloaddition. Both steps in a route of this type are reasonable, since homolytic cleavage reactions of 1,4-diradical vinylogous to **15** and [4 + 2]-cycloaddition reactions of *o*-xylylenes with imines[7] are both well-precedented processes. However, investigations with the specifically deuterium-labeled xylylpyrrolinium salt **18** have led to results which argue against the operation of the *o*-xylylene pathway as well as other more complex sequences for benzoindolizidine generation.

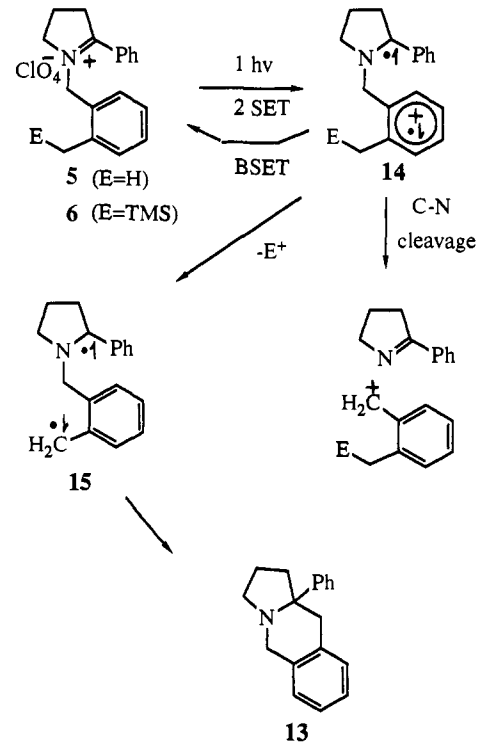
The dideuteriated pyrrolinium perchlorate **18** was prepared by a sequence starting with ethyl toluate. Reduction of this ester with lithium aluminum deuteride provided the benzyl alcohol-d_2 **16**, which was transformed to the iodide **17** by a route analogous to that used for preparation of its protio analogue **11** (see Scheme II above). Benzylation of 2-phenyl-1-pyrroline with **17** and perchlorate anion exchange then gave the crystalline salt **18**.



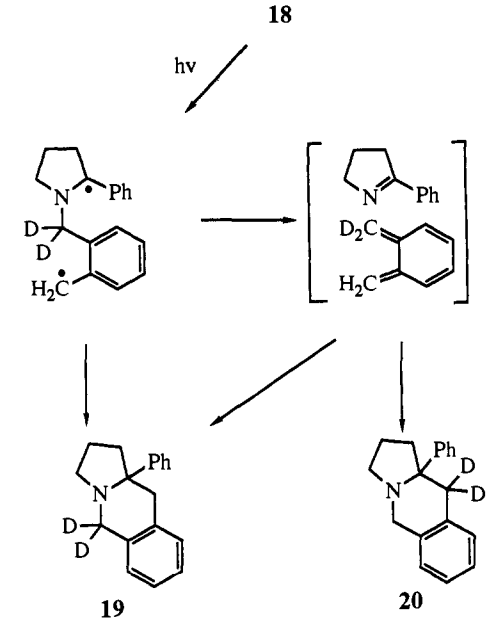
Irradiation of **18** (MeCN, Corex) followed by basic workup and chromatographic separation led to isolation of the corresponding photocyclization product. ^{1}H NMR analysis of this substance demonstrated that it is the 2,2-dideuterioindolizidine **19** uncontaminated (<5%) with the 5,5-dideuterio isomer **20**. This result indicates that the diradical intermediate **15** is not converted to the benzoindolizidine product by a sequence (Scheme IV) involving homolytic cleavage followed by *o*-xylylene–pyrroline cycloaddition. In that event a mixture of **19** and **20** would have been expected from reaction of **18** owing to the pseudosymmetric nature of the xylylene-d_2 intermediate. Of course, our results cannot be used to rule out a two-step process in which cyclo-

(7) Kametani, T.; Takahashi, T.; Honda, T.; Ogasawara, K.; Fukumoto, K. *J. Org. Chem.* **1974**, *39*, 447.

Scheme III



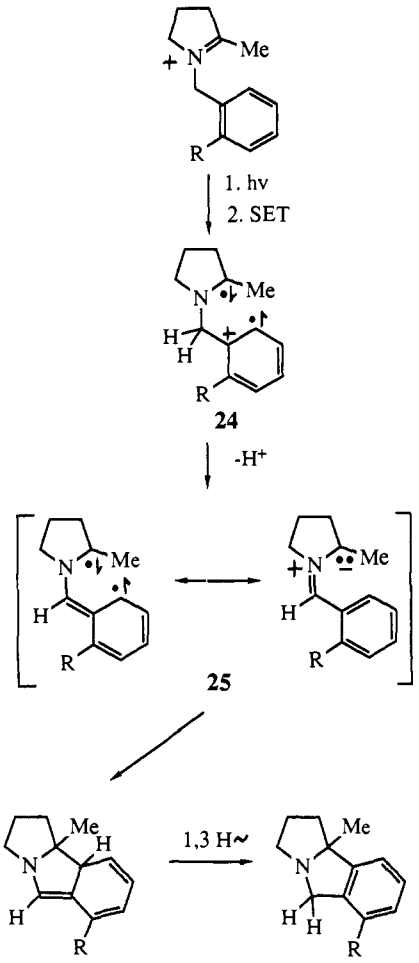
Scheme IV



addition occurs more rapidly than relative rotation of the xylylene and pyrroline species.

Photochemistry of the 2-Methyl-1-pyrrolinium Perchlorates 3 and 4. One of the aims of our exploratory efforts with the *N*-xylylpyrrolinium salts was to probe the photochemistry of closely related arene–iminium cation systems in which electron transfer could be promoted through the excited states of either the donor arene or the acceptor iminium salt chromophores. In the cases described above, the phenyl-conjugated iminium cation grouping is selectively excited, leading to the observed photocyclization and photofragmentation reactions. The absence of conjugation of the iminium cation moiety in the 2-methylpyrrolinium salts **3** and **4** allows for light absorption by the aryl ring when irradiations are conducted with light of wavelength greater than 240 nm. Thus, the photochemistry of these systems should provide useful information about the versatility of this electron-transfer, photochemical methodology in synthetic approaches for N-heterocycle

Scheme V



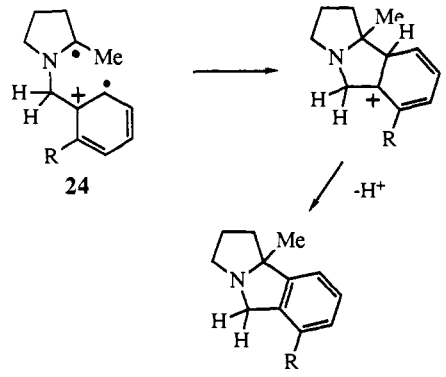
ring construction. Results arising from these efforts have accomplished this purpose and have demonstrated how the chemoselectivities of arene–iminium salt photocyclization reactions can be controlled by substituents which affect the reaction pathways followed by diradical cation intermediates.

