Electron-Transfer-Induced Photochemical Reactions of (Silylallyl)iminium and Benzylpyrrolinium Salts by Dual Diradical and Diradical Cation Cyclization Pathways

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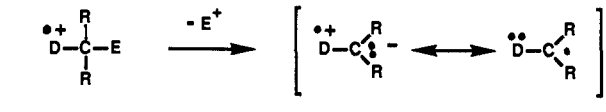
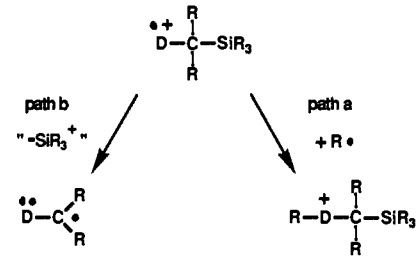
Abstract: The electron-transfer-induced photocyclization reactions of a series of *N*- and *C*-silylmethallyl-substituted iminium and 1-benzyl-1-pyrrolinium salts have been investigated in order to gain information about their mechanistic course and to probe their synthetic potential. The results obtained from these studies demonstrate that diradical cation intermediates formed in these processes can be transformed to products via two competing mechanistic pathways involving radical coupling or loss of allylic or benzylic electrofugal groups. Studies with the ortho CH_3 and ortho CH_2Si-*t*-$BuMe_2$ substituted *N*-benzyl-2-methylpyrrolinium perchlorates show that diradical cation coupling is the predominant mode followed for reaction of the intermediate singlet and triplet cation diradicals in either MeCN, MeOH, or Me_2CO. This pathway leads to exclusive formation of benzopyrrolizidine products. In contrast, the ortho CH_2SiMe_3 analogue photocyclizes in MeCN to form predominantly a benzoindolizidine product via a route involving desilylation of the intermediate cation diradical. The predominance of diradical cation desilylation over radical coupling in the ortho CH_2SiMe_3 system is lessened for reaction in MeOH and enhanced when acetone triplet sensitization is employed. Photocyclizations of the meta OH, OMe, OSi-*t*-$BuMe_2$, CH_3, CH_2Si-*t*-$BuMe_2$, and CH_2SiMe_3 substituted *N*-benzyl-2-methylpyrrolinium perchlorates proceed mainly or exclusively by cation diradical coupling mechanisms and provide the corresponding benzopyrrolizidines in modest to excellent yields. Cyclization in these systems is preferred at the position para to the arene ring substituent, and their selectivity increases as the substituent size increases. The results demonstrate that *N*-benzyliminium salts participate in a new and general photoinduced cyclization reaction that mimics the ground-state Pictet-Spengler analogue and has unique applications in the area of isoindoline synthesis. Similar mechanistic conclusions have been reached in studies with *N*- or *C*-(silylmethallyl)iminium salts containing deuterium labels that enable distinction between photocyclization pathways involving either desilylation or radical coupling of intermediate cation diradicals. In triplet-sensitized reactions of these substances, the desilylation pathway is followed exclusively while, in the direct-irradiation, singlet processes the desilylation and radical coupling modes are competitive. Solvent and substituent effects on the rates of cation diradical coupling have been observed and interpreted in terms of charge localization and frontier orbital considerations.

The area of electron-transfer (SET) photochemistry has been the subject of considerable interest over the past decade.[1] Investigations have focused not only on gaining a detailed understanding of the mechanisms of photochemical reactions operating by SET pathways but also on discovering new and synthetically useful chemical processes. A unique feature of this chemistry comes from the fact that photoinduced SET in donor–acceptor pairs results in the formation of charged and/or neutral radicals that serve as key reactive intermediates. Photoproducts are usually formed in these systems by secondary reaction of these initially formed ion or neutral radicals. Perhaps the most common solution-phase reactions, in which cation radicals participate, involve loss of an electrofugal group (Scheme I). This often occurs readily from a center adjacent to the positively charged radical site and leads to production of a conjugated, neutral radical. The acid–base chemistry of cation radicals bearing α-hydrogens (E = H in Scheme I) exemplifies this reaction type.[2] Similarly, desilylation reactions of α-silyl cation radicals (E = SiR_3 in Scheme I),[3] which mimic the facile Si–C heterolytic bond cleavages seen in related β-silyl carbocations,[4] are often efficient.

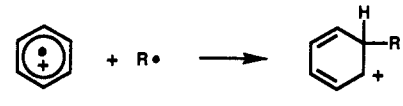
Scheme I



Scheme II



Scheme III



Processes in which the free-radical nature of cation radicals dominates the chemistry have been less often observed in the area of SET photochemistry. Thus, while radical coupling processes of these species are chemically reasonable and of potential use synthetically (see below), they are not a common occurrence when alternate electrofugal group loss pathways are available.[5,6] This

(1) (a) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 410. (b) Fox, M. A. In *Advances in Photochemistry*; Volmman, D. H., Hammond, G. S., Gollnick, K., Eds.; Wiley: New York, 1986; Vol. 13. (c) Mariano, P. S. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: London, 1984; Chapter 3. (d) Davidson, R. S. *Adv. Phys. Org. Chem.* **1983**, *19*, 1.

(2) (a) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472. (b) Sehested, K.; Holcman, J. *J. Phys. Chem.* **1978**, *82*, 651. (c) Nicholas, M.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165. (d) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 2867; *Ibid.* **1988**, *110*, 2872.

(3) (a) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617. (b) Ohga, K.; Yoon, U.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (c) Borg, R. M.; Heuckeroth, R. O.; Lan, A. J.; Quillen, S.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2728. (d) Lan, A. J. Y.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2738.

(4) Clovin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 15–20.

(5) (a) Mazzocchi, P. H.; Fritz, G. *J. Am. Chem. Soc.* **1986**, *108*, 5362. (b) Arnold, D. R.; Wong, P. C.; Marreulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609. (c) Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785.

(6) Cho, I. S.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 1590.

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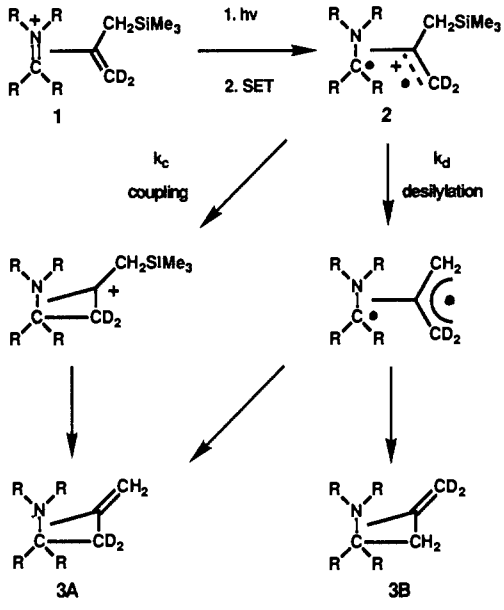
Scheme IV



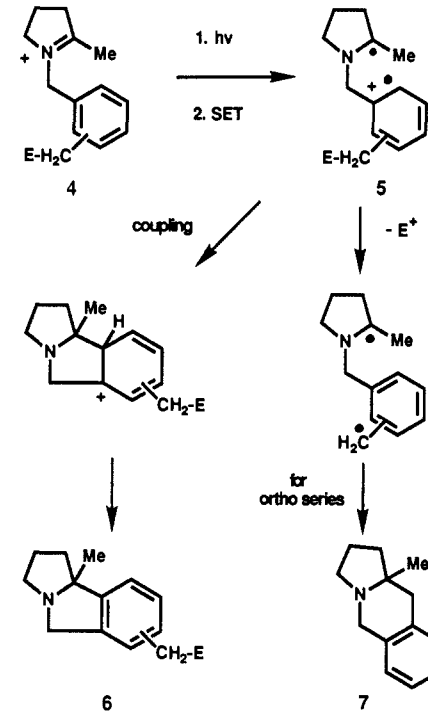
is somewhat surprising in light of the fact that cation radicals arising by donor–acceptor SET are often paired with neutral and anion-radical partners.

The studies described focus on the issue of the dual cationic (i.e., electrofugal group loss) vs radical (i.e., radical coupling) reactivity of cation radicals produced as intermediates in photo-SET reactions. Our goal at the outset of this work was to determine the mechanistic course of processes that proceed via the intermediacy of α-silyl cation radicals (Scheme II). Specifically, radical coupling of these species to neutral radicals (path a) could be competitive with the more typical[3] desilylation process (path b), since the former route leads to generation of stabilized β-silyl cations. This would be particularly relevant in intramolecular systems where radical coupling could have an entropic driving force. Other systems can be envisaged in which stabilization of resulting cations might serve to facilitate radical coupling reactions of radical cations. For example, addition of neutral radicals to arene cation radicals would result in the production of cyclohexadienyl cations, which are identical with those serving as intermediates in familiar electrophilic aromatic substitution reactions (Scheme III). While routes for electrophilic aromatic substitution stimulated by SET are not common,[7] processes of this type involving photogeneration and coupling of arene radical cations could find unique applications in synthetic contexts (see below).

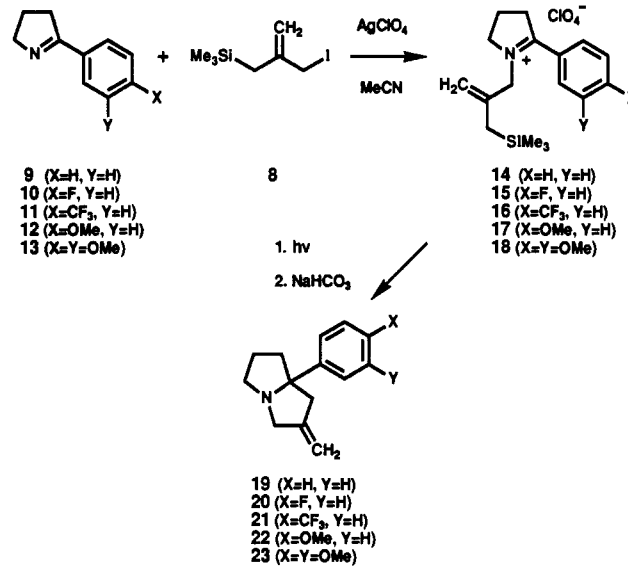
In the studies described below we have explored two types of SET-induced photocyclization reactions that have the potential of operating via the radical cation–neutral radical coupling mechanisms depicted in Schemes II and III or by alternative pathways involving electrofugal ($-H^+$ or $-SiR_3^+$) loss from the charged radical intermediates. Our primary aim was to develop an understanding of the factors (e.g., excited-state multiplicity, solvent, nature and location of substituents, and electrofugal group type) that influence the competition between radical coupling and electrofugal group loss pathways. Information of this type would have synthetic implications, so that these efforts were also designed to develop new and preparatively useful chemistry. In one phase of this study, we have explored photocyclization reactions of a series of regioselectivity deuterium-labeled (silylmethallyl)iminium salts of general structure **1** (Scheme IV). On the basis of earlier results from investigations with intermolecular systems,[3a,b] we anticipated that cyclization reactions of these systems would follow mechanistic routes in which excited-state SET leads to diradical

(7) (a) Cf. Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *26*, 53. (b) Sandararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5235, and references therein.

Scheme V



Scheme VI



cations **2**, which undergo subsequent reaction by desilylation (electrofugal group loss) or cyclization (radical coupling). Distinctions between these competitive pathways would be possible on the basis of an assessment of *d*-isotope distributions in cyclization products **3**. In another, yet related, phase of our investigations, SET photocyclization reactions of substituted 1-benzyl-2-methylpyrrolinium salts **4** (Scheme V) have been probed. These efforts grew out of earlier studies of arene–iminium salt photoaddition[3c] and photocyclization[3d] processes and were designed to evaluate the contributions of cyclization and electrofugal group ($-H^+$ or $-SiR_3^+$) loss reactions available to intermediate cation diradicals **5**. In the ortho-substituted series (**4** where CH_2E is ortho), these pathways would lead to formation of the respective benzopyrrolizidine and benzoindolizidine products **6** (E = H) and **7**.

Results

Synthesis and Photochemistry of 1-(Silylmethallyl)-2-arylpyrrolinium Perchlorates. A series of 1-(silylmethallyl)-2-arylpyrrolinium perchlorates differing in the nature of the para and

Table I. Photoreactions of the (Silylallyl)pyrrolinium Perchlorates **14–18**

pyrrolinium salt	solvent	filter[a]	pyrrolizidine product	% yield
14	MeCN	corex	**19**	58
14	MeOH	corex	**19**	62
15	MeCN	corex	**20**	46
15	MeOH	corex	**20**	55
16	MeCN	vycor	**21**	47
16	MeOH	vycor	**21**	43
17	MeCN	flint	**22**	55
17	MeOH	flint	**22**	50
18	MeCN	flint	**23**	40
18	MeOH	flint	**23**	39

[a] For wavelength cutoff characteristics, see the Experimental Section.

meta substituents on the aromatic groupings were employed in the first phase of this study. These substances were prepared by silver perchlorate promoted allylation of the known 2-aryl-1-pyrrolines **9–13**[8–10] with the Trost[11] [(trimethylsilyl)methyl]allyl iodide (**8**) (Scheme VI). The *N*-[(silylallyl)methyl]-2-aryl-1-pyrrolinium perchlorates **14–18** were formed in this way in yields ranging from 18 to 75%. Irradiations of these salts were conducted on nitrogen-purged solutions (ca. 1×10^{-3} M) in MeCN and MeOH, as solvent employing appropriate glass filters to prevent secondary reactions of the initially formed photoproducts. Basic workup of the photolysates followed by chromatographic separation on silica gel provided the respective pyrrolizidines **19–23**. The yields of these photocyclization processes are recorded in Table I.

Structural assignments to photoproducts **19–23** were made on the basis of their characteristic spectroscopic data and elemental compositions. Especially diagnostic were resonances in the ^{1}H NMR spectrum of each pyrrolizidine indicative of the exocyclic methylene protons at ca. 4.8 ppm and in the ^{13}C NMR spectrum for the methylene carbons at ca. 113 and 138 ppm and quaternary bridgehead carbon at ca. 61 ppm.

Synthesis and Photochemistry of the Regiospecifically Deuterium-Labeled (Silylmethallyl)pyrrolinium Perchlorates. In order to delineate the mechanistic pathways involved in the SET-induced photocyclization reactions of the (silylmethallyl)pyrrolinium salts shown in Scheme VI, regiospecifically deuterium-labeled analogues were required. The tetradeuterio salts **14-d_4–18-d_4** were selected for this purpose since the isotopic labeling patterns in these substances would enable differentiation between potentially competitive diradical cation coupling and electrofugal loss pathways and since preparation of these materials by sequences analogous to those shown in Scheme VI appeared possible. Accordingly, diethyl (trimethylsilyl)methyl)malonate (**24**), prepared by the Knapp[12] procedure, was reduced by using $LiAlD_4$ (98% d_4) under the conditions recommended by Marshall[13] to produce corresponding d_4-silylmethallyl alcohol **25**. The d_4 iodide **26** derived[11] from this alcohol was then used in allylation reactions with the 2-aryl-1-pyrrolines **9–13** to furnish the d_4 perchlorate salts **14-d_4–18-d_4** (Scheme VII).

