Sequential Electron-Transfer–Desilylation Methods for Diradical Photogeneration as Part of Synthetic Routes for Erythrina Alkaloid Synthesis

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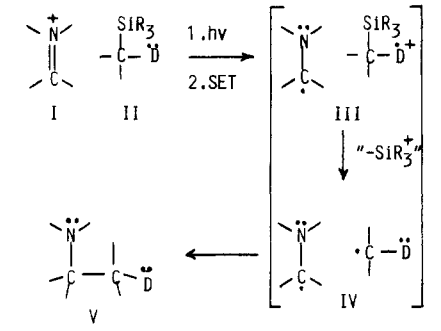
Investigations have been conducted to probe the application of diradical cyclization methods in synthetic approaches to members of the erythrina alkaloid family. For this purpose, a series of [[(trimethylsilyl)-methyl]alkenyl]-3,4-dihydroisoquinolinium perchlorates (**5–11**) have been prepared. These salts have (trimethylsilyl)allyl groupings linked via methylene chains of variable lengths to the 1-position of the hydroisoquinolinium cation nucleus and different N-substituents (e.g., H, Me, and CH_2CO_2Et). Photocyclization reactions of these salts in methanol and acetonitrile, proceeding by sequential electron-transfer–desilylation pathways, lead to generation of the respective spirocyclic products **25–31** in yields ranging from 17 to 88%. Reduction potentials, fluorescence quantum yields, and reaction quantum yields have been measured for a selected number of these hydroisoquinolinium salts in order to gain information about the nature of factors governing the effects of alkenyl chain length, nitrogen substituent, and solvent on photocyclization yields. The 6,7-dimethoxy-[[(trimethylsilyl)methyl]pentenyl]-3,4-dihydroisoquinolinium perchlorate (**35**) has been prepared to probe the mechanistic features of these cyclization processes and to determine whether this methodology is applicable to alkoxy-substituted hydroisoquinolinium salts. Irradiation of **35** in methanol leads to production of the spirocyclic product **36** (60%) formed by a photoinduced, sequential electron-transfer–desilylation pathway, along with a tetracyclic product **37** (15%) arising by intramolecular cycloaddition of the olefin and arene moieties in **35**. Irradiation of **35** in acetonitrile, on the other hand, leads to generation of nearly equal quantities of **36** and **37** (23% and 24%, respectively). Finally, fluoride-induced reactions of the methyl salts **6**, **9**, and **11** were probed in order to determine the relative efficiencies of ionic and diradical cyclization processes. In these cases, the spirocyclic products were produced in low yields along with the corresponding tetrahydroisoquinolines **38–40**. The latter substances are generated by a route involving fluoride ion induced deprotonation followed by disproportionation via hydride transfer between the generated enamine and starting iminium salt functions.

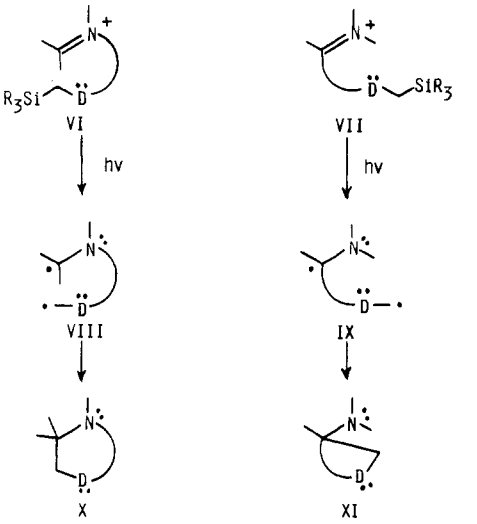
Our investigations in the area of iminium salt photochemistry have uncovered novel and, in some cases, efficient methods for carbon–carbon bond formation.[1] In recent efforts, we have demonstrated that sequences involving excited-state electron transfer and cation diradical desilylation serve as efficient, site-selective methods for radical pair generation.[2] Thus, excitation of either component in systems containing iminium salt (I) and β-trialkylsilyl-substituted electron-donor (II) groupings can induce single electron transfer and lead to production of radical cation pairs (Scheme I). Owing to the high σ_{C-Si}-orbital energy and electropositive character of silicon, the β-silyl cation radicals are prone to undergo rapid[3] desilylation, generating, in a regiocontrolled fashion, radical pair intermediates that are transformed to products through carbon–carbon bond formation.