Irradiation (Vycor) of an acetonitrile solution of the non-silicon-containing *N*-xylylpyrrolinium perchlorate **3** followed by basic workup gave exclusively (55%) a substance identified as the benzopyrrolizidine **22** on the basis of spectroscopic data. Particularly characteristic in this regard are the presence in the ^{1}H NMR spectrum of two methyl singlets at 1.48 and 2.24 ppm and an AB quartet at 3.86 and 4.44 ppm corresponding to the C-5 methyl, arylmethyl, and diastereotopic protons at C-2, respectively. In addition, the 1,2,3-trisubstituted benzene ring in **22** is reflected in the ^{13}C NMR spectrum by the presence of three quaternary aromatic carbons.

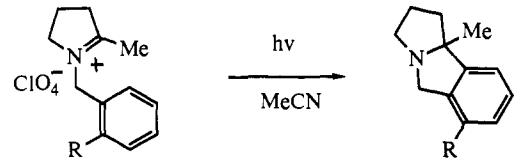
This benzopyrrolizidine-forming, photocyclization reaction of **3** serves as an unique example of an excited-state "Pictet–Spangler" cyclization process which has numerous, synthetically useful, ground-state counterparts. This cyclization reaction also occurs in systems which lack additional alkyl substituents on the aromatic moiety. For example, the *N*-benzylpyrrolinium perchlorate **21**, generated by reaction of the 1-pyrroline **7** with benzyl bromide followed by perchlorate ion exchange, is transformed to the benzopyrrolizidine **23** (80%) upon irradiation in acetonitrile. The close resemblance between the spectroscopic properties of **22** and **23**, except for the difference resulting from the aromatic methyl substituent, serves to evidence the assigned structures.

Initial considerations uncovered two reasonable mechanisms for this novel, high-yielding photocyclization process. Both proceed via the singlet, diradical cation **24** which would be formed by intramolecular electron transfer from the arene donor singlet excited state to the iminium cation groupings. An evaluation of excited- and ground-state electrochemical potentials[1,8] and

Scheme VI

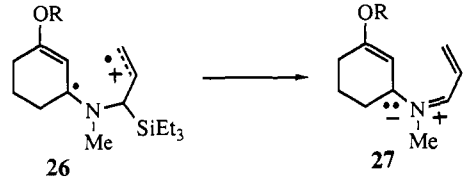


fluorescence quenching data accumulated in our previous studies[1] provides firm support for the expectation that electron transfer in the singlet excited states of **3** and **21** will be highly exoergic and thus rapid. In one mechanistic route, the singlet diradical



3 (R=Me) **22** (R=Me)
21 (R=H) **23** (R=H)

cation **24** formed in this way can be converted to the pyrrolizidine products through a pathway involving deprotonation at the N-benzylic position to produce the vinylazomethine ylide **25** (Scheme V). Pyrrolidine ring formation would then involve 6π-electron electrocyclization of **25** followed by tautomerization. Precedent for the ylide cyclization reaction is found in studies of base-induced cyclization processes of *N*-allylpyrridinium salts.[9] In addition, observations emanating from previous photochemical studies with *N*-(1-(triethylsilyl)allyl)iminium salts have demonstrated that silicon-containing diradical cations related to **24** can undergo rapid desilylation to produce azomethine ylides (e.g., the conversion of **26** to **27**).[10] The close structural and electronic correspondence between the charged diradicals **26** and **24** suggests that deprotonation of the latter system would be a reasonable route for azomethine ylide formation.

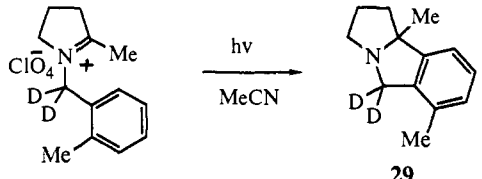


An alternate sequence for benzopyrrolizidine formation from the diradical cation intermediate **24** involves radical coupling prior to proton loss (Scheme VI). The carbon–carbon bond-forming step in this route resembles coupling processes followed by α-amino radicals and arene cation radical uncovered in our previous studies with intermolecular arene–iminium salt systems.[1]

Distinction between these mechanistic alternatives is easily made by the use of deuterium labeling methods. For this purpose, the selectively dideuteriated *N*-xylylpyrrolinium perchlorate **28** was prepared by reaction of 2-methylpyrroline with *o*-methylbenzyl-α,α-d_2 iodide followed by perchlorate ion exchange. The ^{1}H NMR spectrum of the benzopyrrolizidine **29** obtained by

(8) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(9) (a) Pammelet, J. C.; Chucke, J. *Can. J. Chem.* **1970**, *54*, 1971. (b) Tamura, Y.; Tsujmoto, N.; Sumida, Y.; Ikeka, A. *Tetrahedron* **1972**, *28*, 21. (c) Sasaki, T.; Kanematsu, K.; Kakehi, A.; Ito, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2089. (d) Taylor, E. C.; Turchi, I. J. *Chem. Rev.* **1979**, *79*, 181. (e) Huisger, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 947.
(10) Chen, S. F.; Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1983**, *105*, 6160.

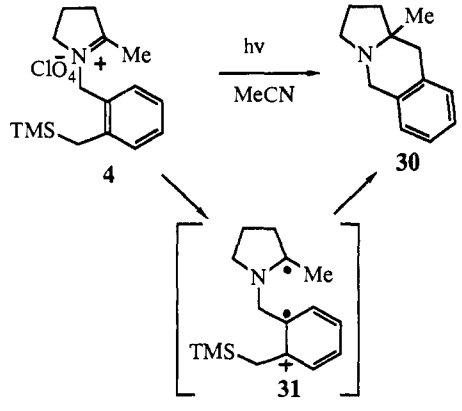
irradiation of **28** lacks resonances corresponding to the diastereotopic C-2 protons. Thus, the two deuteria are retained at the N-benzylic position in the conversion of **28** to the corresponding benzopyrrolizidine. Clearly, the azomethine ylide cyclization mechanism (Scheme V) cannot be operative in these photochemical processes, since a route of this type would have led to exchange of one of the N-benzylic deuteria.