Photocyclization reactions of these (d_4-silylmethallyl)-pyrrolinium salts were conducted under the same direct irradiation conditions (MeCN and MeOH) as used for the protio analogues. The pyrrolizidine products **19-d_4–23-d_4** isolated in pure form by chromatography were produced as mixtures of regioisotopomers (e.g., **19-d_4 A** and **B** from **14-d_4**). In order to determine the effects of solvent polarity, ionic strength, and silophiles, photocyclizations of **17-d_4** in solvents of differing polarity (MeOH, MeCN and

Scheme VII

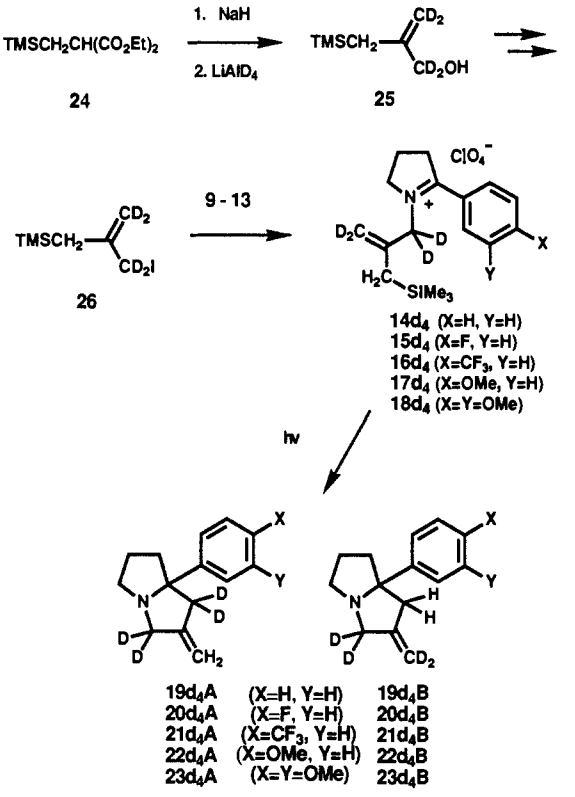


Table II. d_4-Pyrrolizidine **A:B** Isotopomer Ratios Obtained by ^{1}H NMR Analysis of the Products from Direct Irradiations of the d_4-Pyrrolinium Perchlorates **14-d_4–18-d_4**

d_4-pyrrolinium perchlorate	solvent	additive	d_4-pyrrolizidine	**A:B** isotopomer ratio
14-d_4	MeCN		**19-d_4**	1.48 ± 0.05
14-d_4	MeOH		**19-d_4**	1.61 ± 0.02
15-d_4	MeCN		**20-d_4**	1.70 ± 0.10
15-d_4	MeOH		**20-d_4**	1.87 ± 0.06
16-d_4	MeCN		**21-d_4**	1.34 ± 0.03
16-d_4	MeOH		**21-d_4**	1.63 ± 0.05
17-d_4	MeCN		**22-d_4**	2.74 ± 0.01
17-d_4	MeOH		**22-d_4**	3.55 ± 0.10
17-d_4	tBuOH		**22-d_4**	2.31 ± 0.09
17-d_4	MeCN	0.1 M (n-Bu)$_4$NClO$_4$	**22-d_4**	3.05 ± 0.09
17-d_4	MeOH	0.1 M (n-Bu)$_4$NF	**22-d_4**	3.72 ± 0.12
18-d_4	MeCN		**23-d_4**	3.17 ± 0.10
18-d_4	MeOH		**23-d_4**	4.83 ± 0.09

t-BuOH), in MeCN containing 0.1 M (n-Bu)$_4$NClO$_4$ and in MeOH containing 0.1 M (n-Bu)$_4$NF, were also probed. ^{1}H NMR analysis of the purified d_4-pyrrolizidines produced in these reactions (conducted repetitively (ca. three to five times) to provide statistically significant data) was used to determine the regioisotopomer (**A:B**) ratios of each of the pyrrolizidines. Comparisons of the intergrations for the exocyclic methylene H_8-exo and aryl proton resonances after corrections for the 2% protio components of these pyrrolizidines gave the average **A:B** isotopomer ratios recorded in Table II.

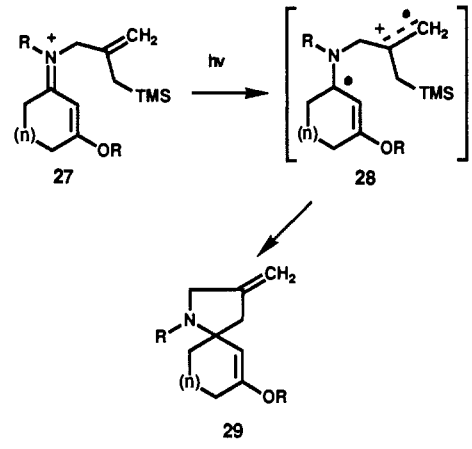
In order to obtain information about the effect of diradical cation multiplicity (singlet vs triplet) on the relative rates of competitive cyclization and desilylation of these intermediates, triplet-sensitized photoreactions of the (d_4-silylmethallyl)-pyrrolinium perchlorates were explored. On the basis of our previous observations,[3a,b] we anticipated that direct irradiation reactions of these substances would be initiated by electron transfer to the singlet excited states of the 2-arylpyrrolinium cation chromophores from the allylsilane donors (see below). Thus, the direct irradiation processes proceed via singlet diradical cation

(8) Mariano, P. S.; Leone-Bay, A. *Tetrahedron Lett.* **1980**, 4581.
(9) Bielawski, J.; Brandange, S.; Lindblom, L. *J. Heterocycl. Chem.* **1978**, *15*, 97.
(10) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136.
(11) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, 5023.
(12) Knapp, S.; O'Connor, U.; Mobilio, D. *Tetrahedron Lett.* **1980**, 4557.
(13) Marshall, J. A.; Anderson, N. H.; Hochstetler, A. R. *J. Org. Chem.* **1967**, *32*, 113.

Table III. d_4-Pyrrolizidine A:B Isotopomer Ratios Obtained by ^{1}H NMR Analysis of the Products from Xanthone-Sensitized Irradiations (MeCN) of d_4-Pyrrolinium Perchlorates **14**-d_4–**16**-d_4

d_4-pyrrolinium perchlorate	d_4-pyrrolizidine	A:B isotopomer ratio
14-d_4	**19**-d_4	0.96 ± 0.01
15-d_4	**20**-d_4	0.99 ± 0.02
16-d_4	**21**-d_4	0.98 ± 0.02

Scheme VIII



intermediates. Triplet diradical cations would be formed if SET was to occur in the iminium cation localized, triplet excited states of these linked donor–acceptor pairs. As a result we have probed the triplet-sensitized reactions of these substances. The aryl ketone xanthone was selected as a suitable sensitizer since it can be selectively irradiated at wavelengths (uranium glass filter, $\lambda >$ 320 nm) where the non-methoxy-substituted arylpyrrolinium perchlorates **14**-d_4-**16**-d_4 do not absorb light. In addition, while the triplet energies of these or related pyrrolinium salts are not easy to measure, they are estimated to be in the 60–62 kcal/mol range on the basis of the excited-state energies[14] of closely analogous styrene derivatives.[15] Thus, triplet energy transfer from xanthone (E_T = 74 kcal/mol)[16] to the arylpyrrolinium cation chromophores in **14**-d_4–**16**-d_4 should be exothermic.

Triplet-sensitized photoreactions of the salts **14**-d_4–**16**-d_4 (2.5×10^{-3} M) with xanthone (1.5×10^{-2} M), MeCN as solvent, and uranium glass filtered light led to production of the respective pyrrolizidines **19**-d_4-**21**-d_4. Control reactions in the absence of xanthone were explored. Under these conditions no pyrrolizidine products were produced. ^{1}H NMR analysis of the pyrrolizidines formed in repetitive triplet-sensitized reactions by using the methods described above enabled determination of the **A:B** regioisotopomer ratios recorded in Table III.

Synthesis and Photochemistry of Other Regiospecifically Deuterium-Labeled (Silylallyl)iminium Salts. The mechanistic course of other allylsilane–iminium salt SET-photocyclization reactions were also probed by using regiospecifically deuterium-labeled substrates. We had shown earlier[17] that cycloalkenylideniminium perchlorates related to **27** undergo cyclization upon direct irradiation to produce spirocyclic amine products of general structure **29** via the pathway depicted in Scheme VIII. In order to determine the contribution of diradical cation **28** cyclization vs desilylation in mechanistic routes for these processes, we have prepared the (d_4-silylmethallyl)-1-cyclohexeniminium perchlorates **32** and **33** by a modification of the sequences previously described.[17] Specifically, deuterioenaminone **31**, generated by N-allylation of β-amino ketone **30** with silylmethallyl iodide **26**, was transformed to the *O*-pivaloyl and *O*-methyl iminium

Scheme IX

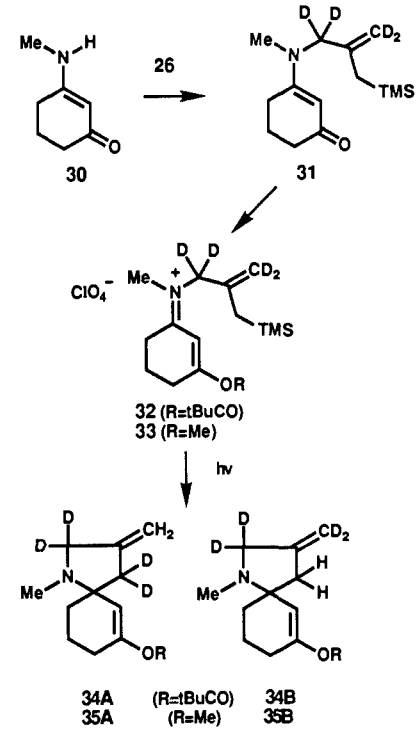


Table IV. A:B Isotopomer Ratios for Spirocyclic Amines **34** and **35** Produced by Direct Irradiations (MeCN) of the Cyclohexeniminium Perchlorates **32** and **33**

cyclohexeniminium salt	stereoisomer ratio	product	A:B isotopomer ratio[b]
32	2.0	**34**	8.8
32	1.4	**34**	7.6
32	0.9	**34**	6.2
33	2.8	**35**	4.8
33	1.8	**35**	4.2

[a] Stereoisomer (*E* vs *Z*) assignments have not been made. [b] The errors for these ratios were determined to be ca. ± 0.02 by multiple measurements for photoreaction of **33**.

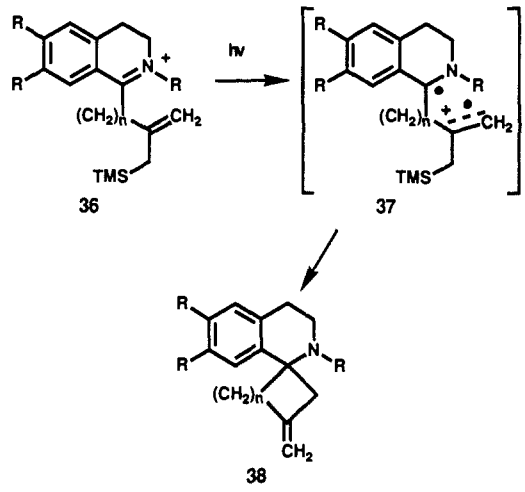
perchlorates **32** and **33** upon $AgClO_4$-induced acrylation or alkylation (Scheme IX). The iminium salts obtained in these ways were mixtures of *E* and *Z* stereoisomers, the relative composition of which could be determined by ^{1}H NMR methods. However, absolute stereochemical assignments to the stereoisomers unfortunately (see below) cannot be unambiguously made on the basis of the accumulated spectroscopic data. Finally, the proportions of *E* and *Z* isomers in both salts can be altered by trituration procedures, owing to their differential solubilities in $CHCl_3$–Et_2O solvent mixtures.

The d_4-iminium salts **32** and **33** of different *EZ*-isomer compositions (Table IV) were irradiated in MeCN solutions and with Corex glass filtered light. Workup of the crude photolysate by treatment with $NaHCO_3$ directly provided pure samples of spirocyclic amines **34** and **35** in high (84–98%) chemical yields (Scheme IX). Deuterium distributions (i.e., regioisotopomer **A:B** ratios) for these substances were determined by ^{1}H NMR intergrations of the exocyclic methylene (ca. 4.9 ppm) and vinyl (ca. 4.4–5.2 ppm) proton resonances. The results are summarized in Table IV. Irradiations of these salts were not conducted in MeOH owing to their instability in this nucleophilic solvent. *EZ* photoisomerization[18] in **32** and **33** occurs under the direct-irradiation conditions, and photostationary states are reached at ca. 50% conversion to the spirocyclic amine products. In addition,

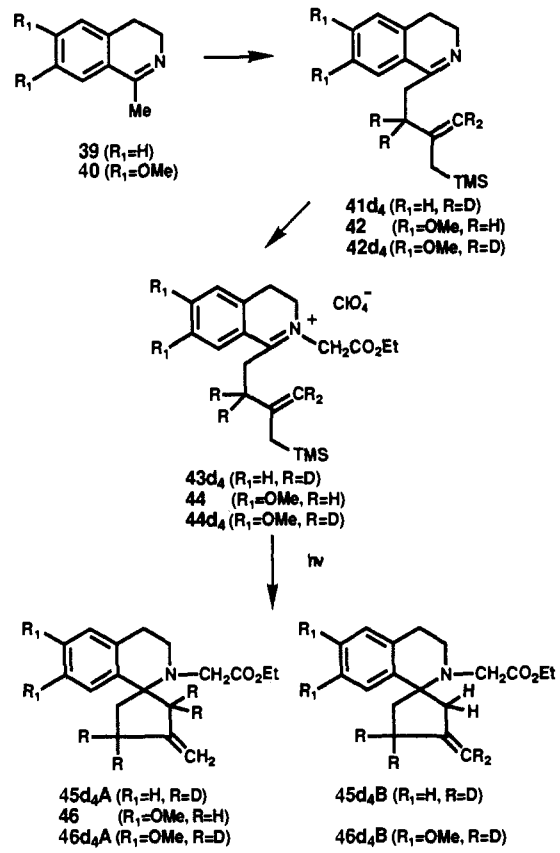
(14) (a) Murov, S. L., *Handbood of Photochemistry*; Marcel Dekker: New York, **1973**; pp 3–22. (b) Evans, D. F. *J. Chem. Soc.* **1959**, 2753.
(15) Mariano, P. S. *Tetrahedron Rep. No. 156* **1983**, *39*, 3879.
(16) Pownall, H. J.; Huber, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 6429.
(17) (a) Ullrich, J.; Chiu, F. T.; Tiner-Harding, T.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 220. (b) Chiu, F. T.; Ullrich, J.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228.

(18) (a) Childs has observed *E,Z* isomerization in the photochemistry of conjugated iminium salts (ref 18b). (b) Childs, R. F.; Dickie, B. *J. Chem. Soc., Chem. Commun.* **1981**, 1268.

Scheme X



Scheme XI



E,Z isomerization is the only pathway detected when these salts are subjected to xanthone triplet-sensitized irradiation.[18]

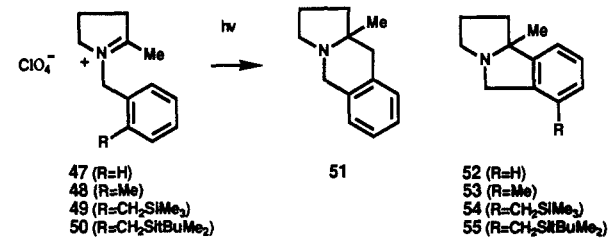
In earlier efforts,[19] we have shown that (silylalkenyl)-3,4-dihydroisoquinolinium salts related to **36** can be easily prepared and efficiently transformed to spirocyclic amines **38** by SET-induced photocyclization processes (Scheme X). The synthetic potential of this methodology has been demonstrated by its application to erythrina alkaloid synthesis.[19b] Our current interest in this chemistry focuses on determining the contributions of diradical cation **37** cyclization and desilylation pathways for photospirocyclization reactions related to the **36** to **38** conversions. The d_4-substituted dihydroisoquinolinium perchlorates **43**-d_4 and **44**-d_4 were selected to probe this question.

The protio analogue of **43**-d_4 has been prepared and subjected to photochemical study earlier.[19a] However, protiodimethoxy-

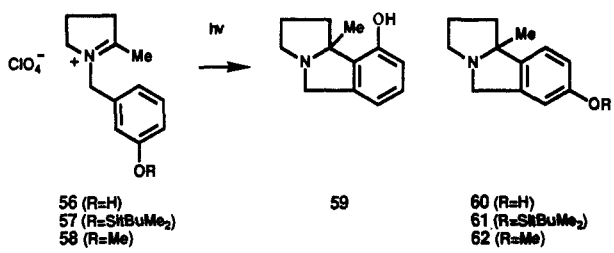
Table V. A:B Isotopomer Ratios for Spirocyclic Tetrahydroisoquinolines **45**-d_4 and **46**-d_4 Produced by Direct Irradiations (MeCN) of the (Silylmethallyl)dihydroisoquinolinium Perchlorates **43**-d_4 and **44**-d_4

dihydroisoquinolinium salt	product	A:B isotopomer ratio
41-d_4	**45**-d_4	1.56 ± 0.04
42-d_4	**46**-d_4	1.96 ± 0.01

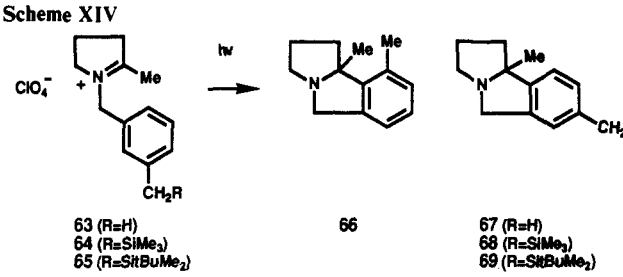
Scheme XII



Scheme XIII



Scheme XIV



dihydroisoquinolinium salt **44** was not included in our initial investigations; thus, we were obliged to prepare this substance and to demonstrate that it undergoes an SET-induced photocyclization reaction. This was easily accomplished starting with the known[20] 1-methyl-3,4-dihydroisoquinoline **40** (Scheme XI), which yielded the silylmethallyl derivative **42** upon metalloenamine generation with *n*-BuLi and C-alkylation with the Trost iodide **8**. $AgClO_4$-assisted N-alkylation of **42** with ICH_2CO_2Et then gave **44**, a substance that undergoes smooth (70%) photocyclization to produce spirocyclic tetrahydroisoquinoline **46** upon irradiation in the MeCN. The d_4-dihydroisoquinolinium salts **43**-d_4 and **44**-d_4 were prepared by the sequences shown in Scheme XI starting with dihydroisoquinolines **39**[21] and **40**.[20] Irradiation (Corex and uranium glass filtered light, respectively, for **43**-d_4 and **44**-d_4) of these perchlorate salts in MeCN solutions gave, after basic workup and chromatographic separation, d_4 spirocyclic amines **45**-d_4 and **46**-d_4 as mixtures of regioisotopomers. Isotopomer (A:B) ratios were determined by ^1H NMR analyses of products from repetitive reactions by integrations of the exocyclic methylene (4.9 ppm) vs either the ester OCH2 (4.2 ppm) of the aryl (7.1 ppm) proton resonances for **45**-d_4 and of the exocyclic methylene (4.9 ppm) vs the aryl (6.5 ppm) proton resonances for **46**-d_4. The results are displayed in Table V.