The overall efficiency noted for these processes, as well as the nature and location of functionality in the generated products, suggests that photoreactions that follow this pathway could serve as the basis for new cyclization methodologies. We envisaged that cyclization of diradical intermediates, formed by photoinduced, sequential electron transfer–desilylation, might comprise a useful procedure for heterocyclic and carbocyclic ring construction as shown in Scheme II. Accordingly, the silicon-containing N- or C-substituted iminium salts VI and VII, produced by ground-state C–N or C–C bond-forming methods starting with appropriate imine and silylmethyl substrates, could serve as precursors of the diradical intermediates

Scheme I



Scheme II



(1) Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130; *Tetrahedron Report 156*, **1983**, *12*, 3845. Mariano, P. S.; Stavinoha, J.; Bay, E. *Tetrahedron* **1981**, *37*, 3385.

(2) (a) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617. (b) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.

(3) Unpublished results of S. M. Farid, S. Mattes, and P. S. Mariano from studies of benzylsilane photoaddition to 9,10-dicyanoanthracene indicate that the benzylsilane cation radical undergoes nucleophile-induced desilylation at a rate in excess of 5×10^9 s^{-1}.

(4) (a) Tiner-Harding, T.; Ullrich, J. W.; Chiu, F. T.; Chen, S. F.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 3360. (b) Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228.

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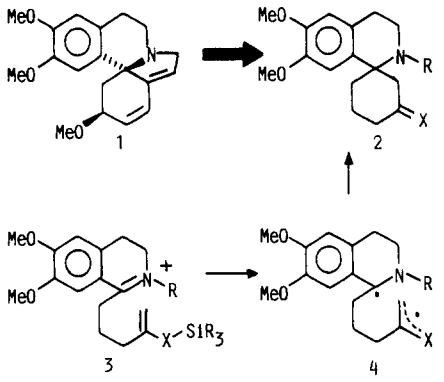
Scheme III

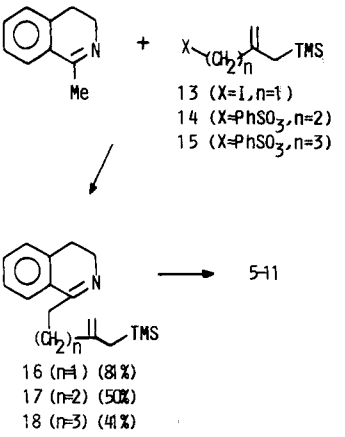


VIII and IX. Final carbon–carbon bond formation in these diradicals would result in production of the N-heterocyclic (X) and carbocyclic (XI) systems shown in Scheme II.