28 **29**

The pathway for benzopyrrolizidine ring formation involving diradical cation cyclization is fully consistent with the results of this labeling study. It is interesting to note that unlike the similarly structured phenyl-substituted diradical cation **14** (E = Me) (Scheme III), the counterpart **24** with the 2-methyl-2-pyrrolidinyl radical center is not prone to homolytic cleavage of the C–N bond. Moreover, cyclization of **24** (R = Me) appears to be much more efficient than proton loss from the CH_3-benzylic position which would have led to production of a 1,6-diradical and eventually to benzoindolizidine formation. This behavior is again different from that of the phenyl-substituted analogue from which benzoindolizidine formation occurs.

The photochemistry of the silicon-substituted *N*-xylyl-2-methylpyrrolinium perchlorate **4** stands in dramatic contrast to that of the protio analogue **3**. In the case of **4**, irradiation (Vycor, MeCN) followed by basic workup and chromatographic separation leads to isolation of only the benzoindolizidine **30** in a 52% yield.

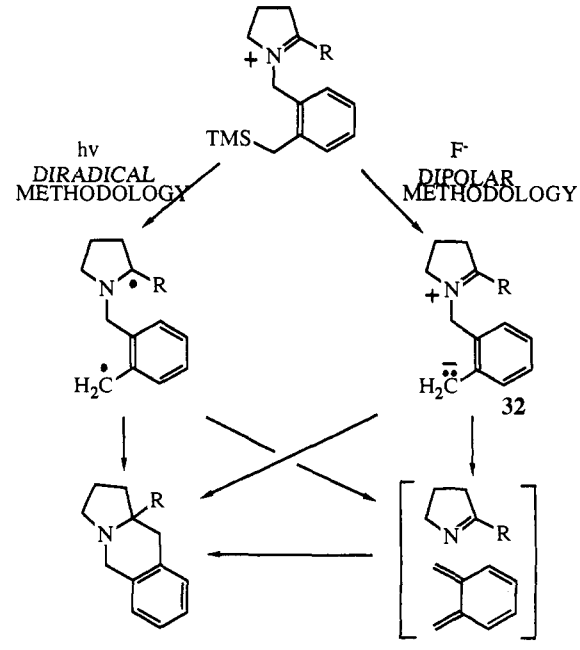


4 **30** **31**

The structure of **30** is clearly evident on the basis of its spectroscopic properties and a comparison with those of the related indolizidine **13**. Careful examination of the crude photolysate failed to reveal the presence of material which could be characterized as a silicon-containing benzopyrrolizidine analogous to **22** or **23**. Thus, the presence of the trimethylsilyl moiety in **4** has resulted in a dramatic alteration in the chemoselectivity of the *N*-xylylpyrrolinium salt photocyclization processes. This marked change appears to be associated with the introduction of a rapid pathway for decay of the intermediate diradical cation **31** through desilylation of cation radical grouping. Thus, we see again the effects of cation radical desilylation on the nature of electron-transfer processes of arene–iminium salt systems.

Dipolar vs. Diradical Cyclization Methodologies. The photocyclization reactions of the silicon-containing *N*-xylylpyrrolinium salts, proceeding by sequential electron-transfer–desilylation mechanisms, represent "diradical cyclization" methodologies for the preparation of N-heterocyclic compounds (Scheme VII). We have described in earlier reports[11] how strategies based upon this

Scheme VII



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methodology can serve as the basis for synthetic approaches for construction of the key ring systems found in several alkaloid families. The complementary charge affinity presented by the iminium cation grouping and carbon–silicon bond[12] in these *N*-xylylpyrrolinium salts gives rise to the possibility that an alternative methodology based upon "dipolar cyclization" processes might be applicable in these systems. Accordingly, fluoride ion induced reactions of these salts, occurring via intermediates which are the reactive equivalent to the dipolar species **32** (Scheme VII),[13] appear to be reasonable for generation of the cyclization products. A cyclization reaction of this type has been uncovered in recent efforts by Takano and his co-workers[14] focusing on the fluoride ion induced transformation of the 2-xylyl-3,4-dihydroisoquinolinium chloride **33** to the protoberberine alkaloid, xylopinine (**34**). The electronic features of the dipolar intermediates **32** suggest that they should also be well suited to homolytic fragmentation processes leading to production of *o*-xylylene and the corresponding pyrrolines (Scheme VII). Fluoride-promoted fragmentation processes of closely related (silylmethyl)benzyl ammonium salts **35** serve as useful methods for o-xylylene synthesis.[15] As discussed above, the *o*-xylylene–imine pairs generated by fragmentation of **32** are capable of participating in Diels–Alder cycloaddition processes which lead to the same types of products as those arising via the dipolar cyclization route. In this way the dipolar and diradical processes could have much in common.

As a result of the methodological similarities between the dipolar and diradical routes outlined in Scheme VII, we have briefly explored the ground-state, fluoride ion promoted chemistry of the silyl-*N*-xylylpyrrolinium perchlorates **4** and **6**. Reaction of **6** with cesium fluoride (5 equiv) in anhydrous acetonitrile at 25 °C led to low-yielding (16%) production of 2-phenyl-1-pyrroline (**10**). None of the benzoindolizidine **13** could be detected in the reaction mixture even by GLC methods. Interestingly, when reactions of either pyrrolinium salt **4** or **6** with cesium fluoride are conducted at higher temperatures in either acetonitrile (85 °C) or absolute ethanol (80 °C) only the respective benzoindolizidines **30** and **13**

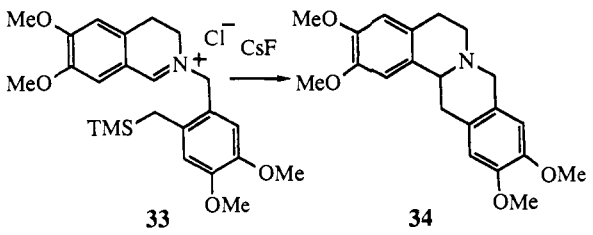
(11) (a) Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228. (b) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1985**, *40*, 5667. (c) Ho, G. D.; Lan, A. J. Y.; Mariano, P. S. *Tetrahedron Lett.* **1985**, 5867.

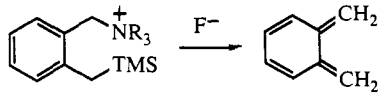
(12) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 97–124.

(13) The actual intermediate in this process may well be an ate complex formed by nucleophilic addition of fluoride to silicon. If, on the other hand, a true dipolar intermediate is involved, the differences between it and the corresponding diradical might be subtle, since they might merely reflect extreme valence bond contributors to one species.