Synthesis and Photochemistry of Substituted *N*-Benzylpyrrolinium Salts. The second phase of our studies probing competitive radical cyclization vs electrofugal group loss pathways

(19) (a) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1985**, *50*, 5667. (b) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 1478.

(20) Spath, E. *Monatsh. Chem.* **1921**, *42*, 97.

(21) Wehrli, P. A.; Schaaer, B. *Synthesis* **1974**, 288.

Table VI. Photoproducts and Yields from Photocyclization Reactions of the Ortho-Substituted Benzylpyrrolinium Perchlorates **48–50**

pyrrolinium salt	irradiation conditions	isolated yield,[a] %	product (yield, %)[b]
48	direct/MeCN	99[c]	**53** (99)
49	direct/MeCN	99	**51** (72), **53** (6), **54** (21)
49	direct/MeOH	99	**51** (48), **53** (48), **54** (3)
50	direct/MeCN	90	**53** (4), **55** (86)
50	direct/MeOH	90	**53** (11), **55** (79)
48	sensit/Me_2CO	99	**53** (99)
49	sensit/Me_2CO	95	**51** (79), **53** (3), **54** (13)
50	sensit/Me_2CO	95	**55** (95)

[a] Total yield of all products. [b] Yields obtained by isolation and ^1H NMR analysis. [c] From ref 3d.

Table VII. Photoproducts and Yields from Photocyclization Reactions of the Meta Oxy Substituted Benzylpyrrolinium Perchlorates **56–58**

pyrrolinium salt	irradiation conditions	isolated yield,[a] %	product (yield, %)[b]
56	direct/MeCN	45	**59** (11), **60** (34)
57	direct/MeCN	83	**60** (21), **61** (62)
58	direct/MeCN	95	**62** (95)
57	sensit/Me_2CO	97	**61** (97)
58	sensit/Me_2CO	97	**62** (97)

[a] Total yield of all products. [b] Yields obtained by isolation and ^1H NMR analysis.

available to diradical cation intermediates formed in the SET-photochemical reaction of donor–iminium salt systems focused on a series of substituted 1-benzyl-2-methylpyrrolinium perchlorates. In preliminary studies with the pyrrolinium salts **47–49**, we had uncovered isolated yet instructive examples of photocyclization processes characteristic of these substances. The efforts reported here represent a thorough investigation and mechanistic analysis of this chemistry. The substituted pyrrolinium perchlorates (Schemes XII–XIV) used in this study were prepared by methods described previously[3d] involving reaction of 2-methyl-1-pyrroline[9] with substituted benzyl iodides followed by perchlorate anion exchange on a Dowex 1 column (ClO_4 form). Synthesis of the benzyl iodides used in these sequences are described in the supplementary material.

Photoreactions of the ortho-substituted benzylpyrrolinium salts **48–50** were conducted under direct (in MeCN and MeOH) and triplet-sensitized (in Me_2CO) conditions. Basic ($NaHCO_3$) workup followed by chromatographic (Florisil) separation afforded benzindolizidine **51** and benzopyrrolizidines **53–55** in the yields recorded in Table VI. The relative yields of photoproducts obtained by isolation matched closely those determined by ^1H NMR analysis of the crude photolysates prior to chromatographic separation. Finally, the structures of the indolizidine and pyrrolizidine products were assigned on the basis of complete and characteristic spectroscopic data.

The meta oxy substituted benzylpyrrolinium salts **56–58** were also subjected to photochemical studies under direct and triplet-sensitized reaction conditions.[22] These substances were found to undergo photocyclizations to produce the benzopyrrolizidines **59–62** shown in Scheme XIII with the efficiencies recorded in Table VII. The arene ring substitution regiochemistry in each of these substances was assigned on the basis of easily recognized aromatic proton coupling patterns in their ^1H NMR spectra. In a similar fashion, the [*m*-methyl- and [*m*-(trialkylsilyl)methyl]-benzyl]pyrrolinium perchlorates **63–65** participate in SET-induced photocyclization processes under direct (MeCN and MeOH) and triplet-sensitized (Me_2CO) conditions to produce benzopyrrolizidines **66–69** depicted in Scheme XIV in the yields recorded in Table VIII. Product structures and arene ring substitution patterns were assigned by use of spectroscopic data. It

(22) Triplet-sensitized reaction of phenolic pyrrolinium salt **56** did not yield the benzopyrrolizidine products presumably due to the fact that phenols are good H atom donors to ketone triplet excited states.

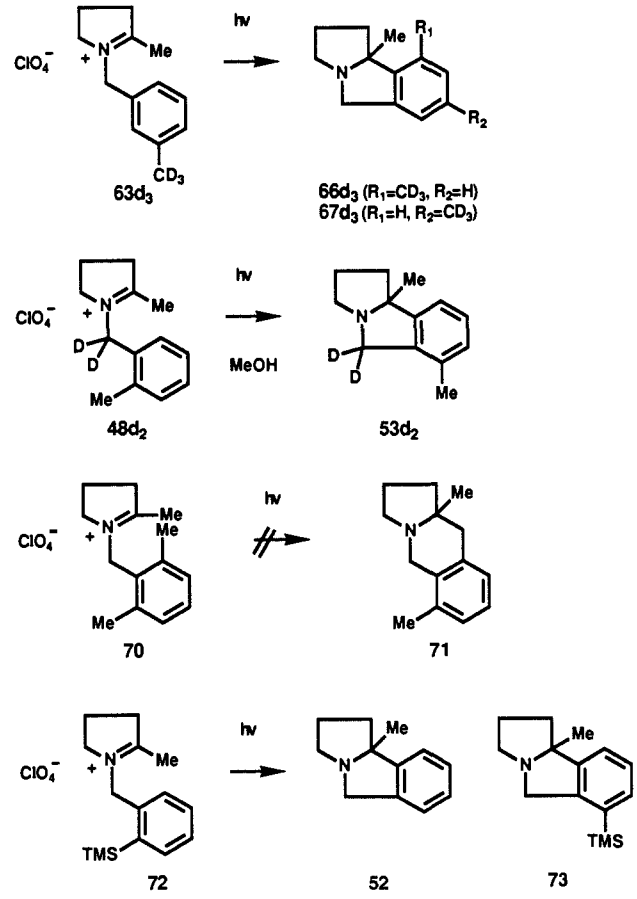
Table VIII. Photoproducts and Yields from Photocyclization Reactions of the [*m*-Methyl- and [*m*-[(Trialkylsilyl)methyl]benzyl]pyrrolinium Perchlorates **63–65**

pyrrolinium salt	irradiation conditions	isolated yield,[a] %	product (yield, %)[b]
63	direct/MeCN	76	**66** (18), **67** (58)
64	direct/MeCN	86	**66** (19), **67** (38), **68** (29)
64	direct/MeOH	90	**66** (32), **67** (55), **68** (3)
65	direct/MeCN	81	**67** (14), **69** (68)
63	sensit/Me_2CO	85	**66** (27), **67** (58)
64	sensit/Me_2CO	95	**66** (32), **67** (42), **68** (21)
65	sensit/Me_2CO	97	**69** (97)

[a] Total yield of all products. [b] Yields obtained by isolation and ^1H NMR analysis.

should be noted that the product distributions from reaction of both the ortho- and meta-substituted salts are not influenced by selective decomposition or interconversion of the primary photoproducts. Accordingly, the photoproducts are stable under the reaction conditions even in the case of *tert*-butyldimethylsilyl ether **61**, which is not transformed to phenol analogue **60** in media used for both the direct and acetone-sensitized process.

Additional experiments have been performed to gain further information about the mechanism and scope of these SET-promoted photocyclization reactions. In order to distinguish between the operation of diradical cation deprotonation and radical cyclization pathways in reaction of the (*m*-methylbenzyl)pyrrolinium salt **63**, photocyclizations of the d_3 analogue, **63**-d_3, were probed.



^1H NMR analysis of the regioisomeric pyrrolizidines produced upon direct (in MeCN or H_2O–MeCN) or acetone-sensitized irradiation showed that these substances (**66**-d_3 and **67**-d_3) were formed with complete retention of the d_3 label. In addition, a d_2 analogue **48**-d_2 of the (*o*-methylbenzyl)pyrrolinium salt containing deuterium substitution at the N-benzylic carbon was subjected to direct irradiation in MeOH.[23] Under these conditions only the d_2-benzopyrrolizidine, **53**-d_2, was formed with no loss of the

(23) The photochemistry of this substance in MeCN was studied earlier.[3d]

isotopic label. (Di-*o*-methylbenzyl)pyrrolinium salt **70** was investigated in order to determine the outcome of the SET-induced process when the diradical cation cyclization pathways is blocked (i.e., to see whether the alternative diradical cation deprotonation pathway leading to benzindolizidine **71** would occur). Upon direct irradiation in MeCN, **70** is essentially inert, with only slow decomposition occurring over extended reaction periods. Finally, with the intent of elucidating whether the regiochemical course of SET-induced photocyclizations of the *N*-benzylpyrrolinium salts can be influenced by factors that effect ground-state electrophilic additions to arenes,[24] we have studied the photochemistry of *o*-trimethylsilyl-substituted salt **72**. Irradiation of this substance in MeCN produces a mixture of the unsubstituted and TMS-substituted benzopyrrolizidines, **52** and **73**, the relative ratios of which are dependent upon the extent of conversion (e.g., **52**:**73** is 10 at 100% conversion, 0.5 at 70%, and 0.14 at 20%). In addition, **73** is transformed to **52** under dark reaction conditions (1 equiv of $HClO_4$ in MeCN), which mimic those present in the photolysis medium before basic workup. Thus, these results demonstrate that the primary photocyclization product arising from **72** is silicon-containing pyrrolizidine **73** and that **52** is formed from **73** by a secondary, acid-catalyzed dark reaction.

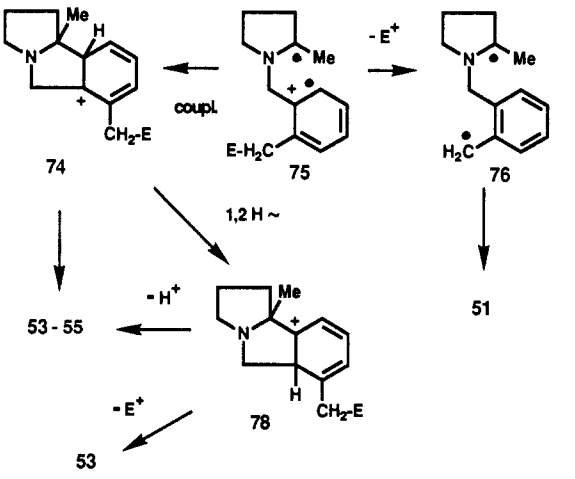
Discussion

The results presented above demonstrate that two competing mechanistic pathways are operable in the SET-induced photochemistry of *N*-(silylmethallyl)- and *N*-benzyl-1-pyrrolinium salts. This conclusion along with several interesting features of the mechanistic duality will be discussed in this section, which has been organized to cover the two classes of reactions separately. The mechanistic conclusions drawn from these studies should apply to a number of photochemical processes that proceed via the intermediacy of charged or zwitterionic diradicals. Consequently, the conclusions should be of general importance.

***N*-Benzylpyrrolinium Salts.** Several interesting and mechanistically relevant trends are present in the observations made in our studies of *N*-benzyl-1-pyrrolinium salt photochemistry. It is important to note at the outset that these trends also have synthetic significance since the photocyclization reactions generate interesting N-heterocyclic ring systems, proceed in high chemical yields, and in some cases occur with high and predictable regioselectivities. Moreover, the unique nature of the benzopyrrolizidine-forming reactions in this series is emphasized by observations that show that the *N*-benzylpyrrolinium salts resist ground-state, Pictet–Spengler-type, cyclizations even under forcing conditions. Thus, the photochemical route for isoindoline ring construction involving the endo-bis-trig cyclization[25] and driven by radical coupling in cationic, 1,5-diradical intermediates represents a unique and potentially useful synthetic methodology.[26]

Turning to mechanistic issues, direct-irradiation reactions of the ortho- and meta-substituted salts are promoted by excitation of the arene chromophores. Intramolecular SET from the excited singlet states of the arene moieties to the ground-state 2-methyl-1-pyrrolinium cation acceptors should be rapid on the basis of ΔG_{SET} considerations[27] and the results of our previous studies with arene–iminium salt systems.[3c,d] For example, 1,2-dimethyl-1-pyrrolinium perchlorate was shown earlier to be an efficient quencher ($k_q \approx 2 \times 10^9$ M^{-1} s^{-1}) for toluene and benzyltrimethylsilane fluorescence. If the rates of decay (fluorescence, ISC, etc.) of the singlet excited arene chromophores in these salts are in the range of those for the xylenes (ca. 3×10^7 s^{-1}),[28] intramolecular SET should be much more efficient (>100 times) than intersystem crossing. As a result, in the direct-irradiation processes intermediate diradical cations should be delivered as singlet species. On the other hand, in the acetone-sensitized reactions, SET from the triplet arenes ($E_T \approx 80$–83 kcal/mol based on the xylene[28] analogy) should occur to give triplet cation diradical intermediates.[29]

Scheme XV

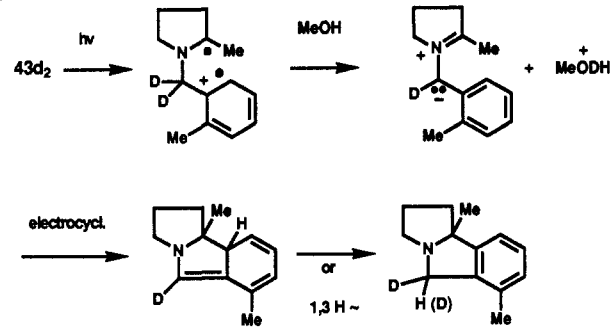


Results from studies of the ortho-substituted *N*-benzylpyrrolinium salts **48**–**50** contain clear examples of how excited-state multiplicity along with the nature of the electrofugal group and solvent influences the mechanistic course of these SET-promoted photocyclizations. In these systems, intramolecular SET generates the cation diradical intermediates **75** (Scheme XV), which partition to tricyclic cations **74** or diradicals **76** by respective radical coupling or electrofugal group loss pathways. The competition between these modes is reflected in the distribution of benzopyrrolizidine (e.g., **53**–**55**) and benzindolizidine (**51**) products. The data in Table VI contain trends in the product distribution that show how competition between the two mechanistic pathways is controlled. Accordingly, benzopyrrolizidines are formed exclusively in direct and sensitized reactions of CH_3- and CH_2S-*t*-$BuMe_2$-substituted salts **48** and **50**. In contrast, benzindolizidine **51** is the major product arising from reaction of CH_2SiMe_3 salt **49**. The proportion of **51** formed in the latter reaction increases with a change in solvent from MeOH to MeCN and when the process is triplet sensitized. Finally and at first glance surprisingly, direct-irradiation reactions of CH_2SiMe_3 and CH_2Si-*t*-$BuMe_2$ salts **49** and **50** also give non-silicon-containing benzopyrrolizidine **53**.

These observations are in clear accord with processes in which the relative rates of electrofugal group loss vs radical coupling in diradical cations **75** are controlled by the nature of the electrofugal group, solvent polarity, and multiplicity. As we have shown earlier,[3,30] the rates of Me_3Si loss from benzyl- and allylsilane cation radicals far exceed those for deprotonation and are larger than those for Me_2-*t*-BuSi loss. These are expected results since (1) in the current reactions and those probed earlier, the cation radicals are formed in the absence of a strongly basic partner capable of promoting proton abstraction[31] and (2) desilylation of cation radicals most probably requires participation by a nucleophile. Accordingly, singlet cation diradical **75** partitions more rapidly to diradical **76** when E = Me_3Si, while radical coupling to form cation **74** is favored when E = H or Me_2-*t*-BuSi.