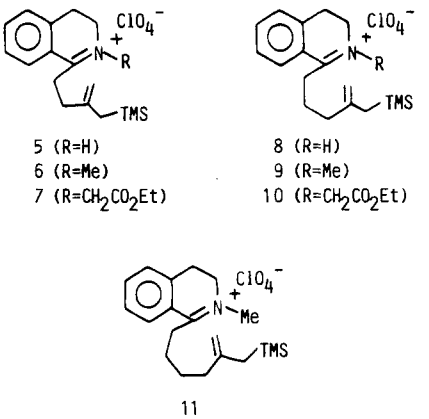
In previous investigations,[2] we have probed the heterocyclic ring-forming process exemplified by the conversion of VI to X as part of synthetic approaches to members of the harringtonine alkaloid family. These studies have shown that diradical generation by sequential electron-transfer–desilylation routes and cyclization are highly efficient processes. In addition, the synthetic utility of this heterocyclization method was further demonstrated by the high-yielding photoconversion of 1-[*o*-[(trimethylsilyl)-methyl]benzyl]-1-pyrrolinium perchlorates to the corresponding benzoindolizidine products[5a] and of *N*- and 1-*o*-xylyl-3,4-dihydroisoquinolinium salts to products possessing the basic skeleton of members of the protoberberine and spirobenzyl isoquinoline alkaloid families.[5b] Another phase of our efforts in this area is focused on the application of the diradical cyclization method to construction of carbocyclic ring systems. We chose to test the feasibility of this procedure in the context of a general approach to fabrication of the tetracyclic skeleton found in members of the erythrina alkaloid family, exemplified by erysotrine **1**.[6] The strategy under study is outlined in Scheme III and employs photocyclization of appropriately substituted 1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinolinium salts **3**. Thus, cyclization of the diradical intermediate **4** should generate the key spirocyclic BC-ring juncture of erysotrine. Installation of the Δ^3-pyrroline D-ring and CD-ring functionality manipulation would then be required to complete a synthesis of this substance.

We have now completed exploratory efforts designed to probe the scope and generality of the key diradical cyclization process to be used for carbocyclic ring formation in this strategy. Discussed below are the results of this study that indicate that (1) syntheses of the requisite 1-[[(trimethylsilyl)methyl]alkenyl]-3,4-dihydroisoquinolinium salts related to **3** are easily accomplished by short sequences involving alkylative addition of appropriate silylalkenyl substrates to 2-methyl-3,4-dihydroisoquinoline, (2) efficiencies of the ring-forming photoprocesses of these salts are a sensitive function of the natures of the alkenyl side chain, nitrogen substituent, and solvent, and (3) construction of the tricyclic ring system required for an erythrina alkaloid synthetic approach following the design presented in Scheme III is feasible.

Scheme IV



Synthesis of the 1-(Silylalkenyl)-3,4-dihydroisoquinolinium Perchlorates. The dihydroisoquinolinium perchlorates **5–11**, differing in the nature of the nitrogen



substituent and chain length separating the iminium salt acceptor and allylsilane donor functions, were selected to probe the scope and generality of the above-described photocyclization methodology. These salts were readily prepared by the alkylative methods outlined in Scheme IV. Accordingly, the metallo enamine derived by deprotonation of 2-methyl-3,4-dihydroisoquinoline reacts with the known allylic iodide **13**[7] and the homologous alkenyl benzenesulfonates **14** and **15** to generate the alkenyldihydroisoquinolines **16–18**. The benzenesulfonates used for these alkylation processes were prepared in situ from the corresponding alcohols **21** and **24** by sequential treatment with *n*-BuLi and $PhSO_2Cl$.

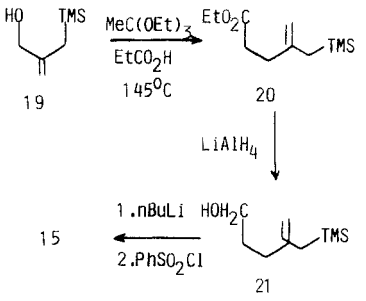
It is important to note that all attempts to convert the silyl alcohols **21** and **24** to the corresponding alkenyl halides under a variety of conditions result in undesired desilylation. For example, bromide formation by treatment of these substances with either PBr_3 or Ph_3P/CBr_4 leads cleanly to production of the desilylated, unsaturated bromides. Likewise, the unstable mesylate derivatives of **21** and **24** can be prepared but are transformed to the corresponding desilylated iodides when treated immediately after their formation with NaI in acetone. Attempts to build in a resistance to desilylation by replacing the trimethylsilyl group in **24** by the more resilient triethylsilyl moiety did not alter the course of halide-forming reactions. Finally, the benzenesulfonate derivatives **14** and **15** do not survive attempts at isolation owing to surprisingly rapid protodesilylation, yielding the corresponding alkenyl benzenesulfonates lacking silicon. Thus, the exceptional

(5) (a) Lan, A. J. Y.; Quillen, S. Q.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6439. (b) Ho, G. D.; Lan, A. J. Y.; Mariano, P. S. *Tetrahedron Lett.* **1985**, *26*, 5867.