(14) Takano, S.; Numata, H.; Ogasawara, K. *J. Chem. Soc., Chem. Commun.* **1982**, 769.

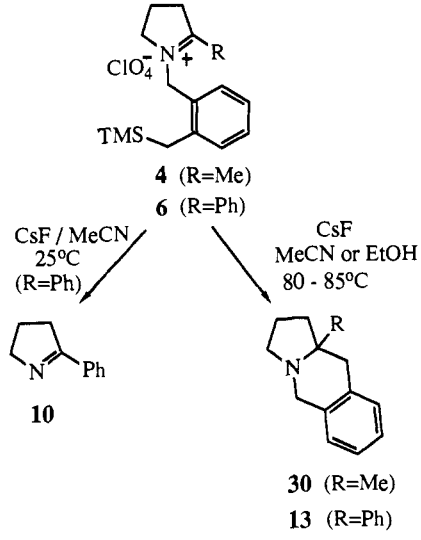
(15) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863; **1981**, *103*, 476.



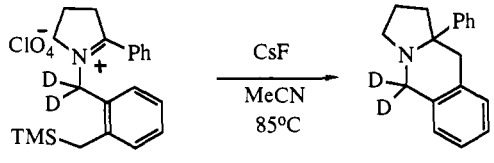


35

are formed in variable (12–31%) yields. The observed temperature effect noted in this albeit preliminary study is consistent with observations reported by Takano,[14] who noted that xylopinine (**34**) formation from **33** occurs only when reactions are conducted in refluxing ethanol.



In order to determine if the temperature-dependent cyclization process noted above is due to the operation of a dipolar fragmentation–cycloaddition mechanism, studies were conducted on the specifically deuteriated *N*-xylylpyrrolinium salt **18**. Reaction of **18** with cesium fluoride in acetonitrile at 85 °C furnished only the 2,2-dideuterioindolizidine **19**. This result strongly suggests that the dipolar cyclization route is responsible for the fluoride-induced cyclization reaction.



While the factors governing the nature of the dipolar cyclization processes are not clear at this time,[16] it is obvious that this methodology is far less efficient than the photochemical approaches described for generation of benzoindolizidines from the corresponding silicon-substituted *N*-xylylpyrrolinium salts. It is important to note that this same conclusion was reached in earlier efforts with allylsilane–iminium salt systems in which the efficiencies of sequential electron-transfer–desilylation routes were compared to those of closely related fluoride ion induced, dipolar cyclization pathways.[17]

(16) Studies of this type are currently being conducted by G. D. Ho and P. S. Mariano.

Experimental Section

General. NMR spectra were recorded with $CDCl_3$ solutions by using a Varian XL-200, XL-100, and EM-360 or a Bruker AM-400 instrument. 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-500-56 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 a Dupont 21-390, Hitachi RMU-6E, or VG-7070 instrument. Elemental analyses were performed by F. Kasler at the University of Maryland. Gas chromatographic analyses were performed on a Varian-940 (FID) instrument. Melting points are reported uncorrected. Column chromatography was performed by using Merck Silica Gel (230–400 mesh). Molecular distillations were conducted at reduced pressure with a Kugelrohr apparatus.

Preparative photolyses were conducted by use 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 each irradiation was followed by NMR, UV, or GLC, and, when ca. 75% of the starting material (iminium salt or arene) had been consumed, the photolysis was terminated and the photolysate was concentrated in vacuo. The residue was dissolved in $CHCl_3$, washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated in vacuo to give a residue which was subjected to chromatographic separation.

Preparation of *o*-((Trimethylsilyl)methyl)benzyl Alcohol (12). This substance was prepared by a different method than that developed earlier by Swenton.[4] A solution of *o*-methylbenzyl alcohol (10 g, 0.08 mol), *n*-butyllithium (272 mL, 1.5 M, 0.4 mol), and tetramethylethylenediamine (0.4 mol) in THF was stirred at 25 °C for 3. 5 h under N_2, poured into saturated $NaHCO_3$, and extracted with Et_2O. The ethereal layer was washed with 3% aqueous H_2SO_4 and saturated $NaHCO_3$, dried, and concentrated in vacuo, giving the crude O,C-bissilylated compound: ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 0.10 (s, 9 H), 2.10 (s, 2 H), 4.61 (s, 2 H), 6.8–7.5 (m, 4 H). A solution of this bis(trimethylsilyl) compound in 80 mL of 1:1 THF–H_2O containing 2 mL of H_2SO_4 was stirred for 2 h, poured into saturated $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with saturated $NaHCO_3$, dried, and concentrated, giving after molecular distillation (0.1 torr, 75 °C) 13.9 g (87%) of *o*-((trimethylsilyl)methyl)benzyl alcohol (**12**). Spectroscopic data not included in the original description of this substance[4] include the following: ^{13}C NMR δ −1.4 (Me_3Si), 22.8 (CH_2Si), 63.4 (CH_2O), 124.4, 127.5, 128.1, 129.3 (aromatic), 137.2, 138.6 (aromatic).

Preparation of *o*-((Trimethylsilyl)methyl)benzyl Bromide (9). A solution of the benzyl alcohol **12** (2.83 g, 0.015 mol) in 20 mL of Et_2O containing triphenylphosphine (4.20 g, 0.016 mol) and carbon tetrabromide (5.31 g, 0.016 mol) was stirred at 25 °C for 0.5 h, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (hexane) to yield 3.65 g (97%) of the desired bromide **9**: IR ($CHCl_3$) 2955, 1250, 1153, 845, 605 cm^{-1}; ^1H NMR δ 0.00 (s, 9 H), 2.24 (s, 2 H), 6.697–7.30 (m, 4 H); ^{13}C NMR δ −1.4 ($Si(CH_3)_3$), 23.2 ($ArCH_2S$), 32.6 ($ArCH_2Br$), 124.6, 128.5, 129.5, 130.5 (aromatic nonquaternary), 133.8, 139.5 (quaternary aromatic); mass spectrum, *m/e* (relative intensity) 256 (2), 258 (3), 178 (3), 177 (12), 104 (100); high-resolution mass spectrum, *m/e* 256.0257, 258.0246 ($C_{11}H_{17}SiBr$ requires 258.0230).