(24) (a) For example, Miller[24b] has shown how the Me_3Si group can be used to control the regiochemistry of Pictet–Spengler cyclizations. (b) Miller, R. B.; Tsang, T. *Tetrahedron Lett.* **1988**, 6715.
(25) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.
(26) The generality of this process is currently being explored. Preliminary observations suggest that isoindoline ring formation by this photo-SET pathway represents a viable methodology.
(27) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(28) See ref 14a.
(29) (a) Singlet energy transfer from acetone to the arenes is not possible owing to the short (<2-ns) lifetime of the acetone singlet, low concentrations of the salts used (ca. 4 mM), and possible endothermic nature of the process. (b) Triplet energy transfer appears to occur even though the xylene and acetone triplets are close in energy.
(30) In a private communication, we have learned that J. P. Dinnocenzo and his co-workers have shown that the rate of benzylsilane cation radical desilylation decreases upon bulky substituent replacement at silicon.
(31) (a) Examples have been reported showing that deprotonation is faster than desilylation in α-silyl cation radicals when strongly basic partners are available.[31b] (b) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J.-U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

Scheme XVI

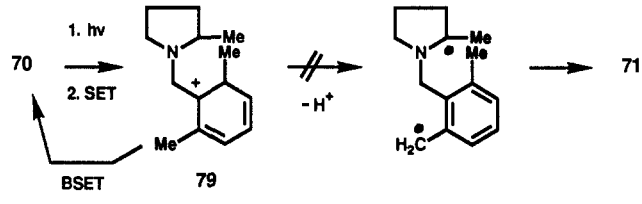


Tricyclic cyclohexadienyl cation **74** appears to react to form neutral products either by direct loss of the ring proton (the normal electrophilic aromatic substitution pathway) or by a prior hydride 1,2-shift followed by desilylation from the benzylic position and tautomerization. Methyl-substituted benzopyrrolizidine **53** formed from **49** and **50** is most probably derived by this sequence. Interestingly, the yields of **53** increase when the solvent is changed from MeCN to MeOH in a manner consistent with solvent silophilicity (oxygen vs nitrogen nucleophile).

Solvent also appears to play a significant role in governing the rates of electrofugal group loss and/or radical-cation coupling of intermediate cation diradicals related to **75**. This effect is indicated by the change in the indolizidine to pyrrolizidine ratio (**51**:**53** + **54**) derived from Me_3Si salt **49** from 2.7 in MeCN to 0.9 in MeOH. At first glance, these results seem counterintuitive since it is expected that in the cation diradical (**75**, E = Me_3Si) desilylation would be faster in the more silophilic MeOH. In light of this, we are led to conclude that solvent polarity (Z(MeOH) = 83.6 vs Z(MeCN) = 71.3) facilitates radical coupling in **75** presumably by stabilization of the transition state for formation of a more localized cation **74**. This effect, alluded to earlier[3c] in rationalizing product distributions from arene–iminium salt photoadditions, appears to be general since it also plays a role in SET photocyclizations of (silylmethallyl)pyrrolinium salts.

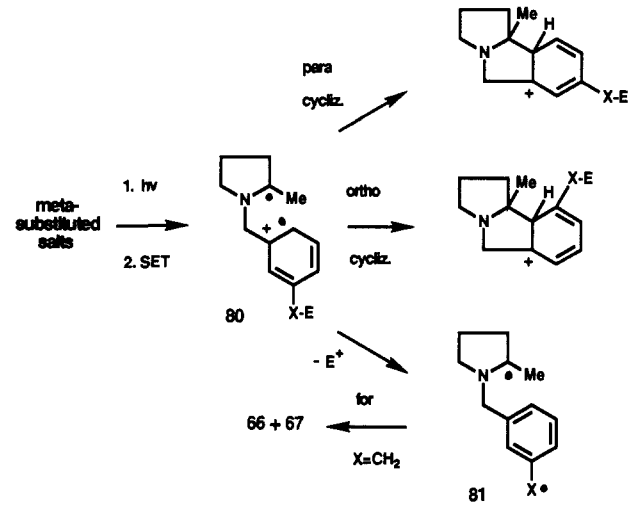
A small yet diagnostic change occurs in the **51**:**53** + **54** ratio from photoreaction of Me_3Si salt **49** when acetone triplet sensitization is employed. While this observation could simply be a manifestation of the solvent polarity effect noted above (Z-(Me_2CO) = 65.7), it also could reflect a control offered by multiplicity (singlet vs triplet) on the rate of radical coupling in diradical cation intermediate **75**. Accordingly, radical coupling in triplet **75** would be determined by the rate of intersystem crossing, while the rate of desilylation to furnish diradical **76** would not be altered by multiplicity.

The above results indicate that cation diradicals related to **75** undergo electrofugal group loss with rates that are dependent upon the electrofugal group in the following order: Me_3Si > Me_2-*t*-BuSi > H. Additional observations suggest that cation radical deprotonation rates are exceedingly slow. This, in reaction of *o*-dimethylsalt **70** where radical coupling in intermediate cation diradical **79** is sterically blocked (see diagram) deprotonation is



not even competitive with back-SET, since **70** is photochemically unreactive. It also should be noted that a mechanism for pyrrolizidine formation from the *N*-benzylpyrrolinium salts, involving deprotonation of cation diradical **75** at the N-benzylic position followed by 6π-electron electrocyclization and tautomerization (Scheme XVI), can be ruled out on the basis of results of past[3d] and current studies especially with d_2 salt **48**-d_2. As observed earlier[3d] for reaction in MeCN, irradiation of **48**-d_2 in MeOH leads to exclusive production of **53**-d_2, a substance that completely

Scheme XVII

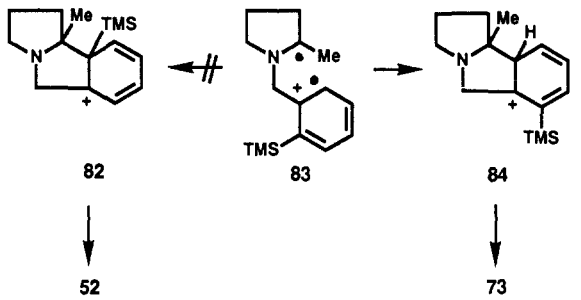


retains the d_2 label. Exchange of hydrogen at the *N*-benzylic center with either the arene ring of the solvent protons (emphasizing the need to look at the reaction in MeOH) would have occurred for cyclization by the benzylic deprotonation-electrocyclization pathway.

Studies with meta-substituted *N*-benzylpyrrolinium salts **56**–**58** and **63**–**65** have provided further information about the factors influencing the chemistry of cation diradical intermediates. In these systems distinction between the competitive pathways for photocylization is not as clearly made on the basis of product analysis. This is due to the fact that the radical coupling and electrofugal group loss routes in these cases can give the same types (i.e., benzopyrrolizidines) of products. However, the trends observed in product distributions appear to parallel (in terms of electrofugal group, steric, solvent, and multiplicity effects) those seen in reactions of the ortho-substituted analogues. For example, direct irradiations of meta MeO and Me_2-*t*-BuSiO salts **57** and **58** give exclusively pyrrolizidines (**60**–**62**) with arene ring substituents para (rather than ortho) to the cyclization bond. A minor product formed in phenol **56** photocyclization is ortho-cyclized substance **59**. In addition, triplet sensitization of **57** leads to formation of silicon-containing para product **61** solely. Results from investigations with the meta Me and R_3SiCH_2 salts **63**–**65** display similar trends. Reaction of meta Me salt **63** under direct-irradiation conditions gives a mixture of para (major) and ortho (minor) cyclized products **67** and **66**, respectively. Deuterium labeling techniques (i.e., studies with **63**-d_3) demonstrate that neither of these products arises by a pathway involving deprotonation of intermediate cation diradical **80** (X–E = Me, Scheme XVII). Likewise, photocyclization of Me_2-*t*-BuSiCH_2 salt **65** gives predominantly or exclusively silicon-containing para product **69**, depending on whether the process is initiated by direct or acetone-sensitized irradiation. Moreover, even non-silicon-containing product **67** arising from the MeCN direct-irradiation reaction of **65** contains the methyl group para to the cyclization bond. Finally, Me_3SiCH_2 salt **64** produces a mixture of ortho- and para-cyclized products **66** and **67** + **68**, respectively. In this system, like with its ortho analogue **49**, a change in the solvent from MeCN to MeOH causes an increase in the non-silicon-containing products (**66** and **67**). Also, the acetone-sensitized reaction of **64** gives substantially more non-TMS product as compared to the direct process in MeCN.

On the basis of these observations, we conclude that the major, if not exclusive, pathway followed in all but the meta Me_3SiCH_2 salt reactions involves radical coupling in the diradical cation intermediate (**80** in Scheme XVII). The ortho:para selectivities for these cyclizations appear to be governed by steric factors and range from ca. 0.3 for HO and Me salts (**56** and **63**) to 0 from the MeO, Me_2-*t*-BuSiO, and Me_2-*t*-BuSiCH_2 salts (**58**, **57**, and **65**). The steric control of regiochemistry in these processes is further demonstrated by the photochemistry of ortho Me_3Si salt

Scheme XVIII



72 where the major primary photoreaction produces silicon-containing pyrrolizidine **73**. This result indicates that, unlike typical electrophilic substitutions with arylsilanes,[24,32] formation of Me_3Si-stabilized cyclohexadienyl cation **82** (Scheme XVIII) is disfavored in competition with the sterically more favorable process leading to cation **84**.

The larger amount of ortho cyclization product **66** arising in photocyclization of the meta Me_3SiCH_2 salt as compared to Me analogue **63** along with the predominance of non-silicon-containing products combines to suggest that desilylation is competitive with radical coupling in intermediate cation radical **80** (X–E = Me_3SiCH_2) when Me_3Si loss from the benzylic position is possible. The diradical (**81**, E = CH_2, Scheme XVII) produced by Me_3Si loss in this intermediate is transformed to either **66** or **67** by ortho or para bonding in the benzylic radical moiety.

***N*- and *C*-(Silymethallyl)iminium Salts.** Studies with the regioisotopically labeled (d_4-silylmethallyl)iminium salts have provided additional observations demonstrating the general nature of intramolecular SET processes that operate by competitive electrofugal group loss and radical coupling pathways. At the outset of these efforts, we anticipated that d_4-iminium salts of general structure **1** (Scheme IV) would be useful in probing this mechanistic duality. Our proposal was that the isotope labels in the products of photocyclization of these substances would allow determination of contributions made by desilylation (k_d) and radical coupling (k_c) of cation diradical intermediates **2**. As shown in Scheme IV, cyclization by the latter mode would provide isotopomers **3A** while the former mode would give mixtures of **3A** and **3B**. In order to establish a direct correspondence between the isotopomer ratios **3A**/**3B** and the rate constant ratios k_c/k_d, knowledge about the effects of deuterium substitution on cation and neutral diradical coupling is required. Clearly, an inverse isotope effect on radical coupling in **2** would bias the product ratios in the direction of isotopomer **3A** and thus make the observed k_c/k_d ratio larger than in the protio systems. In addition, an inverse isotope effect on cyclization of the neutral diradical formed by cation diradical desilylation would have the same net effect.

It is difficult to gain direct information about isotope effects on radical coupling in diradical cations. However, more is known about similar processes of neutral radicals. Crawford[33] has reported results that suggest that no isotope effect exists for **1,1-d_2**-allyl radical combination reactions. Further pertinent information on this point is found in our observation that the isotopomer ratios obtained in xanthone triplet-sensitized reactions of (silylmethallyl)pyrrolinium salts **14-d_4**–**16-d_4** are nearly unity (Table III). These results support a proposed mechanistic scheme (1) in which radical coupling is slow relative to desilylation in triplet diradical cation intermediates and (2) where there are little if any inverse isotope effects on coupling in the resulting diradicals. If this conclusion is correct, the **3A**/**3B** isotopomer ratios in products formed by photocyclizations of the (d_4-silylmethallyl)iminium salts can be directly translated into a ratio of rate constants for radical coupling (k_c) and desilylation (k_d) of diradical cation intermediates.

In Table IX are listed the k_c/k_d ratios determined from pyrrolizidine isotopomer ratios from photocyclizations of the (d_4-silylmethallyl)-1-pyrrolinium perchlorates **14-d_4**–**18-d_4**. A number of trends in these data are fully supportive of the conclusions arrived at by analyzing the *N*-benzylpyrrolinium salt reactions discussed above. Accordingly, these SET-induced photoreactions appear to operate by two mechanistic pathways involving diradical cation coupling and desilylation. Change in solvent from MeCN to MeOH results in increases in the k_c/k_d ratios. These effects, which can be also mimicked by adding the salt *n*-Bu_4NClO_4, are most probably due to solvent polarity (ionic strength), which alters k_c in the manner described above for the *N*-benzyl analogues. It should be noted that attempts to enhance the rates of cation diradical desilylation by adding the silophilic reagent *n*-Bu_4NF results in little if any change in k_d. The observed change in k_c/k_d for reaction of **17-d_4** in proceeding from MeOH (1.18) to 0.1 M NBu_4BF in MeOH (1.36) suggests that a change in ionic strength is the dominant effect caused by this fluoride salt.

Table IX. Ratio of Rate Constants for Radical Coupling and Desilylation of Diradical Cation Intermediates in the Singlet SET Photocyclizations of (d_4-Silylmethyallyl)pyrrolinium Perchlorates

d_4-silylmethallyl salt	product	k_c/k_d MeCN	k_c/k_d MeOH
14-d_4	**19-d_4**	0.24 ± 0.02	0.30 ± 0.01
15-d_4	**20-d_4**	0.35 ± 0.05	0.44 ± 0.03
16-d_4	**21-d_4**	0.17 ± 0.02	0.32 ± 0.03
17-d_4	**22-d_4**	0.87 ± 0.05	1.18 ± 0.02
17-d_4	**22-d_4**	(1.02 ± 0.04)[a]	(1.36 ± 0.06)[b]
18-d_4	**23-d_4**	1.18 ± 0.02	1.92 ± 0.04

[a] Containing 0.1 M *n*-Bu_4NClO_4. [b] Containing 0.1 μ *n*-Bu_4NF.

A particularly interesting feature of the data given in Table IX concerns the changes noted in k_c/k_d with variations in the aryl ring substituents. The k_c/k_d ratios increase in the series *p*-CF_3 < *p*-H < *p*-F < *p*-OMe < *m,p*-$(OMe)_2$. These effects are most certainly a consequence of variations in k_c, since it is difficult to imagine how changes in the arene ring moieties could alter cation diradical desilylation rates. The changes noted for k_c parallel the electron-releasing abilities (e.g., σ^+) of the substituents that are transmitted to the α-amino benzylic radical centers. These results can be understood in terms of an FMO analysis. Accordingly, increases in the α-amino benzylic radical SOMO energies engendered by electron-donating group substitution should enhance the rates of their coupling reactions with highly electron deficient cation radicals.[34] A similar effect is observed in SET-induced photocyclizations of d_4-silylmethallyl-substituted dihydroisoquinolinium perchlorates **43-d_4** and **44-d_4**, where k_c/k_d ratios from MeCN reactions are 0.28 ± 0.02 and 0.48 ± 0.01, respectively.

The largest k_c/k_d ratios observed in this study are for photoreactions of (silylmethallyl)-1-cyclohexeniminium salts **32** and **33**. These range from 2.62 to 3.91 for the *O*-pivaloyl (**32**) and 1.6 to 1.8 for the *O*-methyl (**33**) cyclizations in MeCN. An interpretation of this phenomenon and the observed effects of C=N isomerism on the k_c/k_d ratios (Table IV) is difficult to make at this time since we have been unable to assign stereochemistry to the C=N *E* and *Z* isomers and since *EZ* isomerization occurs under the irradiation conditions.

Finally, it is important to note that alternate explanations for the results obtained from studies with the (silylmethallyl)iminium salts do exist. For example, product isotopomer ratios in these systems could be solely or partly governed by the relative rates of bond rotation and radical coupling. It is possible that SET, desilylation, and radical coupling in these processes could be rapid and occur at rates that are competitive with C–C and C–N conformational changes. If so, conformational preferences for SET in singlet excited states of the (silylmethallyl)iminium salts would be important. Thus, if SET is more efficient in U-type conformer **82** and ensuing steps are fast in the singlet manifold,[35]

(32) See ref 4 for examples of electrophilic aromatic substitution reactions with arylsilanes in which desilylation in the predominant pathway.

(33) Al-Sader, B. H.; Crawford, R. J. *Can. J. Chem.* **1970**, *48*, 2745.

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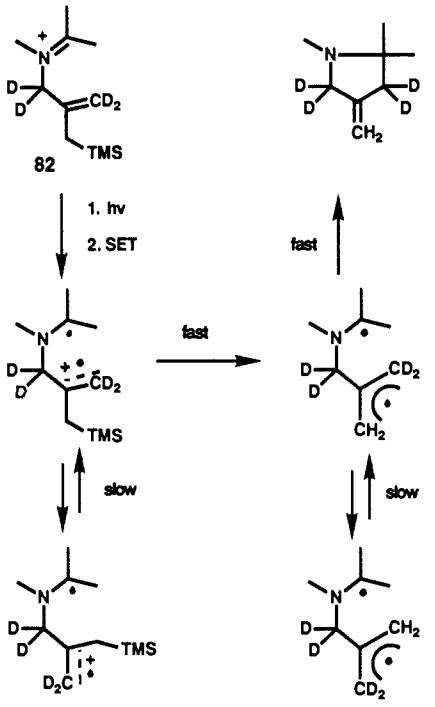
(35) (a) Jaffe, A. B.; Skinner, K. J.; McBride, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 8510. (b) Weir, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *118*, 526. Johnston, L.; Scaiano, J. C.; Sheppard, J.; Bays, J. P. *Ibid.* **1986**, *124*, 493. Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819. (c) Zimmt, M. B.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 3618.



a preference for isotopomer **3A** would be seen even if a cation diradical coupling route is not followed. The near-unity isotopomer ratios observed in triplet reactions of **14**-d_4–**16**-d_4 could also fit this mechanistic scheme since in these cases triplet diradicals would be produced and radical coupling could be slow since it requires prior intersystem crossing. Consequently, bond rotations at this stage could fully equilibrate diradical conformers. On the other hand, if this mechanistic scenario were correct, it would be difficult to understand the observed substituent and solvent effects. These appear to be more consistent with sequences involving competitive desilylation and radical coupling of diradical cation intermediates.

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H NMR spectra were recorded at either 200 or 400 MHz, and ^{13}C NMR were recorded at 50 MHz. Proton chemical shifts are reported (ppm) with residual $CHCl_3$ (7.25) in $CDCl_3$ or d_5-acetone (2.04) in d_6-acetone used as internal standards. Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), AB q (AB quartet), and m (multiplet). Carbon chemical shifts are reported (ppm) relative to $CDCl_3$ (77.0) or d_6-acetone (29.8) as internal standards. Carbon resonance assignments are aided by INEPT results. IR spectra were recorded on a Perkin-Elmer Lambda 5 instrument (cm^{-1}). UV spectra were recorded on a Perkin-Elmer 281 instrument. Mass spectrometric data were obtained by using low-resolution (Hitachi RMU-6E) and high-resolution (VG-7700) instruments.

Photolyses were conducted with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well with appropriate glass filters (Vycor ($\lambda > 240$ nm), Corex ($\lambda > 280$ nm), Pyrex ($\lambda > 290$ nm), flint ($\lambda > 305$ nm), and uranium ($\lambda > 320$ nm)) on nitrogen-purged solutions. The general workup procedure unless otherwise specified involved concentration of the photolysate in vacuo, dilution of the residue with aqueous saturated. $NaHCO_3$, and extraction with $CHCl_3$. The $CHCl_3$ extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the crude product mixture.

Molecular distillations were performed with a Kugelrohr apparatus. Preparative chromatographic separations were accomplished by using the following: flash column chromatography, Merck EM Type 60 (230–400-mesh) silica gel; column chromatography, Fisher Florisil (100–200 mesh); preparative thin-layer chromatography, Merck Type 60GF-254 silica gel. Drying of all organic layers obtained in workup of preparative reactions was by use of anhydrous Na_2SO_4. Substituted phenyl-1-pyrrolines **9–13** were prepared according to the method described by Bielawski[9] from *N*-vinyl-i-pyrrolidone and substituted phenyllithiums. The desired pyrrolines had spectral properties identical with those previously reported.[8-10]

Preparation of *N*-[(Silylmethyl)allyl]pyrrolinium Perchlorates 14–18 and 14-d_4–18-d_4. To solutions of 2-aryl-1-pyrrolines **9–13** (2 mmol) and silver perchlorate (2 mmol) in acetonitrile (10 mL) at 0 °C were added dropwise 2-[(trimethylsilyl)methyl]allyl iodide (**8**) or its tetradeuterio analogue **26** (2.2 mmol) in acetonitrile (5 mL). After addition, the reaction mixtures were stirred at 25 °C for 3 days in the dark and then filtered through Celite. The filtrates were concentrated in vacuo to afford viscous liquids, which were subjected to column chromatography on Florisil (2% MeOH–$CHCl_3$ as eluant), yielding the desired pyrrolinium perchlorate salts **14–18** and **14-d_4–18-d_4**. Spectroscopic data for the all protiopyrrolinium perchlorate salts are as follows:

14: UV (CH_3CN) λ_{max} 263 nm (ϵ 9100); ^{1}H NMR −0.18 (s, 9 H, $Si(CH_3)_3$), 1.43 (s, 2 H, CH_2-Si), 2.44 (p, J = 7.8 Hz, 2 H, H-4), 3.65 (t, J = 7.8 Hz, 2 H, H-3), 4.33 (s, 2 H, NCH_2C=C), 4.39 (t, J = 7.8 Hz, 2 H, H-5), 4.90, 4.94 (s, 2 H, vinyl H), 7.44–7.64 (m, 5 H, aryl H); ^{13}C NMR −2.1 ($Si(CH_3)_3$), 18.0 (CH_2Si), 23.8 (C-4), 40.8 (C-3), 57.3 (NCH_2C=C), 60.5 (C-5), 112.8 (C=CH_2), 126.7, 127.9, 129.2, 133.7, 137.8 (*C*=CH_2), 88.9 (C-2); IR ($CHCl_3$) 1650, 1250, 1090, 850; mass spectrum, m/e (relative intensity) 271 (M^+ − $HClO_4$, 27), 196 (16), 158 (69), 145 (11), 143 (22), 77 (27), 73 (100); high-resolution mass spectrum, m/e 271.1765 ($C_{17}H_{25}NSi$ requires 271.1756).

15: UV (CH_3CN) λ_{max} 266 nm (ϵ 8700); ^{1}H NMR −0.12 (s, 9 H, $Si(CH_3)_3$), 1.49 (s, 2 H, CH_2Si), 2.47 (p, J = 7.6 Hz, 2 H, H-4), 3.72 (t, J = 7.6 Hz, 2 H, H-3), 4.33 (s, 2 H, NCH_2C=C), 4.40 (t, J = 7.6 Hz, 2 H, H-5), 4.91, 4.96 (s, 2 H, vinyl H), 7.18–7.28 (m, 2 H, aryl H ortho to F), 7.7–7.8 (m, 2 H, aryl H meta to F); ^{13}C NMR −1.8 ($Si(CH_3)_3$), 18.3 (CH_2Si), 24.3 (C-4), 41.0 (C-3), 57.7 (NCH_2C=C), 61.0 (C-5), 112.7 (C=CH_2), 117.0 (d, J = 22.3 Hz, C-3′), 123.0 (C-1′), 131.4 (d, J = 9.7 Hz, C-2′), 138.24 (*C*=CH_2), 165.8 (d, J = 258.4 Hz, C-4′), 188.0 (C-2); IR ($CHCl_3$) 1655, 1600, 1090, 845; mass spectrum, m/e (relative intensity) 289 (M^+ −$HClO_4$, 31), 217 (3), 176 (98), 163 (3), 161 (25), 95 (3), 73 (100); high-resolution mass spectrum, m/e 289.1651 ($C_{17}H_{24}NSiF$ requires 289.1662).

16: UV (CH_3CN) λ_{max} 247 nm (ϵ 8050); ^{1}H NMR −0.14 (s, 9 H, $Si(CH_3)_3$), 1.47 (s, 2 H, CH_2Si), 2.54 (p, J = 7.9 Hz, 2 H, H-4), 3.76 (t, J = 7.9 Hz, 2 H, H-3), 4.32 (s, 2 H, NCH_2), 4.48 (t, J = 7.9 Hz, 2 H, H-5), 4.92, 4.96 (s, 2 H, vinyl H), 7.77 and 7.91 (AB q, J = 8.4 Hz, 4 H, aryl H); ^{13}C NMR−1.9 ($Si(CH_3)_3$), 18.4 (CH_2Si), 24.3 (C-4), 41.7 (C-3), 57.9 (NCH_2), 61.3 (C-5), 113.6 (=CH_2), 123.1 (q, J = 273.5 Hz, CF_3), 126.4 (q, J = 2.9 Hz, C-3′), 128.6 (C-2′), 130.5 (C-1′), 135.1 (q, J = 33.1 Hz, C-4′), 137.9 (*C*=CH_2), 188.9 (C-2); IR ($CHCl_3$) 2930, 1645, 1325, 1090; mass spectrum, m/e (relative intensity 339 (M^+ − $HClO_4$, 10), 226 (6), 213 (9), 215 (5), 145 (25), 73 (100); high-resolution mass spectrum, m/e 339.1632 ($C_{18}H_{24}F_3NSi$ requires 339.1630).

17: UV (CH_3CN) λ_{max} 310 nm (ϵ 14 000); ^{1}H NMR −0.08 (s, 9 H, $Si(CH_3)_3$), 1.49 (s, 2 H, CH_2Si), 2.39 (p, J = 7.8 Hz, 2 H, H-4), 3.66 (t, J = 7.8 Hz, 2 H, H-3), 3.84 (s, 3 H, OCH_3), 4.32 (t, J = 7.8 Hz, 2 H, H-5), 4.36 (s, 2 H, NCH_2C=C), 4.84, 4.92 (s, 2 H, vinyl H), 6.98 (d, J = 9.0 Hz, 2 H, aryl H, ortho to OMe), 7.67 (d, J = 9.0 Hz, 2 H, aryl H, meta to OMe); ^{13}C NMR −1.6 ($Si(CH_3)_3$), 18.6 (CH_2Si), 24.6 (C-4), 39.9 (C-3), 55.8 (OCH_3), 57.8 (NCC=C), 60.5 (C-5), 111.2 (C=CH_2), 115.1 (C-3′), 118.6 (C-1′), 131.8 (C-2′), 138.8 (*C*=CH_2), 164.9 (C-4′), 186.5 (C-2); IR ($CHCl_3$) 2955, 1650, 1630, 1090; mass spectrum, m/e (relative intensity) 301 (M^+ − $HClO_4$, 26), 229 (15), 188 (100), 175 (7), 173 (52), 107 (2), 73 (75); high-resolution mass spectrum, m/e 301.1854 ($C_{18}H_{27}NOSi$ requires 301.1862).

18: UV (CH_3CN) λ_{max} 297 nm (ϵ 7400), 336 (6800); ^{1}H NMR −0.09 (s, 9 H, $Si(CH_3)_3$), 1.48 (s, 2 H, CH_2Si), 2.41 (p, J = 7.9 Hz, 2 H, H-4), 3.68 (t, J = 7.9 Hz, 2 H, H-3), 3.87 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.33 (t, J = 7.9 Hz, 2 H, H-5), 4.40 (s, 2 H, NCH_2C=C), 4.85 (s, 2 H, vinyl H), 4.93 (s, 2 H, vinyl H), 6.95 (d, J = 8.5 Hz, 1 H, aryl H), 7.27–7.33 (m, 2 H, aryl H); ^{13}C NMR −1.7 ($Si(CH_3)_3$), 18.6 (CH_2Si), 24.4 (C-4), 40.2 (C-3), 56.3, 56.5 (OCH_3), 57.8 (NCH_2C=C), 60.7 (C-5), 111.5 (C-5′), 111.7 (C=CH_2), 111.9 (C-2′), 118.9 (C-1′), 123.4 (C-6′), 139.0 (*C*=CH_2), 149.8 (C-3′), 154.6 (C-4′), 187.2 (C-2); IR ($CHCl_3$) 2955, 1640, 1250, 1090; mass spectrum, m/e (relative intensity) 331 (M^+ − $HClO_4$, 27), 259 (9), 218 (68), 205 (9), 203 (33), 73 (100); high-resolution mass spectrum, m/e 331.1974 ($C_{19}H_{29}NO_2Si$ requires 331.1967).

Photolyses (Direct Irradiation) of Protio- and Deuteriopyrrolinium Perchlorates 14–18 and 14-d_4–18-d_4. Irradiation of solutions of the protio (**14–18**) and deuterio (**14-d_4–18-d_4**) salts were carried out under identical conditions (see Tables I and II). The crude product mixtures obtained from workup of the photolysates (see general section) were subjected to column chromatographic separations on silica gel (3% MeOH–$CHCl_3$), giving the desired pyrrolizidines **19–23** and their d_4 analogues **19-d_4–23-d_4**, respectively. The regioisotopomer (**A**:**B**) ratios for d_4-pyrrolizidines **19-d_4–23-d_4** were determined by ^{1}H NMR methods (see Results and Table II). Spectroscopic data for **19–23** area as follows:

19: ^{1}H NMR 1.63–2.03 (m, 4 H, H-6 and H-7), 2.62–2.78 (m, 3 H, H-4 and H-8), 3.13–3.23 (m, 1 H, H-8), 3.30 (d, J = 14.6 Hz, 1 H, H-2), 3.73 (d, J = 14.6 Hz, 1 H, H-2), 4.80 (s, 2 H, vinyl H), 7.01–7.45 (m,

5 H, aryl H); ^{13}C NMR 24.8 (C-7), 39.8 (C-6), 46.7 (C-4), 55.4 (C-8), 59.9 (C-2), 76.3 (C-5), 105.3 (=CH_2), 125.7 (C-2'), 125.9 (C-4'), 128.0 (C-3'), 149.1 (C-1'), 149.5 (C-3); IR ($CHCl_3$) 2920, 1680, 1260, 1020; mass spectrum, *m/e* (relative intensity), 199 (M^+, 100), 198 (68), 144 (88), 122 (68), 77 (17); high-resolution mass spectrum, *m/e* 199.1351 ($C_{14}H_{17}N$ requires 199.1361).

20: ^{1}H NMR 1.61–2.08 (m, 4 H, H-6 and H-7), 2.62–2.78 (m, 3 H, H-4 and H-8), 3.12–3.22 (m, 1 H, H-8), 3.30 (d, J = 14.6 Hz, 1 H, H-2), 3.73 (d, J = 14.6 Hz, 1 H, H-2), 4.83 (s, 2 H, vinyl H), 6.88–7.02 (m, 2 H, aryl H, ortho to F), 7.33–7.46 (m, 2 H, aryl H, meta to F); ^{13}C NMR 24.9 (C-7), 39.9 (C-6), 46.8 (C-4), 55.4 (C-8), 59.9 (C-2), 75.8 (C-5), 105.4 (=CH_2), 114.6 (d, J = 20.6 Hz, C-3'), 127.2 (d, J = 7.7 Hz, C-2'), 144.9 (C-1'), 149.3 (C-3), 161.3 (d, J = 243.8 Hz, C-4'); IR ($CHCl_3$) 2940, 1600, 1500, 1150, 835; mass spectrum, *m/e* (relative intensity) 217 (M^+, 82), 216 (63), 162 (100), 122 (44), 95 (13); high-resolution mass spectrum, *m/e* 217.1254 ($C_{14}H_{16}NF$ requires 217.1267).

21: ^{1}H NMR 1.62–2.17 (m, 4 H, H-6 and H-7), 2.61–2.83 (m, 3 H, H-4 and H-8), 3.13–3.24 (m, 1 H, H-8), 3.32 (d, J = 14.6 Hz, 1 H, H-2), 3.71 (d, J = 14.6 Hz, 1 H, H-2), 4.82 (s, 2 H, vinyl H), 7.49–7.59 (m, 4 H, aryl H); ^{13}C NMR 24.9 (C-7), 40.1 (C-6), 46.8 (C-4), 55.6 (C-8), 59.9 (C-2), 76.3 (C-5), 105.8 (C=CH_2), 124.4 (q, J = 271.8 Hz, CF_3) 124.9 (q, $J \approx$ 3.9 Hz, C-3'), 126.1 (C-2'), 128.2 (q, J = 32.1 Hz, C-4'), 148.9 (C-3), 153.5 (C-1'); IR ($CHCl_3$) 2965, 1330, 1170, 1130, 1070; mass spectrum, *m/e* (relative intensity) 267 (M^+, 100), 266 (75), 213 (13), 212 (85), 198 (11), 145 (25), 122 (65); high-resolution mass spectrum, *m/e* 266.1157 ($C_{15}H_{15}NF_3$ requires 266.1157).

22: ^{1}H NMR 1.62–2.08 (m, 4 H, H-6 and H-7), 2.63–2.78 (m, 3 H, H-4 and H-8), 3.12–3.21 (m, 1 H, H-8), 3.31 (d, J = 14.6 Hz, 1 H, H-2), 3.74 (d, J = 14.6 Hz, 1 H, H-2), 3.78 (s, 3 H, OCH_3), 4.82 (s, 2 H, vinyl H), 6.78–6.86 (m, 2 H, aryl H, ortho to OMe), 7.32–7.40 (m, 2 H, aryl H meta to OMe); ^{13}C NMR 24.7 (C-7), 39.6 (C-6), 46.6 (C-4), 55.1 (OCH_3), 55.2 (C-8), 59.7 (C-2), 75.9 (C-5), 105.3 (=CH_2), 113.3 (C-3'), 126.7 (C-2'), 140.9 (C-1'), 149.5 (C-3), 157.8 (C-4'); IR ($CHCl_3$) 2920, 1608, 1500, 1235; mass spectrum, *m/e* (relative intensity), 229 (M^+, 69), 228 (44), 174 (100), 122 (24), 107 (1); high-resolution mass spectrum, *m/e* 229.1472 ($C_{15}H_{19}NO$ requires 229.1466).