Preparation of *o*-((Trimethylsilyl)methyl)benzyl Iodide (11). A solution of the benzyl bromide **45** (0.58 g, 0.23 mmol) in 70 mL of acetone was stirred at 25 °C for 4 min, poured into saturated $NaHCO_3$, and extracted with Et_2O. The ethereal layer was dried and concentrated in vacuo, giving 0.65 g (94%) of the pure benzyl iodide **11**: IR ($CHCl_3$) 2950, 1160, 850 cm^{-1}; ^1H NMR δ 0.00 (s, 9 H), 2.16 (s, 2 H), 4.38 (s, 2 H), 6.91–7.30 (m, 4 H); ^{13}C NMR δ −1.3 ($Si(CH_3)_3$), 6.2 (CH_2I), 24.0 (CH_2Si), 124.9, 128.2, 129.9, 130.1, 135.0, 139.2 (aromatic); high-resolution mass spectrum, *m/e* 304.0138 ($C_{11}H_{17}SiI$ requires 304.032).

Preparation of 2-Methyl-1-(*o*-xylyl)-1-pyrrolinium Perchlorate (3). A solution of 2-methyl-1-pyrroline (**7**) (0.50 g, 6.0 mmol) and α-bromo-*o*-xylene (**18**) (2.60 g, 14.0 mmol) in anhydrous ether was stirred at 25 °C under N_2 for 16 h. The crystalline pyrrolinium bromide (0.85 g, 53%) was separated by filtration: ^1H NMR 2.00–2.48 (m, 2 H), 2.32 (s, 3 H), 2.75 (s, 3 H), 2.54 (t, 2 H), 4.03 (t, 2 H), 5.09 (s, 2 H), 7.28 (s, 4 H). This material was subjected to ion exchange by passing a MeOH solution through a Dowex-1 column (ClO_4^- form) to provide, after recrystallization from EtOH, 0.42 g (23%) of pure pyrrolinium perchlorate **3**: ^1H NMR δ 2.00–2.48 (m, 2 H), 2.29 (s, 3 H), 2.64 (s,

(17) We have found that diradical cyclization processes induced by sequential electron-transfer–desilylation pathways are superior to corresponding fluoride ion promoted cyclizations in a number of different systems (ref 11a and 11b).

3 H), 3.10–3.62 (br t, 2 H), 3.67–4.21 (br t, 2 H), 4.98 (s, 2 H), 7.23 (s, 4 H); ^{13}C NMR δ 18.2 ($ArCH_3$), 18.8 (N=CCh_3), 19.5 (pyrroline C-4), 41.8 (pyr C-3), 53.0 (pyr C-5), 60.8 (NCH_2), 127.9, 130.2, 130.5, 132.1 (aryl), 130.3, 138.5 (aryl), 194.2 (C=N); UV (CH_3CN) λ_{max} 264 nm (482); mass spectrum, *m/e* (relative intensity) 188 (M – ClO_4^-, 10.6), 187 (27.1), 172 (53.5), 105 (100); high-resolution mass spectrum, *m/e* 188.1417 (M – ClO_4^-) ($C_{13}H_{18}N$ requires 188.1394).

Preparation of 2-Methyl-1-(*o*-((trimethylsilyl)methyl)benzyl)-1-pyrrolinium Perchlorate (4). An acetonitrile solution of the (trimethylsilyl)benzyl bromide **9** (700 mg, 2.7 mmol) and 500 mg (6.0 mmol) of 2-methyl-1-pyrroline (**7**) containing silver perchlorate (540 mg) was stirred for 1.0 h and filtered. Concentration in vacuo of the filtrate gave a residue which was subjected to silica gel column chromatography (2% CH_3OH–$CHCl_3$) to generate 402 mg (41%) of the pure trimethylsilylated xylylpyrrolinium perchlorate **4**: ^{1}H NMR δ 0.00 (9 H), 2.17 (s, 2 H, Me_3SiCH_2), 2.22 (m, 2 H), 2.62 (s, 3 H, CH_3), 3.43 (t, 2 H, pyr H-3), 4.00 (t, 2 H, pyr H-5), 4.97 (s, 2 H, NCH_2), 6.96–7.43 (m, 4 H, aromatic); ^{13}C NMR δ –1.8 ($SiMe_3$), 17.6 (CH_3), 17.7 ($SiCH_2$), 23.5 (pyrroline C-4), 40.9 (pyr C-3), 52.0 (pyr C-5), 59.6 (NCH_2), 125.4, 128.9, 129.1, 130.0 (aromatic), 126.6, 139.9 (aromatic), 192.5 (C=N); UV (CH_3CN) λ_{max} 271 nm (1250); mass spectrum, *m/e* (relative intensity) 259 (M – $HClO_4$, 23.5), 244 (14.5), 186 (8.7), 177 (20.5), 172 (15.1), 104 (16.2); high-resolution mass spectrum, *m/e* 259.1747 ($C_{16}H_{25}NSi$ requires 259.1738).

Preparation of 1-(2′-Methylbenzyl)-2-phenyl-1-pyrrolinium Perchlorate (5). A solution of 2-phenyl-1-pyrroline (**10**) (5.00 g, 0.034 mol) and 4.6 mL (0.034 mol) of 2-(bromomethyl)toluene (**8**) in 10 mL of anhydrous tetrahydrofuran was stirred for 70.5 h under an N_2 atmosphere. Filtration provided a white, hydroscopic powder (4.50 g) characterized as the pyrrolinium bromide. This material was immediately converted to the more easily handled perchlorate salt by ion exchange with the use of Dowex-1 resin. Concentration of the methanol eluant from this column gave 3.32 g of 28% of 1-(2′-methylbenzyl)-2-phenyl-1-pyrrolinium perchlorate (**5**): mp 118.5–120 °C; IR ($CHCl_3$) 3010, 1640, 1600, 1445, 1370, 1090, 620 cm^{-1}; ^{1}H NMR δ 2.09 (s, 3 H, $ArCH_3$), 2.1–2.8 (m, 2 H, pyrroline H-4), 3.84 (t, 2 H, pyrroline H-3), 4.28 (t, 2 H, pyrroline H-5), 5.22 (s, 2 H, NCH_2Ar), 7.32 (s, 4 H, aryl), 7.75 (m, 5 H, Ph); UV (CH_3CN) λ_{max} 261 nm (ϵ 11 000).

Anal. Calcd for $C_{18}N_{20}NClO_4$: C, 61.80; H, 5.76; N, 4.00. Found: C, 61.81; H, 5.80; N, 3.88.