23: ^{1}H NMR 1.69–2.08 (m, 4 H, H-6 and H-7), 2.69–2.78 (m, 3 H, H-4 and H-8), 3.12–3.23 (m, 1 H, H-8), 3.30 (d, J = 14.7 Hz, 1 H, H-2), 3.72 (d, J = 14.7 Hz, 1 H, H-2), 3.83, 3.87 (s, 6 H, OCH_3), 4.83 (s, 2 H, vinyl H), 6.75–7.05 (m, 3 H, aryl H); ^{13}C NMR 24.8 (C-7), 39.8 (C-6), 46.8 (C-4), 55.3 (C-8), 56.0 (OCh_3), 59.9 (C-2), 76.1 (C-5), 105.2 (=CH_2), 109.9 (C-2'), 111.1 (C-5'), 117.7 (C-6'), 142.0 (C-1'), 147.4 (C-4'), 148.8 (C-3'), 149.6 (C-3); IR ($CHCl_3$) 2960, 1510, 1465, 1255; mass spectrum, *m/e* (relative intensity) 259 (M^+, 85), 258 (44), 205 (19), 204 (100), 123 (34); high-resolution mass spectrum 259.1566 ($C_{16}H_{21}NO_2$ requires 259.1572).

Xanthone (Triplet) Sensitized Photoreactions of the Pyrrolinium Perchlorates 14-d_4–18-d_4. N_2-purged solutions of the deuteriopyrrolinium perchlorates **14**-d_4–**18**-d_4 (0.9–2.0) × 10^{-3} M) and xanthone ((5.1–10.0) × 10^{-3} M) in acetonitrile were irradiated for 12 h with uranium glass filtered light. The photolysates were concentrated in vacuo and subjected to the normal workup procedure, giving residues that were dissolved in Et_2O and filtered. The filtrates were extracted with 10% HCl. The aqueous extracts were made basic (pH 10) with aqueous NaOH and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving oils that were subjected to column chromatography on silica gel (3.5% MeOH–$CHCl_3$) and giving the corresponding pyrrolizides **19**-d_4–**23**-d_4 as regioisotopomeric (**A**:**B**) mixtures that were subjected to ^{1}H NMR analysis (see Table III).

***1,1,3,3-d*$_4$-2-[(Trimethylsilyl)methyl]-2-propen-1-ol (25) and Derived Mesylate and Iodide 26.** Tetradeuterio alcohol **25** was prepared by the method of Marshall[13] from reduction of the enolate of diethyl [(trimethylsilyl)methyl]malonate (see ref 12 and supplementary material for preparation) with $LiAlD_4$ (98% d_4). The spectroscopic properties of d_4 alcohol **25** were similar to those reported for the protio analogue. In addition, the corresponding tetradeuterio mesylate and tetradeuterio iodide **26** were prepared by the procedures identical with those reported for the protio analogues, and these had spectral properties similar to those previously recorded.[11] Characteristic spectroscopic data are as follows:

25: ^{1}H NMR 0.01 (s, 9 H, $Si(CH_3)_3$, 1.50 (s, 2 H, CH_2Si); ^{13}C NMR −1.5 ($Si(CH_3)_3$), 23.1 (CH_2Si), 146.6 (C-2).

Mesylate of 25: ^{1}H NMR 0.02 (s, 9 H, $Si(CH_3)_3$), 1.56 (s, 2 H, CH_2Si), 2.98 (s, 3 H, SO_2CH_3); ^{13}C NMR −1.6 ($Si(CH_3)_3$), 22.8 (CH_2Si), 7.9 (SO_2CH_3), 139.7 (C-2).

26: ^{1}H NMR 0.01 (s, 9 H, $Si(CH_3)_3$), 1.69 (s, 2 H, CH_2Si); ^{13}C NMR −1.3 ($Si(CH_3)_3$), 24.9 (CH_2Si), 144.5 (C-2).

3-[*N*-Methyl-*N*-[1,1,3,3-*d*$_4$-2-[(trimethylsilyl)methyl]-2-propen-1-yl]amino]cyclohex-2-en-1-one (31). The d_4 enaminone **31** was prepared by the method previously[17] described for corresponding protio analogue involving N-allylation with **26** of 3-(methylamino)cyclohex-2-enone **30**.

Preparation of Tetradeuterated *N*-Cyclohexeniminium Perchlorates 32 and 33. The deuterio iminium perchlorates **32** and **33** as mixtures of *E* and *Z* isomers were prepared by methods previously described[17] for the protio analogues.

Photolyses (Direct Irradiation) of *d*$_4$-Cyclohexeniminium Perchlorates 32 and 33. Irradiation of solutions of iminium salts **32** and **33** (1×10^{-3} M) comprised of different relative amounts of *E* and *Z* isomers in acetonitrile were conducted with Corex filtered light. The photolysates were subjected to the general workup procedure (general section), which provided pure samples of regiosotopomeric mixtures of the d_4 spirocyclic amine products **34** and **35**. ^{1}H NMR analysis provided the regioisotopomer (**A**:**B**) ratios recorded in Table IV.

1-[*2,2,4,4-d*$_4$-3-[(Trimethylsilyl)methyl]-3-buten-1-yl]-3,4-dihydroisoquinoline (41-*d*$_4$). This compound was prepared by the route previously[19a] described for the synthesis of analoguous protiodihydroisoquinoline.

6,7-Dimethoxy-1-[3-[(trimethylsilyl)methyl]-3-buten-1-yl]-3,4-dihydroisoquinoline (42). To a −78 °C solution of 6,7-dimethoxy-1-methyl-3,4-dihydroxyisoquinoline (**40**) (410 mg, 2 mmol) in 3 mL of anhydrous THF was added slowly 2.4 mmol of *n*-butyllithium in hexane and tetramethylenediamine (280 mg, 2.4 mmol). The reaction mixture was warmed to 25 °C, stirred for 3 h, cooled to −78 °C, and then quenched by dropwise addition of the allylic iodide **8** (0.55 g, 2.15 mmol) in 2 mL of THF. The reaction mixture was then stirred at 25 °C for 24 h, poured into water, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving a residue that was subjected to Florisil column chromatography (2% MeOH −98% $CHCl_3$) to yield 550 mg (86%) of the desired dihydroisoquinoline **42**: ^{1}H NMR −0.02 (s, 9 H, $Si(CH_3)_3$), 1.56 (d, 2 H, J = 0.5 Hz, CH_2Si), 2.28 (t, J = 9.9 Hz, 2 H, H-2'), 2.57 (t, J = 7.5 Hz, 2 H, H-4), 2.80 (t, J = 9.9 Hz, 2 H, H-1'), 3.60 (t, J = 7.5 Hz, 2 H, H-3), 3.87, 3.89 (s, 3 H, OCH_3), 4.52, 4.63 (s, 2 H, vinyl H), 6.66, 6.97 (s, 2 H, H-5 and H-8); ^{13}C NMR −1.4 ($Si(CH_3)_3$), 25.8, 26.8 (C-4 and CH_2Si), 34.6 (C-1'), 35.6 (C-2'), 46.9 (C-3), 55.9, 56.2 (OCH_3), 107.0 (C=CH_2), 108.6 (C-5), 110.3 (C-8), 121.8 (C-9), 131.6 (C-10), 147.2 (C-7), 147.4 (*C*-CH_2), 150.7 (C-6), 166.3 (C-1); IR ($CHCl_3$) 2930, 1625, 1265, 1140, 855; mass spectrum, *m/e* (relative intensity) 331 (M^+, 27), 330 (46), 316 (23), 258 (100), 244 (21), 203 (4), 73 (13); high-resolution mass spectrum, *m/e* 331.1974 ($C_{19}H_{29}O_2NSi$ requires 331.1968).

6,7-Dimethoxy-1-[*2,2,4,4-d*$_4$-3-[(trimethylsilyl)methyl]-3-buten-1-yl]-3,4-dihydroisoquinoline (42-*d*$_4$). Tetradeuteriodihydroisoquinoline **42**-d_4 was prepared by the method described above for **42** with d_4-allyl iodide **25**.

***N*-[(Ethoxycarbonyl)methyl]-1-[*2,2,4,4-d*$_4$-[(trimethylsilyl)methyl]-3-buten-1-yl]-3,4-dihydroisoquinolinium Perchlorate (43-*d*$_4$).** This salt was made by use of a method different from that reported[19a] previously for synthesis of its protio analogue. To a solution of 3,4-dihydroisoquinoline **41**-D_4 (1 mmol) and silver perchlorate (1 mmol) in acetonitrile (3 mL) at 0 °C was added ethyl iodoacetate (1 mmol) dropwise at 0 °C. After addition, the reaction mixture was stirred at 25 °C for 3 days in the dark and then filtered through Celite. The filtrate was concentrated in vacuo to afford a viscous liquid that was subjected to column chromatography on Florisil (2% MeOH–$CHCl_3$ as eluent) affording the desired salt **43**-d_4 (90%) with spectroscopic properties identical with those of the known[19a] material.

***N*-[(Ethoxycarbonyl)methyl]-6,7-dimethoxy-1-[3-[(trimethylsilyl)methyl]-3-buten-1-yl]-3,4-dihydroisoquinolinium Perchlorate (44).** To a solution of 3,4-dihydroisoquinoline **42** (1 mmol) and silver perchlorate (1 mmol) in acetonitrile (3 mL) at 0 °C was added ethyl iodoacetate (1 mmol) dropwise at 0 °C. After addition, the reaction mixture was stirred at 25 °C for 3 days in the dark and then filtered through Celite. The filtrate was concentrated in vacuo to afford a viscous liquid that was triturated with ether to obtain pure perchlorate salt **44**: ^{1}H NMR −0.06 (s, 9 H, $Si(CH_3)_3$), 1.29 (t, J = 7.1 Hz, 3 H, CH_3), 1.45 (s, 2 H, CH_2Si), 2.20 (dd, J = 7.4, 7.9 Hz, 2 H, H-2'), 3.18 (m, 4 H, H-4 and H-1'), 3.86 (s, 3 H, OCH_3), 3.96–4.04 (7, 5 H, OCH_3 and H-3), 4.26 (q, J = 7.1 Hz, 2 H, OCH_2), 4.55, 4.61 (s, 2 H, vinyl H), 4.91 (s, 2 H, NCH_2CO_2), 6.90, 7.16 (s, 2 H, H-5 and H-8); ^{13}C NMR −1.6 ($Si(CH_3)_3$), 14.0 (CH_3), 25.6, 26.5 (C-4, CH_2Si), 30.2 (C-1'), 35.9 (C-2'), 52.4 (C-3), 56.4, 56.8 (OCH_3), 63.2 (NCH_2CO_2), 109.2 (C=CH_2), 111.0, 112.2 (C-5 and C-8), 118.6 (C-9), 134.9 (C-10), 144.0 (C-7), 148.8 (*C*=CH_2), 157.1 (C-6), 166.2 (CO_2), 179.3 (C-1); IR ($CHCl_3$) 3029, 1748, 1388, 1096, 855; mass spectrum, *m/e* (relative intensity) 417 ($M^+ - HClO_4$, 5), 344 (48), 272 (81), 258 (35), 205 (28), 190 (12), 73 (64); high-resolution mass spectrum, *m/e* 417.2371 ($C_{23}H_{35}O_4NSi$ requires 417.2335).

***N*-[(Ethoxycarbonyl)methyl]-6,7-dimethoxy-1-[*2,2,4,4-d*$_4$-3-[(trimethylsilyl)methyl]-3-buten-1-yl]-3,4-dihydroisoquinolinium Perchlorate (44-*d*$_4$).** Tetradeuteriodihydroisoquinolinium perchlorate **44**-d_4 was prepared from tetradeuteriodihydroisoquinoline **42**-d_4 by the method described above for preparation of **44**.

Photolyses (Direct Irradiation) of the d_4-3,4-Dihydroisoquinolinium Perchlorates 43-d_4 and 44-d_4. Irradiations were conducted on N_2-purged MeCN solutions of d_4-dihydroisoquinolinium perchlorates **43**-d_4 and **44**-d_4. The photolysates were subjected to the general workup procedure, yielding residues that were subjected to column chromatographic separation on silica gel ($CHCl_3$ as eluant) and giving the desired products **45**-d_4 and **46**-d_4. The ratios of isotopomers (**A**:**B**) in these products were determined by ^1H NMR methods (see Table V).

Photolyses (Direct Irradiation) of *N*-[(Ethoxycarbonyl)methyl]-6,7-dimethoxy-1-[3-[(trimethylsilyl)methyl]-3-buten-1-yl]-3,4-dihydroisoquinolinium Perchlorate (44). A N_2-purged solution of dihydroisoquinolinium salt **44** (1.5×10^{-3} M) in acetonitrile was irradiated with a uranium glass filtered light. The photolysate was concentrated in vacuo and subjected to the general workup procedure (general section). The residue obtained was subjected to column chromatography on silica gel ($CHCl_3$ as eluent), giving the spirocyclic product **45** (74%): ^1H NMR 1.23 (t, J = 7.1 Hz, 3 H, CH_3), 2.00–3.00 (m, 8 H, H-4, H-2′, H-4′, H-5′), 3.10–3.40 (m, 2 H, H-3), 3.25 (s, 2 H, NCH_2CO_2), 3.76, 3.82 (s, 6 H, OCH_3), 4.16 (q, J = 7.1 Hz, 2 H, OCH_2), 4.90, 4.95 (s, 2 H, vinyl H), 6.52, 6.74 (s, 2 H H-5 and H-8); ^{13}C NMR 14.2 (CH_3), 23.8 (C-4), 31.6 (C-4′), 40.2 (C-5′), 45.3 (C-3), 46.7 (C-2′), 51.9 (NCH_2CO_2), 55.8, 55.9 (OCH_3), 60.6 (OCH_2), 67.9 (C-1), 105.8 ($C{=}CH_2$), 109.6, 111.6 (C-8 and C-5), 125.4 (C-9), 134.8 (C-10), 147.2, 147.4 (C-6 and C-7), 151.9 (C-3′), 171.8 (CO_2); IR ($CHCl_3$) 2935, 1725, 1500, 1455, 1250; mass spectrum, m/e (relative intensity) 345 (M^+, 66), 344 (34), 330 (38), 316 (72), 272 (100), 258 (54), 244 (94); high-resolution mass spectrum, m/e 345.1924 ($C_{20}H_{27}O_4$ requires 345.1940).

General Procedure for Preparation of the 2-Methyl-1-(substituted benzyl)-1-pyrrolinium Perchlorates. A mixture of 2-methyl-1-pyrroline[9] (0.33–0.50 g, 4.0–6.0 mmol) and an equimolar amount of a selected benzyl iodide (see supplementary material) in CH_2Cl_2 (0.2–0.5 mL) was stirred at 0 °C for 0.5 h under an Ar atmosphere and at 25 °C for 2 h. The resulting thick oil or solid was triturated with pentane–ether to give the corresponding pyrrolinium iodide. The iodide salt was converted to the desired perchlorate salt by elution in a methanol solution (150–200 mL) through a Dowex 1 ion-exchange column (ClO_4 form). Concentration of the methanol eluant in vacuo gave pure pyrrolinium perchlorate that was normally used without further purification. In the case of crystalline substances, analytically pure samples were obtained by recrystallization from CH_3OH. The following salts were prepared in this way.

2-Methyl-1-[*o*-[(*tert*-butyldimethylsilyl)methyl]benzyl]-1-pyrrolinium perchlorate (50): yield 75%; mp 150–152 °C; UV(CH_3CN) λ_{max} 273 nm (ϵ 1280); ^1H NMR −0.12 (s, 6 H, $Si(CH_3)_2$), 0.94 (s, 9 H, $SiC(CH_3)_3$), 2.12 (s, 2 H, $ArCH_2Si$), 2.25 (p, 2 H, H-4), 2.60 (s, 3 H, 2-CH_3), 3.42 (t, 2 H, H-3), 4.00 (t, 2 H, H-5), 4.95 (s, 2 H, $ArCH_2N$), 7.04–7.29 (m, 4 H); ^{13}C NMR −6.3 ($Si(CH_3)_2$), 16.7 ($SiC(CH_3)_3$), 17.75 (C-4), 17.80 (2-CH_3), 19.0 ($ArCH_2Si$), 26.5 ($SiC(CH_3)_3$), 41.4 (C-3), 52.2 (C-5), 59.8 ($ArCH_2$), 125.5, 128.4, 129.3, 130.5 (aryl CH), 126.7, 140.0 (aryl quaternary), 192.3 (C-2); IR ($CHCl_3$) 2930, 2860, 1660, 1450, 1250, 1080, 840; mass spectrum, m/e (relative intensity) 301 (M^+ − $HClO_4$, 18), 244 (12), 162 (10), 83 (54); high-resolution mass spectrum, m/e 301.2211 ($C_{19}H_{31}NSi$ requires 301.2226).

2-Methyl-1-(*m*-hydroxybenzyl)-1-pyrrolinium perchlorate (56): yield 75%; UV (CH_3CN) λ_{max} 277 nm (ϵ 2020); ^1H NMR (acetone-d_6) 2.26 (p, 2 H, H-4), 2.70 (s, 3 H, 2-CH_3), 3.41 (t, 2 H, H-3), 4.21 (t, 2 H, H-5), 5.06 (s, 2 H, $ArCH_2$), 6.94 (m, 3 H), 7.24 (t, 1 H, aryl H-5), 8.62 (br s, 1 H, OH); ^{13}C NMR (acetone-d_6) 17.7 (2-CH_3), 18.7 (C-4), 41.6 (C-3), 54.5 (C-5), 60.7 ($ArCH_2$), 116.5, 117.0, 120.7, 131.1 (aryl CH), 133.5, 158.8 (aryl quaternary), 193.7 (C-2); IR (neat) 3360 (br, OH), 1670, 1600, 1590, 1460, 1090, 620; mass spectrum, m/e (relative intensity), 189 (M^+ − $HClO_4$, 11), 107 (100), 83 (44); high-resolution mass spectrum, m/e 189.1149 ($C_{12}H_{15}ON$ requires 189.1154).

2-Methyl-1-[*m*-(*tert*-butyldimethylsiloxy)benzyl]-1-pyrrolinium perchlorate (57): yield 80%; mp 120–121 °C; UV (CH_3CN) λ_{max} 277 nm (ϵ 1690); ^1H NMR 0.18 (s, 6 H, $Si(CH_3)_2$), 0.95 (s, 9 H, $SiC(CH_3)_3$), 2.22 (p, 2 H, H-4), 2.62 (s, 3 H, 2-CH_3), 3.37 (t, 2 H, H-3), 4.02 (t, 2 H, H-5), 4.91 (s, 2 H, $ArCH_2$), 6.76–6.93 (m, 3 H), 7.27 (t, 1 H, aryl H-5); ^{13}C NMR −4.4 ($Si(CH_3)_2$), 17.8 (2-CH_3 and C-4), 18.4 (SiC), 18.2 (C-4), 25.6 ($SiC(CH_3)_3$) 41.1 (C-3), 54.4 (C-5), 59.8 ($ArCH_2$), 120.8, 121, 121.6, 130.8 (aryl CH), 131.7, 156.5 (aryl quaternary), 192.2 (C-2); IR ($CHCl_3$) 2930, 2860, 1670, 1610, 1600, 1490, 1450, 1290, 1260, 1090, 840; mass spectrum, m/e (relative intensity) 303 (M^+ − $HClO_4$, 45), 288 (9), 246 (20), 221 (25), 83 (38), 75 (100); high-resolution mass spectrum, m/e 303.2027 ($C_{18}H_{29}SiON$ requires 303.2018).

2-Methyl-1-(*m*-methoxybenzyl)-1-pyrrolinium perchlorate (58): yield 88%; UV (CH_3CN) λ_{max} 276 nm (ϵ 2030); ^1H NMR 2.21 (p, 2 H, H-4), 2.62 (s, 3 H, 2-CH_3), 3.36 (t, 2 H, H-3), 3.80 (s, 3 H, OCH_3), 4.00 (t, 2 H, H-5), 4.93 (s, 2 H, $ArCH_2$), 6.88–6.93 (m, 3 H), 7.30 (t, 1 H, aryl H-5); ^{13}C NMR 17.5 (2-CH_3), 17.6 (C-4), 40.8 (C-3), 54.1 (C-5), 55.3 (OCH_3), 59.4 ($ArCH_2$), 114.4, 115.2, 121.2, 130.4 (aryl CH), 131.5, 160.1 (aryl quaternary), 192.1 (C-2); IR ($CHCl_3$) 3010, 1670, 1600, 1270, 1205, 1090; mass spectrum, m/e (relative intensity) 203 (M^+ − $HClO_4$, 24), 188 (6), 121 (100), 83 (7); high-resolution mass spectrum, m/e 203.1311 ($C_{13}H_{17}ON$ requires 203.1310).

2-Methyl-1-(*m*-methylbenzyl)-1-pyrrolinium perchlorate (63): yield 72%; UV (CH_3CN) λ_{max} 266 nm (ϵ 488); ^1H NMR (acetone-d_6) 2.22 (p, 2 H, H-4), 2.35 (s, 3 H, $ArCH_3$), 2.72 (s, 3 H, 2-CH_3), 3.40 (t, 2 H, H-3), 4.11 (t, 2 H, H-5), 5.11 (s, 2 H, $ArCH_2$), 7.24–7.33 (m, 4 H); ^{13}C NMR (acetone-d_6) 17.6 (2-CH_3), 18.4 (C-4), 21.2 ($ArCH_3$), 41.3 (C-3), 54.4 (C-5), 60.3 ($ArCH_2$), 126.9, 129.6, 130.3, 130.4 (aryl CH), 131.9, 139.7 (aryl quaternary), 193.4 (C-2); IR (neat) 2940, 1670, 1180, 620; mass spectrum, m/e (relative intensity) 187 (M^+ − $HClO_4$, 23), 172 (5), 105 (100), 83 (15); high-resolution mass spectrum, m/e 187.1358 ($C_{13}H_{17}N$ requires 187.1361).

2-Methyl-1-[*m*-[(trimethylsilyl)methyl]benzyl]-1-pyrrolinium perchlorate (64): yield 84%; mp 109–110.5 °C; UV (CH_3CN) λ_{max} 274 nm (ϵ 890); ^1H NMR −0.05 (s, 9 H, $Si(CH_3)_3$), 2.10 (s, 2 H, $ArCH_2Si$), 2.22 (p, 2 H, H-4), 2.63 (s, 3 H, 2-CH_3), 3.38 (t, 2 H, H-3), 4.01 (t, 2 H, H-5), 4.91 (s, 2 H, $ArCH_2N$), 6.94–7.03 (m, 3 H), 7.24 (t, 1 H, aryl H-5); ^{13}C NMR −2.0 ($Si(CH_3)_3$), 17.7 (C-4), 17.8 (2-CH_3), 26.9 ($ArCH_2Si$), 40.1 (C-3), 54.6 (C-5), 59.7 ($ArCH_2N$), 124.3, 128.3, 129.1, 129.4 (aryl CH), 130.1, 142.5 (aryl quaternary), 191.9 (C-2); IR ($CHCl_3$) 2950, 1670, 1600, 1250, 1090, 850; mass spectrum, m/e (relative intensity) 259 (M^+ − $HClO_4$, 43), 177 (34), 73 (100); high-resolution mass spectrum, m/e 259.1757 ($C_{16}H_{25}NSi$ requires 259.1756).

2-Methyl-1-[*m*-[(*tert*-butyldimethylsilyl)methyl]benzyl]-1-pyrrolinium perchlorate (65): yield 81%; mp 110–111 °C; ^1H NMR −0.14 (s, 6 H, $Si(CH_3)_2$), 0.89 (s, 9 H, $SiC(CH_3)_3$), 2.11 (s, 2 H, $ArCH_2Si$), 2.23 (p, 2 H, H-4), 2.64 (s, 3 H, 2-CH_3), 3.38 (t, 2 H, H-3), 4.05 (t, 2 H, H-5), 4.92 (s, 2 H, $ArCH_2N$), 6.92–7.21 (m, 3 H), 7.25 (t, 1 H, aryl H-5); ^{13}C NMR −6.4 ($Si(CH_3)_3$), 16.7 ($SiC(CH_3)_3$), 17.8 (2-CH_3), 17.9 (C-4), 22.8 ($ArCH_2Si$), 26.5 ($SiC(CH_3)_3$), 41.1 (C-3), 54.8 (C-5), 55.9 ($ArCH_2N$), 124.3, 128.6, 129.5, 129.6 (aryl CH), 130.2, 142.9 (aryl quaternary), 192.0 (C-2); IR ($CHCl_3$) 2930, 2850, 1670, 1605, 1250, 1090, 825; mass spectrum, m/e (relative intensity) 301 (M^+ − $HClO_4$, 9), 244 (M^+ − $HClO_4$ − $C(CH_3)_3$, 5), 219 ($(TBDMS)CH_2ArCH_2^+$, 5), 83 (10); high-resolution mass spectrum, m/e 301.2236 ($C_{19}H_{31}SiN$ requires 301.2226).

2-Methyl-1-(2′,6′-dimethylbenzyl)-1-pyrrolinium perchlorate (70): yield 64%; mp 151–153 °C dec; ^1H NMR 2.14 (p, 2 H, H-4), 2.31 (s, 6 H, $Ar(CH_3)_2$), 2.64 (s, 3 H, 2-CH_3), 3.37 (t, 2 H, H-3), 3.74 (t, 2 H, H-5), 5.05 (s, 2 H, $ArCH_2$), 7.23–7.05 (m, 3 H); ^{13}C NMR 17.7 (C-4), 17.8 (2-CH_3), 20.0 ($Ar(CH_3)_3$), 41.1 (C-3), 49.1 (C-5), 58.4 ($ArCH_2$), 129.2, 129.9 (aryl CH), 127.0, 138.7 (aryl quaternary), 191.9 (C-2); IR ($CHCl_3$) 3020, 2970, 1665, 1470, 1250, 1095; mass spectrum, m/e (relative intensity) 201 (M^+ − $HClO_4$, 15), 186 (85), 119 (100), 83 (10); high-resolution mass spectrum, m/e 201.1514 ($C_{14}H_{19}N$ requires 201.1517).

2-Methyl-1-[*o*-(trimethylsilyl)benzyl]-1-pyrrolinium perchlorate (72): yield 65%; mp 179–181 °C dec; ^1H NMR 0.36 (s, 9 H, $Si(CH_3)_3$), 2.28 (p, 2 H, H-4), 2.62 (s, 3 H, 2-CH_3), 3.45 (t, 2 H, H-3), 4.05 (t, 2 H, H-5), 5.12 (s, 2 H, $ArCH_2$), 7.10–7.58 (m, 4 H); ^{13}C NMR 0.1 ($Si(CH_3)_3$), 17.9 (2-CH_3), 18.1 (C-4), 41.0 (C-3), 54.5 (C-5), 60.1 ($ArCH_2$), 126.4, 128.4, 130.5, 135.5 (aryl CH), 135.6, 139.5 (aryl quaternary), 193.5 (C-2); IR ($CHCl_3$) 2020, 2960, 1675, 1255, 1220, 1100, 840; mass spectrum, m/e (relative intensity) 245 (M^+3 − $HClO_4$, 38), 230 (26), 163 (100), 83 (26); high-resolution mass spectrum, m/e 245.1619 ($C_{15}H_{23}NSi$ requires 245.1600).

General Procedure for Direct Irradiation of 2-Methyl-1-(benzyl substituted)-1-pyrrolinium Perchlorates. A nitrogen-purged solution of the 2-methyl-1-(substituted benzyl)-1-pyrrolinium perchlorate (0.5–0.9 mmol) in MeCN (120 mL) was irradiated with Vycor glass filtered light ($\lambda \geq 240$ nm). The reaction progress was followed by ^1H NMR (200 mHz). Irradiation was stopped when characteristic proton resonances of the starting salt had completely disappeared. In order to determine product ratios accurately, photoreactions were conducted at least two times. The crude photolysate obtained from each photoreaction was subjected to workup procedures involving addition of either solid $NaHCO_3$ or aqueous saturated $NaHCO_3$ either prior to or following concentration in vacuo. Extraction with $CHCl_3$ followed by drying and concentration in vacuo gave a residue that was subjected to Florisil column chromatography, giving pure photoproducts. In each case, ^1H NMR analysis of the crude product mixtures prior to separation was used to determine photoproduct ratios, and the ratios matched closely those obtained by product isolation. Photoreactions under the conditions described above were also conducted on MeOH and Me_2CO (pyrex filter) solutions. The results are recorded in Tables VI–VIII.

Irradiation of 2-Methyl-1-[*o*-[(trimethylsilyl)methyl]benzyl]-1-pyrrolinium Perchlorate (49). Reexamination of the Photoproduct Dis-

tribution. Photoreaction of pyrrolinium perchlorate **49** reported earlier[3d] was conducted under the conditions previously described. Two minor photoproducts, 2',5-dimethyl-3,4-benzopyrrolizidine (**53**) (6%) and 2'-[(trimethylsilyl)methyl]-5-methyl-3,4-benzopyrrolizidine (**54**) (21%), not previously reported were detected in addition to 6-methyl-3,4-benzindolizidine (**51**) (72%), which had been previously isolated and identified.[3d]

54: H NMR −0.01 (s, 9 H, $Si(CH_3)_3$), 1.37 (s, 3 H, 5-CH_3), 1.67–2.03 (m, 4 H, H-6 and H-7), 2.58 (m, 1 H, H-8 endo), 3.24 (m, 1 H, H-8 exo), 3.77 and 4.29 (ABq, J = 15.2 Hz, 2 H, H-2), 6.82 (d, J = 7.5 Hz, 1 H, H-3'), 6.87 (d, J = 7.5 Hz, 1 H, H-5'), 7.12 (t, J = 7.5 Hz, 1 H, H-4'); mass spectrum, m/e (relative intensity) 259 (M^+, 71), 244 (100), 231 (17), 216 (5), 187 (23), 73 (57); high-resolution mass spectrum, m/e 259.1765 ($C_{16}H_{25}SiN$ requires 259.1756).

Irradiation of 2-Methyl-1-[*o*-[(*tert*-butyldimethylsilyl)methyl]-benzyl]-1-pyrrolinium Perchlorate (50). Formation of 2'-[(*tert*-Butyldimethylsilyl)methyl]-5-methyl-3,4-benzopyrrolizidine (55). Photoreaction gave 2-[(*tert*-butyldimethylsilyl)methyl]benzopyrrolizidine **55** (86%) and 2-methyl-3,4-benzopyrrolizidine **53** (4%).

55: ^{1}H NMR −0.14 (s, 6 H, $Si(CH_3)_3$), 0.91 (s, 9 H, $SiC(CH_3)_3$), 1.36 (s, 3 H, 5-CH_3), 1.72–1.98 (m, 4 H, H-6 and H-7), 1.96 (s, 2 H, $ArCH_2Si$), 2.57 (m, 1 H, H-8 endo), 3.21 (m, 1 H, H-8 exo), 3.71 and 4.22 (AB q, J = 15.1 Hz, 2 H, H-2), 6.84 (t, J = 7.7 Hz, 2 H, H-3' and H-5'), 7.11 (t, J = 7.5 Hz, 1 H, H-4'); ^{13}C NMR −6.3 ($Si(CH_3)_2$), 16.6 ($SiC(CH_3)_3$), 19.1 ($ArCH_2Si$), 25.4 (C-7), 26.4 ($SiC(CH_3)_3$), 29.3 (5-CH_3), 38.9 (C-6), 56.8 (C-8), 58.2 (C-2), 76.0 (C-5), 117.6, 126.5, 127.4 (aryl CH) 135.4, 136.4, 148.8, (aryl quaternary); IR ($CHCl_3$) 2960, 2850, 1590, 1465, 1250, 1145, 900, 830, 820; mass spectrum, m/e (relative intensity) 301 (M^+, 20), 286 (100), 273 (3), 258 (36), 244 (12), 186 (6), 115 (1); high-resolution mass spectrum, m/e 301.2234 $C_{19}H_{31}NSi$ requires 301.2226).

Irradiation of 2-Methyl-1-(*m*-hydroxybenzyl)-1-pyrrolinium Perchlorate (56). Formation of 3'- and 5'-Hydroxy-5-methyl-3,4-benzopyrrolizidine (60 and 59). The regioisomeric 3'- and 5'-hydroxy-5-methyl-3,4-benzopyrrolizidines **60** and **59** were obtained following column chromatography in 34% and 11% yields, respectively, by preparative silica gel TLC (12% CH_3OH–88% $CHCl_3$).

59: R_f 0.2; ^{1}H NMR 1.50 (s, 3 H, 5-CH_3), 1.78–2.29 (m, 4 H, H-6 and H-7), 2.61 (m, 1 H, H-8 endo), 3.32 (m, 1 H, H-8 exo), 3.8 and 4.41 (AB q, J = 15.4 Hz, 2 H, H-2), 6.61 (d, J = 7.8 Hz, 1 H, H-2'), 6.71 (d, J = 7.4 Hz, 1 H, H-4'), 7.08 (t, J = 7.6 Hz, 1 H, H-3'); mass spectrum, m/e (relative intensity) 189 (M^+, 9), 188 (3), 174 (100), 161 (8), 146 (3); high-resolution mass spectrum, m/e 189.1154 ($C_{12}H_{15}NO$ requires 189.1154).