Preparation of 1-(2′-((Trimethylsilyl)methyl)benzyl)-2-phenyl-1-pyrrolinium Perchlorate (6). A solution of 2-phenyl-1-pyrroline (**10**) (0.72 g, 0.5 mmol) and *o*-((trimethylsilyl)methyl)benzyl iodide (**11**) (1.51 g, 0.50 mmol) was stirred under N_2 for 9 h at 25 °C. The resultant thick oil was triturated with Et_2O to give the pyrrolinium iodide (1.64 g, 74%) as a crystalline solid. This substance was converted to the desired pyrrolinium perchlorate by elution of a methanol solution through a Dowex-1 ion-exchange column (ClO_4^- form) followed by concentration and recrystallization from EtOH. This gave 1.08 g (51%) of pure pyrrolinium perchlorate **6**: mp 144–146 °C; IR ($CHCl_3$) 1650, 1450, 1260, 1100, 860 cm^{-1}; ^{1}H NMR δ –0.21 (s, 9 H, Me_3Si), 1.83 (s, 2 H, CH_2SiMe_3), 2.33–2.49 (m, 2 H, pyrroline H-4), 3.68 (t, 2 H, pyrroline H-3), 4.26 (t, 2 H, pyrroline H-5), 5.14 (s, 2 H, NCH_2), 7.00–7.31, 7.57–7.93 (m, 9 H, aryl); ^{13}C NMR δ –2.0 (Me_3Si) 18.1 (C-4 pyrroline), 23.3 (CH_2Si), 40.9 (C-3 pyrroline), 53.6 (C-5 pyrroline), 60.0 (NCH_2), 125.3, 126.9, 127.0, 128.4, 129.3, 129.4, 129.5, 130.0, 133.8, 140.0 (aromatic), 187.7 (C=N); UV (CH_3CN) λ_{max} 262 nm (ϵ 9400).

Anal. Calcd for $C_{21}H_{28}NSiClO_4 \cdot (^1/_3H_2O)$: C, 58.93; H, 6.59; N, 3.27; Cl, 8.38. Found: C, 59.17; H, 6.78; N, 3.15; Cl, 8.28.

Irradiation of 2-Methyl-1-(*o*-xylyl)-1-pyrrolinium Perchlorate (3). Formation of the Benzopyrrolizidine 22. A nitrogen-purged solution of the xylylpyrrolinium perchlorate **3** (100 mg, 0.35 mmol) in 120 mL of CH_3CN was irradiated with Vycor filtered light for 3.5 h and concentrated in vacuo. The residue was dissolved in $CHCl_3$, washed with $NaHCO_3$, dried, and concentrated in vacuo to provide 65 mg (100%) of nearly pure (ca. 90%) benzopyrrolizidine **22**. Preparative TLC gave 35 mg (54%) of pure **22**: ^{1}H NMR δ 1.48 (s, 3 H, CH_3), 1.92 (m, 4 H, pyrrolidine H-3, H-4), 2.24 (s, 3 H, CH_3), 2.64–2.70 (dd, 1 h, pyrrolidine H-5 endo), 3.39–3.47 (dd, 1 H, pyrrolidine H-5 exo), 3.86 and 4.44 (ABq, 2 H, NCH_2), 6.98–7.25 (m, 3 H); ^{13}C NMR δ 18.6 (CCH_3), 25.5 (pyr C-4), 29.0 (aryl CH_3), 39.1 (pyr C-3), 57.0 (pyr C-5), 58.1 (NCH_2), 77.3 (pyr C-2), 119.3, 128.1 (aryl CH), 132.7, 137.0, 147.8 (aryl quaternary); mass spectrum, *m/e* (relative intensity) 187 (M^+, 18), 172 (M^+ – CH_3, 100), 157 (9); high-resolution mass spectrum, *m/e* 187.1356 ($C_{13}H_{17}N$ requires 187.1351).

Irradiation of 2-Methyl-1-(*o*-((trimethylsilyl)methyl)benzyl)-1-pyrrolinium Perchlorate (4). Preparation of the Benzoindolizidine 30. An N_2-purged solution of the pyrrolinium perchlorate **4** (160 mg, 0.44 mmol) in 120 mL of CH_3CN was irradiated with Vycor filtered light for 3.25 h. The photolysate was subjected to the familiar workup procedure (see above), yielding 96 mg of the crude benzoindolizidine **30** (ca. 60% purity). Final purification was by preparative GLC (1.5 ft × 0.5 in., ~10% OV-101, 130 °C) and gave 43 mg (52%) of **30**: ^{1}H NMR δ 0.97 (s, 3 H, CH_3), 1.76 (m, 4 H, pyrrolidine H-3 and H-4), 2.62 (d, 1 H, pyr H-5 endo), 2.82 (d, 1 H, pyr H-5 exo), 2.84 (m, 2 H, CCH_2Ar), 3.75 and 3.93 (AB-q, 2 H, NCH_2), 7.08–7.17 (m, 4 H, aromatic); ^{13}C NMR δ 20.0 (CH_3), 21.0 (pyrrolidine C-4), 39.0 (pyr C-3), 39.8 (CCH_2Ar), 49.6 (pyr C-5), 51.6 (NCH_2), 59.4 (pyr C-2), 125.8, 126.5, 129.2 (aromatic), 134.0, 134.8 (aromatic); mass spectrum, *m/e* (relative intensity) 187 (M^+, 14), 172 (M – CH_3, 100), 104 (26); high-resolution mass spectrum, *m/e* 187.1356 ($C_{13}H_{17}N$ requires 187.1351).

Irradiation of 1-(2′-Methylbenzyl)-2-phenyl-1-pyrrolinium Perchlorate (5). Preparation of Benzoindolizidine 13. A nitrogen-purged solution of 1-(2′-methylbenzyl)-2-phenyl-1-pyrrolinium perchlorate (**5**) (300 mg, 0.85 mmol) in spectrograde methanol was irradiated with Corex filtered light in a preparative apparatus for 4 h. Concentration of the crude photolysate afforded a residue which was dissolved in $CHCl_3$, washed with saturated $NaHCO_3$ and brine, dried, and concentrated in vacuo, yielding an oil which was subjected to chromatographic separation by TLC (silica gel, 1:1 ether–hexane). This gave 19 mg (17%) of 2-phenyl-1-pyrroline (**10**) and 38 mg (18%) of pure benzoindolizidine **13**: IR ($CHCl_3$) 2940, 1605, 1500, 1450, 700 cm^{-1}; ^{1}H NMR δ 1.75 (m, 3 H), 2.10 (m, 1 H), 2.67 (q, 1 H), 2.92 and 3.10 (ABq, 2 H), 3.21 (m, 1 H), 3.74 and 3.80 (ABq, 2 H), 7.1–7.2 (m, 7 H, aromatic), 7.55 (dd, 2 H, aromatic); ^{13}C NMR δ 22.2, 36.8, 41.6, 50.0, 53.1, 65.5, 125.5, 125.7, 125.9, 126.3, 126.4, 127.9, 128.3, 135.3, 136.3, 149.0; mass spectrum, *m/e* (relative intensity) 249 (64), 220 (12), 172 (76), 170 (17), 144 (77), 118 (27), 104 (100), 91 (24); high-resolution mass spectrum, *m/e* 249.1500 ($C_{18}H_{19}N$ requires 249.1507).