60: R_f 0.1; ^{1}H NMR 1.39 (s, 3 H, 5-CH_3), 1.75–2.04 (m, 4 H, H-6 and H-7), 2.65 (m, 1 H, H-8 endo), 3.25 (m, 1 H, H-8 exo), 3.76 and 4.32 (AB q, J = 15.4 Hz, 2 H, H-2), 6.58 (d, J = 2.2 Hz, 1 H, H-2'), 6.69 (dd, J = 8.1, 2.2 Hz, 1 H, H-4'), 6.96 (d, J = 8.1 Hz, 1 H, H-5'); ^{13}C NMR (acetone-d_6) 25.7 (C-7), 27.3 (5-CH_3), 39.4 (C-6), 57.7 (C-8), 59.3 (C-2), 81.6 (C-5), 110.2, 116.9, 123.6 (aryl CH) 136.3, 137.7, 158.8 (aryl quaternary); IR (neat) 3340 (br), 2960, 1600, 1450, 1280, 1100, 620; mass specrum, m/e (relative intensity) 189 (M^+, 22), 188 (4), 174 (100), 161 (26), 146 (11); high-resolution mass spectrum, m/e 189.1155 ($C_{12}H_{15}ON$ requires 189.1154).

Irradiation of 2-Methyl-1-[*m*-(*tert*-butyldimethylsiloxy)benzyl]-1-pyrrolinium Perchlorate (57). Formation of 3'-(*tert*-Butyldimethylsiloxy)-5-methyl-3,4-benzopyrrolizidine (61). Photoreaction provided 3'-(*tert*-butyldimethyolsiloxy)-5-methyl-3,4-benzopyrrolizidine (**61**) in 62% yield and 3'-hydroxy-5-methyl-3,4-benzopyrrolizidine (**60**) in a 21% yield. The ratio of **61** to **60** decreases when the crude photolysate is concentrated without prior base treatment.

61: mp 135–136 °C (ether); ^{1}H NMR 0.18 (s, 6 H, $Si(CH_3)_2$), 0.97 (s, 9 H, $SiC(CH_3)_3$), 1.36 (s, 3 H, 5-CH_3), 1.69–1.99 (m, 4 H, H-6 and H-7), 2.59 (m, 1 H, H-8 endo), 3.22 (m, 1 H, H-8 exo), 3.74 and 4.29 (AB q, J = 15.3 Hz, 2 H, H-2), 6.59 (d, J = 2.2 Hz, 1 H, H-2'), 6.69 (dd, J = 8.1, 2.2 Hz, 1 H, H-4'), 6.96 (d, J = 8.1 Hz, 1 H, H-5'); ^{13}C NMR −4.4 ($Si(CH_3)_2$), 18.1 ($SiC(CH_3)_3$), 25.7 ($SiC(CH_3)_3$), 25.8 (C-7), 29.2 (5-CH_3), 39.0 (C-6), 56.8 (C-8), 58.7 (C-2), 75.6 (C-5), 113.9, 119.2, 122.5 (aryl CH), 140.5, 141.6, 155.0 (aryl quaternary); IR ($CHCl_3$) 2920, 2850, 1610, 1485, 1280, 960, 840; mass spectrum, m/e (relative intensity) 303 (M^+, 37), 288 (100), 275 (4), 246 (2); high-resolution mass spectrum, m/e 303.1996 ($C_{18}H_{29}OSiN$ requires 303.2018).

Irradiation of 2-Methyl-1-(*m*-methoxybenzyl)-1-pyrrolinium Perchlorate (58). Formation of 3'-Methoxy-5-methyl-3,4-benzopyrrolizidine (62). Photoreaction gave 3'-methoxy-5-methyl-3,4-benzopyrrolizidine (**62**) as a sole product in 95% yield.

62: ^{1}H NMR 1.35 (s, 3 H, 5-CH_3), 1.19–1.69 (m, 4 H, H-6 and H-7), 2.57 (m, 1 H, H-8 endo), 3.20 (m, 1 H, H-8 exo), 3.75 (s, 3 H, OCH_3), 3.77 and 4.30 (AB q, J = 15.2 Hz, 2 H, H-2), 6.60 (d, J = 2.2 Hz, 1 H, H-2'), 6.75 (dd, J = 8.2 and 2.2 Hz, 1 H, H-4'), 7.02 (d, J = 8.2 Hz, 1 H, H-5'); ^{13}C NMR 25.6 (C-7), 29.3 (5-CH_3), 30.9 (C-6), 55.4 (OCH_3), 56.7 (C-8), 58.8 (C-2), 75.3 (C-5) 107.8, 113.6, 122.5 (aryl CH), 140.8, 141.2, 159.2 (aryl quaternary); IR ($CHCl_3$) 2940, 1610, 1490, 1260, 1210, 1145, 1080, 1020, 920; mass spectrum, m/e (relative intensity) 203 (M^+, 25), 202 (13), 188 (100), 175 (23), 160 (10); high-resolution mass spectrum, m/e 203.1306 ($C_{13}H_{17}NO$ requires 203.1310).

Irradiation of 2-Methyl-1-(*m*-methylbenzyl)-1-pyrrolinium Perchlorate (63). Formation of 3',5- and 5',5-Dimethyl-3,4-benzopyrrolizidines (67 and 66). Photoreaction provided 5',5-dimethyl-3,4-benzopyrrolizidine (**66**) and 3',5-dimethyl-3,4-benzopyrrolizidine (**67**) in yields of 18% and 58%, respectively.

66: ^{1}H NMR 1.45 (s, 3 H, 5-CH_3), 2.08 (m, 4 H, H-6 and H-7), 2.34 (s, 3 H, $ArCH_3$), 2.53 (m, 1 H, H-8 endo), 3.32 (m, 1 H, H-8 exo), 3.72 and 4.36 (AB q, J = 15.4 Hz, 2 H, H-2), 7.03 (m, 2 H, H-2' and H-4'), 7.14 (t, 1 H, H-3'); mass spectrum, m/e (relative intensity) 187 (M^+, 5), 186 (8), 172 (100), 159 (7), 144 (5); high-resolution mass spectrum, m/e 187.1630 ($C_{13}H_{17}N$ requires 187.1361).

67: ^{1}H NMR 1.38 (s, 3 H, 5-CH_3), 1.97 (m, 4 H, H-6 and H-7), 2.33 (s, 3 H, $ArCH_3$), 2.59 (m, 1 H, H-8 endo), 3.24 (m, 1 H, H-8 exo), 3.79 and 4.34 (AB q, J = 15.3 Hz, H-2), 6.97 (s, 1 H, H-2'), 7.04 and 7.05 (s, 2 H, H-4' and H-5'); ^{13}C NMR 21.2 ($ArCH_3$), 25.6 (C-7), 29.2 (5-CH_3), 39.0 (C-6), 56.8 (C-8), 58.7 (C-2), 75.7 (C-5), 121.8, 123.3, 128.3 aryl CH), 136.6, 139.4, 146.1 (aryl quaternary); mass spectrum, m/e (relative intensity) 187 (M^+, 14), 186 (3), 172 (100), 159 (18), 144; high-resolution mass spectrum, m/e 187.1358 ($C_{13}H_{17}N$ requires 187.1361).

Irradiation of 2-Methyl-1-[*m*-[(trimethylsilyl)methyl]benzyl]-1-pyrrolinium Perchlorate (64). Formation of 3'-[(Trimethylsilyl)-methyl]-5-methyl-3,4-benzopyrrolizidine (68). Photoreaction gave the 5',5-dimethyl- (**66**), 3',5-dimethyl- (**67**), and 3'-[(trimethylsilyl)-methyl]-5-methyl-3,4-benzopyrrolizidines (**68**) in yields of 19%, 38%, and 29%, respectively.

68: ^{1}H NMR −0.03 (s, 9 H, $Si(CH_3)_3$), 2.00 (m, 4 H, H-6 and H-7), 2.05 (s, 2 H, $ArCH_2Si$), 2.54 (m, 1 H, H-8 endo), 3.20 (m, 1 H, H-8 exo), 3.84 and 4.48 (AB q, J = 15.2 Hz, 2 H, H-2), 6.78 (s, 1 H, H-2'), 6.88 (d, J = 7.8 Hz, 1 H, H-4'), 6.98 (d, J = 7.8 Hz, 1 H, H-5'); mass spectrum, m/e (relative intensity) 259 (M^+, 43), 258 (5), 244 (100), 263 (21), 186 (16), 73 (78); high-resolution mass spectrum, m/e 259.1734 ($C_{16}H_{25}NSi$ requires 259.1756).

Irradiation of 2-Methyl-1-[*m*-[(*tert*-butyldimethylsilyl)methyl]-benzyl]-1-pyrrolinium Perchlorate (65). Formation of 3'-[(*tert*-Butyldimethylsilyl)methyl]-5-methyl-3,4-benzopyrrolizidine (69). Photoreaction gave 3'-[(*tert*-butyldimethylsilyl)methyl]-5-methyl-3,4-benzopyrrolizidine (**69**) and 3',5-dimethyl-3,4-benzopyrrolizidine (**67**) in yields of 68% and 14%, respectively.

69: ^{1}H NMR −0.13 (s, 6 H, $Si(CH_3)_2$), 0.89 (s, 9 H, $SiC(CH_3)_3$), 1.36 (s, 3 H, 5-CH_3), 1.74–1.97 (m, 4 H, H-6 and H-7), 2.05 (s, 2 H, $ArCH_2Si$) 2.58 (m, 1 H, H-8 endo), 3.21 (m, 1 H, H-8 exo), 3.74 and 4.29 (AB q, J = 15.2 Hz, 2 H, H-2), 6.77 (s, 1 H, H-2'), 6.84 (d, J = 7.4 Hz, 1 H, H-4'), 6.96 (d, J = 7.4 Hz, 1 H, H-5'); ^{13}C NMR −6.4 ($Si(CH_3)_2$), 16.7 ($SiC(CH_3)_3$), 22.3 ($ArCH_2Si$), 25.6 (C-7), 26.5 ($SiC(CH_3)_3$), 29.3 (5-CH_3), 39.0 (C-6), 56.7 (C-8), 58.9 (C-2), 75.5 (C-5), 121.5, 122.3, 127.4 (aryl CH), 139.1, 139.4, 144.8 (aryl quaternary); IR ($CHCl_3$) 2920, 2850, 1610, 1465, 1250, 1160, 850, 825; mass spectrum, m/e (relative intensity) 301 (M^+, 31), 286 (100), 273 (6), 258 (15), 244 (22), 186 (5), 115 (3); high-resolution mass spectrum, m/e 301.2214 ($C_{19}H_{31}NSi$ requires 301.2226).

Irradiation of 2-Methyl-1-[*o*-(trimethylsilyl)benzyl]-1-pyrrolinium Perchlorate (72). Formation of 2'-(Trimethylsilyl)-5-methyl-3,4-benzopyrrolizidine (73). ^{1}H NMR analysis of the crude photolysate showed it to contain a mixture of 2'-(trimethylsilyl)-5-methyl-3,4-benzopyrrolizidine (**73**) and the known 5-methyl-3,4-benzopyrrolizidine (**52**)[3d] in a 2:1 ratio. Chromatographic separation gave **73** in a 46% yield. Aliquots of the photolysate were analyzed by ^{1}H NMR after various conversions. Product **73**:**52** ratios (approximate conversion percentages) were 7:1 (20%) and 2:1 (70%).

73: ^{1}H NMR 0.26 (s, 9 H, $Si(CH_3)_3$), 1.39 (s, 3 H, 5-CH_3), 1.70–2.03 (m, 4 H, H-6 and H-7), 2.60 (m, 1 H, H-8 endo), 3.27 (m, 1 H, H-8 exo), 3.87 and 4.40 AB q, J = 15.2 Hz, 2 H, H-2), 7.12–7.32 (m, 3 H); ^{13}C NMR −0.8 ($Si(CH_3)_3$), 25.4 (C-7), 29.2 (5-CH_3), 39.0 (C-6), 56.7 (C-8), 59.6 (C-2), 75.2 (C-5), 123.0, 126.9, 132.5 (aryl CH), 134.5, 144.1, 147.7 (aryl quaternary); IR ($CHCl_3$) 2960, 1705, 1250, 1215; 840; mass spectrum, m/e (relative intensity) 245 (M^+, 22), 230 (100), 217 (13), 73 (44); high-resolution mass spectrum, m/e 245.1589 ($C_{15}H_{23}NSi$ requires 245.1600).

General Procedure for Acetone-Sensitized Irradiation of 2-Methyl-1-(benzyl substituted)-1-pyrrolinium Perchlorates. Nitrogen-purged solutions of the pyrrolinium perchlorates (0.4–0.8 mmol) in 100 mL of acetone were irradiated with Pyrex filtered light ($\lambda > 290$ nm). Photolysates were subjected to the same workup procedures used in the direct

irradiation reactions. 2-Methyl-1-(*m*-hydroxybenzyl)-1-pyrrolinium perchlorate was inert under the acetone-sensitized reaction conditions. Control irradiations with Pyrex filtered light, in which CH_3CN was employed as solvent, led to no conversion of the salts. Product yields and distributions were determined by using the same procedures described for direct irradiation reactions.

Preparation of 2-Methyl-1-(*m*-(d_3-methyl)benzyl)-1-pyrrolinium Perchlorate (63-d_3). This substance was prepared following the procedure used for the preparation of the protio analogue: ^{1}H NMR (acetone-d_6) 2.22 (p, 2 H, H-4), 2.35 (p, residual CD_2H), 2.72 (s, 3 H, 2-CH_3), 3.40 (t, 2 H, H-3), 4.11 (t, 2 H, H-5), 5.11 (s, 2 H, $ArCH_2$), 7.24-7.33 (m, 4 H).

Irradiation of 2-Methyl-1-(*m*-(d_3-methyl)benzyl)-1-pyrrolinium Perchlorate (63-d_3). Irradiation of the d_3-pyrrolinium perchlorate **63-d_3** in CH_3CN and 0.2% H_2O-CH_3CN (for direct irradiation) or in acetone (for sensitized irradiation) and workup were carried out as described previously for the protio analogue. This afforded a mixture of 3'-(trideuteriomethyl)-(**67-d_3**)- and 5'-(trideuteriomethyl)-5-methyl-3,4-benzopyrrolizidine (**66-d_3**) each of which was shown by ^{1}H NMR to have completely (ca. 97%) retained the d_3 label.

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Supplementary Material Available: Experimental procedures for the preparation of benzyl chlorides, benzyl alcohols, and ortho and meta substituted benzyl iodide (6 pages). Ordering information is given on any current masthead page.

Intermediates in the Ene Reactions of Singlet Oxygen and *N*-Phenyl-1,2,4-triazoline-3,5-dione with Olefins

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Abstract: The reaction between singlet oxygen and *cis*- and *trans*-2-butene-*1,1,1-d*$_3$ has been studied. The product isotope effects (k_H/k_D) were found to be 1.38 and 1.25, respectively. Similarly, *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) reacts readily with these substrates and shows isotope effects that are larger (5.36, 1.29) but in the same direction. 2-Methyl-1-propene-3,3,3-d_3 is unreactive with singlet oxygen but reacts easily with PTAD with a product isotope effect of 1.25. The intermolecular (kinetic) and intramolecular (product) isotope effects on the reactions of singlet oxygen with *cis*-1,4-diphenyl-2-butene were found to be 1.07 and 1.50, respectively. cis-Butene is 18 times more reactive with singlet oxygen than the trans isomer. Ene reactions for both singlet oxygen and PTAD probably proceed through the reversible formation of an intermediate with structural requirements similar to a perepoxide or aziridinium imide, respectively.

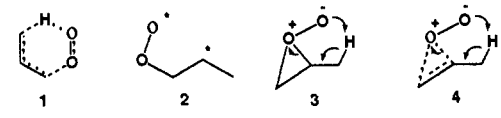
Although the mechanism of the ene reaction of singlet oxygen with olefins has been studied for many years by many research groups, it is still the subject of controversy.[1-6] At least four mechanisms have been proposed for this reaction: (1) a concerted reaction in which the characteristic bond shifts take place through a cyclic transition state (**1**), (2) formation of a zwitterionic or diradical intermediate in which the C-O bond forms first (**2**), (3) formation of a perepoxide intermediate (**3**), and (4) formation of an exciplex (**4**) with a geometry similar to that of **3**. These possibilities are shown in Scheme I.

The concerted mechanism was generally accepted for many years because neither the rate nor the product distribution of ene reactions is sensitive to solvent, many attempts to trap intermediates had been unsuccessful, and there is little evidence for the Markovnikov directivity which would be anticipated for intermediates of type **2**.[7-9]

A diradical mechanism for the reactions of singlet oxygen with many types of substrates was suggested by Goddard and Harding on the basis of GVB calculations.[10] However, this intermediate has not found much support because it would not be expected to give the observed high stereoselectivity if it had sufficient lifetime to rotate around the former double bond.

Evidence for dipolar intermediates in reactions of singlet oxygen has come mainly from substrates in which the cation would be expected to be stabilized by oxygen or by conjugation with a double bond or aromatic system. For example, Jefford demonstrated solvent incorporation in [2 + 2] reactions in the methoxynorbornene system.[11] Jefford has also trapped zwitterionic intermediates by addition to carbonyls in similar systems.[12,13]

Scheme I. Proposed Mechanisms for the Ene Reaction of Singlet Oxygen (* = radical or charge)



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