Irradiation of 1-(2′-((Trimethylsilyl)methyl)benzyl)-2-phenyl-1-pyrrolinium Perchlorate (6). Preparation of Benzoindolizidine 13. A nitrogen-purged solution of the pyrrolinium perchlorate **6** (100 mg, 0.024 mmol) in 160 mL of CH_3CN was irradiated with Corex filtered light in a preparative apparatus for 45 min. The crude photolysate was concentrated, giving a residue which was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with saturated $NaHCO_3$, dried, and concentrated in vacuo, giving an oil which was subjected to silica gel column chromatography yielding 28 mg (40%) of the benzoindolizidine **13**. This substance has equivalent chemical and physical properties to the photoproduct arising by irradiation of the pyrrolinium perchlorate **5**.

Preparation of 1-Benzyl-2-methyl-1-pyrrolinium Perchlorate (21). A solution of 2-methyl-1-pyrroline (**7**) (1.0 g, 12.0 mmol) and benzyl iodide in ether was stirred at 25 °C for 6 h. Concentration in vacuo followed by chromatography on silica gel (3% CH_3OH–$CHCl_3$) gave 1.21 g of the crude iodide salt, which was subjected to ion exchange by eluting a CH_3OH solution through Dowex-1 (ClO_4^- form). Concentration of the CH_3OH eluant gave 1.13 g (34%) of the pure benzylpyrrolinium perchlorate **21**: ^{1}H NMR δ 2.23 (m, 2 H), 2.61 (s, 3 H), 3.36 (t, 2 H), 3.93 (t, 2 H), 4.97 (s, 2 H), 7.42 (s, 5 H); ^{13}C NMR δ 17.0 (N=CCH_3), 17.3 (pyr C-4), 40.4 (pyr C-3), 53.7 (pyr C-5), 59.3 (NCH_2), 128.6, 128.9, 128.9 (aryl), 129.9 (aryl), 192.0 (C=N); UV (CH_3CN) λ_{max} 257 nm (383); mass spectrum, *m/e* (relative intensity) 173 (M – $HClO_4$, 28.4), 91 (100), 82 (8.4), 77 (9.2); high-resolution mass spectrum, *m/e* 173.1195 ($C_{12}H_{15}N$ requires 173.1186).

Irradiation of 1-Benzyl-2-methyl-1-pyrrolinium Perchlorate (21). Preparation of the Benzopyrrolizidine 23. A solution of the benzylpyrrolinium perchlorate **21** (200 mg, 0.73 mmol) in 120 mL was irradiated with Vycor filtered light for 3.5 h and concentrated in vacuo. The residue was dissolved in $CHCl_3$, washed with $NaHCO_3$, dried, and concentrated in vacuo, giving 102 mg (81%) of the benzopyrrolizidine **23** in ca. 95% purity. This material was not subjected to further purification: ^{1}H NMR δ 1.42 (s, 3 H, CH_3), 1.83 (m, 4 H, pyrrolidine H-3, H-4), 2.59 (dd, 1 H, pyr H-5 endo), 3.34 (dd, 1 H, pyr H-5 exo), 8.84 and 4.46 (ABq, 2 H, NCH_2), 7.16 (m, 4 H, aromatic); ^{13}C NMR δ 25.4 (pyr C-4), 29.0 (CH_3), 38.8 (pyr C-3), 57.7 (pyr C-5), 58.7 (N-CH_2), 75.8 (pyr C-2), 121.9, 122.6, 126.7, 127.2 (aromatic CH), 139.0, 148.8 (aromatic); mass spectrum, *m/e* (relative intensity) 173 (23), 158 (M^+ – CH_3, 100), 145 (M^+ – C_2H_4, 22); high-resolution mass spectrum, *m/e* 173.1208 ($C_{12}H_{15}N$ requires 173.1212).

Preparation of *o*-Methylbenzyl-α,α-d_2 Iodide. This substance was prepared starting with ethyl *o*-methylbenzoate by the following procedure. Reaction of the ester (0.50 g, 3.0 mmol) with $LiAlD_4$ (0.10 g, 2.4 mmol) in Et_2O gave after workup 0.39 g (100%) of *o*-methylbenzyl-α,α-d_2 alcohol **16**: (^{1}H NMR δ 2.37 (s, 3 H), 3.64 (s, 1 H), 6.98–7.38 (m, 4 H), suggesting 95% dideuterium incorporation). A solution of the alcohol (5.4 g, 44 mmol), triphenylphosphine (13.5 g, 44 mmol), and CBr_4 (17.1 g, 44 mmol) in Et_2O was stirred at 40 °C for 3 h, filtered, and concentrated in vacuo, giving a residue from which 7.90 g of pure (98%) xylyl-d_2 bromide was separated by silica gel column chromatography (hexane) (^{1}H NMR δ 2.42 (s, 3 H), 7.10–7.42 (m, 4 H), indicating

95% dideuterium incorporation). A 250-mL methyl ethyl ketone solution of 21.0 g of NaI and 8.4 g of the xylyl-d_2 bromide was stirred at 60 °C for 2 h, filtered, and concentrated in vacuo, giving a residue which was dissolved in $CHCl_3$. The $CHCl_3$ solution provided, after being washed with saturated $NaHCO_3$, dried, and concentrated in vacuo, 6.3 g (62%) of the xylyl-α,α-d_2 iodide (^{1}H NMR δ 2.21 (s, 3 H), 6.90–7.26 (m, 4 H), indicating 95% dideuterium incorporation).

Preparation of 2-Methyl-1-(*o*-xylyl-α,α-d_2)-1-pyrrolinium Perchlorate (28). A mixture of 2.5 g (30 mmol) of 2-methyl-1-pyrroline (**7**) and 6.37 g (27 mmol) of *o*-methylbenzyl-α,α-d_2 iodide in Et_2O was stirred at 25 °C for 16 h, which yielded 6.35 g of a crystalline iodide salt which was separated by filtration, dissolved in MeOH, and eluted through a Dowex-1 ion-exchange column (ClO_4^- form) to provide, after concentration in vacuo and recrystallization from EtOH, 1.98 g (23%) of the pure xylyl-d_2-pyrrolinium perchlorate **28**: ^{1}H NMR δ 2.00–2.51 (m, 2 H), 2.32 (s, 3 H), 2.62 (s, 2 H), 3.35 (t, 2 H), 3.95 (t, 2 H), 7.34 (s, 4 H); ^{13}C NMR δ 18.1, 18.8, 19.4, 41.8, 51.8, 60.73, 127.8, 130.2, 130.2, 130.5, 132.1, 138.4, 194.2; mass spectrum, *m/e* (relative intensity) 190 (M – ClO_4, 5.5), 189 (30.6), 174 (76.5), 107 (100), 82 (17.2); high-resolution mass spectrum, *m/e* 190.1535 ($C_{13}H_{16}ND_2$ requires 190.1506).

Irradiation of 2-Methyl-1-(*o*-xylyl-α,α-d_2)-1-pyrrolinium Perchlorate (28). Deuterium Labeling Study of the Mechanism for Benzopyrrolizidine Formation. A solution of the *o*-xylyl-d_2-pyrrolinium perchlorate **28** (150 mg, 0.52 mmol) in 120 mL of CH_3CN was irradiated with Vycor filtered light for 3.5 h. The photolysate was concentrated in vacuo, diluted with aqueous $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving 89 mg of the benzopyrrolizidine-d_2 **29**. The extent and location of deuterium incorporation of this material were evaluated by use of ^{1}H NMR and mass spectrometries. Specifically, the high-resolution mass spectrum contained a peak at *m/e* 189.1483 ($C_{13}H_{15}ND_2$ requires 189.1480) with nearly the same relative intensity as that of the diprotio analogue **22**. The ^{1}H NMR spectrum displayed the total absence of the AB quartet at δ 3.86 and 4.44 (corresponding to the isoindoline NCH_2) and the presence of resonances corresponding to all other hydrogens.

Preparation of 2-Phenyl-1-(*o*-((trimethylsilyl)methyl)benzyl-α,α-d_2)-1-pyrrolinium Perchlorate (18). *o*-Methylbenzyl-α,α-d_2 alcohol **16** was converted to *o*-((trimethylsilyl)methyl)benzyl-α,α-d_2 iodide **17** by using the same procedure used to convert the *o*-methylbenzyl alcohol to iodide derivative **11** as described above. A mixture of the iodide **17** (1.40 g) and 2-phenyl-1-pyrroline (**10**) (0.7 g) was stirred at 25 °C for 20 h, giving a solid which was dissolved in MeOH and eluted through a Dowex-1 ion-exchange column (perchlorate ion form) to yield 1.50 g (77%) of the desired perchlorate salt **18**. This material was purified by recrystallization from EtOH: ^{1}H NMR δ 0.00 (s, 9 H, Me_3Si), 2.10 (s, 2 H), 2.55–2.72 (br q, 2 H), 2.92 (t, 2 H), 4.46 (t, 2 H), 7.18–7.52 (br m, 5 H), 7.78–8.05 (br m, 4 H).

Irradiation of 2-Phenyl-1-(*o*-((trimethylsilyl)methyl)benzyl-α,α-d_2)-1-pyrrolinium Perchlorate (18) in CH_3CN. A nitrogen-purged solution of the pyrrolinium-d_2 perchlorate **18** (70 mg, 0.17 mmol) in 150 mL of CH_3CN was irradiated with Corex filtered light for 45 min, diluted with aqueous $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving a residue which was subjected to silica gel chromatography (10% Et_2O–hexane) to yield 13 mg (32%) of the pure benzoindolizidine **19**. The deuterium content and location were assessed by ^{1}H NMR analysis: ^{1}H NMR δ 1.60–1.88 (br m, 3 H), 2.10 (m, 1 H), 2.67 (q, 1 H), 3.09 and 3.19 (AB q, 2 H), 3.21 (t, 1 H), 7.03–7.64 (br m, 9 H).

Reaction of 2-Phenyl-1-(*o*-((trimethylsilyl)methyl)benzyl)-1-pyrrolinium Perchlorate (6) under Fluoride Ion Induced Desilylation Conditions. A CH_3CN solution (50 mL) of the pyrrolinium perchlorate **6** (70 mg, 0.11 mmol) and 130 mg of CsF (0.85 mmol) was stirred at 25 °C for 40 h, concentrated in vacuo, diluted with aqueous $NaHCO_3$, and extracted with $CHCl_3$. Concentration in vacuo of the $CHCl_3$ layer gave 68 mg of a residue which was shown by GLC methods to contain exclusively 2-phenyl-1-pyrroline (**10**) and not to contain any of the benzoindolizidine **13**.

An ethanol (10-mL) solution of 50 mg (0.12 mmol) of the pyrrolinium perchlorate **6** and 110 mg (0.60 mmol) of CsF was stirred at 80 °C under N_2 for 20 h, cooled to 25 °C, filtered, and concentrated in vacuo, giving a residue which was shown by ^{1}H NMR and GLC methods to contain 8 mg (27%) of the benzoindolizidine **13** and none of 2-phenyl-1-pyrroline (**10**).

An reaction identical with that above with the exception that acetonitrile was used as solvent at 85 °C provided the benzoindolizidine **13** in a 31% yield and none of 2-phenyl-1-pyrroline (**10**).

Reaction of 2-Methyl-1-(*o*-((trimethylsilyl)methyl)benzyl)-1-pyrrolinium Perchlorate (4) under Fluoride Ion Induced Desilylation Conditions. An ethanol (10-mL) solution of 50 mg (0.14 mmol) of 2-methyl-1-(*o*-((trimethylsilyl)methyl)benzyl)-1-pyrrolinium perchlorate (**4**) and 130 mg (0.70 mmol) of CsF was stirred at 85 °C under N_2 for 20 h, cooled to 25 °C, filtered, and concentrated in vacuo, giving a residue which was shown by ^{1}H NMR and GLC to contain 3 mg (12%) of the benzoindolizidine **30**.

Fluoride Anion Induced Desilylation and Cyclization of Phenyl-1-(*o*-((trimethylsilyl)methyl)benzyl-α,α-d_2)-1-pyrrolinium Perchlorate (18) in CH_3CN at 85 °C. A solution of 50 mg (0.12 mmol) of the pyrrolinium perchlorate **18** in 10 mL of CH_3CN containing 120 mg (0.60 mmol) of CsF was stirred for 20 h at 85 °C, filtered, and concentrated in vacuo. The residue was subjected to silica gel chromatography (10% Et_2O–hexane) yielding 2 mg (7%) of the indolizidine **19**. ^{1}H NMR spectroscopic analysis indicated the content and location of deuterium as being identical with those in the product **19** obtained by irradiation of the pyrrolinium perchlorate **18**.

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