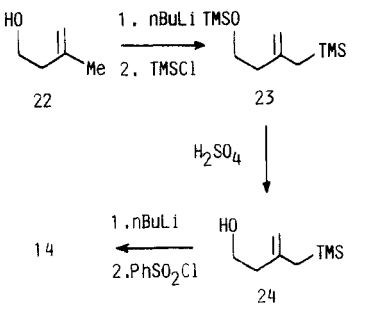
(6) Cf. The Erythrina Alkaloids in: Manske, R. H. F., Ed. "Alkaloids"; Academic Press: New York: 1967, Vol. X, Chapter 12, p 483; 1960; Vol VII, Chapter 11, p 201; 1960; Vol II, Chapter 14, p 499.

(7) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 5023.

Scheme V



Scheme VI



lability of the halide and ester derivatives of **21** and **24** is remarkable when contrasted to the homologue, 2-[(trimethylsilyl)methyl]-2-propen-1-ol where the ester and iodide are exceptionally stable species.

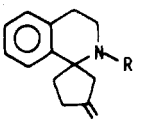
The ortho ester Claisen rearrangement procedure[8] was used to prepare 4-[(trimethylsilyl)methyl]-4-penten-1-ol (**21**) (Scheme V). Accordingly, the known allylic alcohol **19**[9] was converted to the silylpentenoate ester **20** by propionic acid catalyzed reaction with triethyl orthoacetate. Reduction of **20** with LAH led to formation of the desired alcohol. The (trimethylsilyl)butenol **24** was cleanly generated (Scheme VI) by application of the Trost[9] allyl–hydroxyl bis-silylation, monodesilylation procedure starting with the commercially available, 3-methyl-3-buten-1-ol (**22**).

N-Alkyldihydroisoquinolinium perchlorate formation from the intermediate dihydroisoquinolines **16–18** was accomplished by alkylation with either methyl iodide or ethyl α-iodoacetate followed by perchlorate ion exchange on a Dowex X-1 column and chromatographic purification on Florisil. The N–H salts were generated in situ by treatment of the corresponding hydroisoquinolines with 70% $HClO_4$. It is significant that the allylsilane functions in the N-protonated hydroisoquinolines **5** and **8** do not undergo protodesilylation[10] on the time scales required for salt formation and photocyclization.

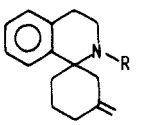
Photochemistry of the (Silylalkenyl)dihydroisoquinolinium Perchlorates. The photochemistry of the (silylalkenyl)dihydroisoquinolinium perchlorates **5–11** was investigated in order to explore the feasibility of diradical cyclization processes driven by photoinduced electron transfer–desilylation and to probe the effect of chain length, nitrogen substitution, and solvent on reaction efficiency. Irradiations of the salts were performed on nitrogen-purged solutions (ca. 1–4 mM) of the perchlorate salts in acetonitrile or methanol with Corex- ($\lambda > 280$ nm) filtered light. The photoreactions were monitored by UV spectroscopic methods and terminated when decreases in the absorbancies corresponding to the λ_{max} for the dihydroisoquinolinium chromophores ceased. Basic workup of the photolysates followed by chromatographic purifications on Florisil provided the spirocyclic photoproducts **25–31** in yields ranging from 17 to 88% (see Table I).

Table I. Results of Photocyclization Reactions of the (Silylalkenyl)dihydroisoquinolinium Perchlorates

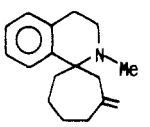
dihydroisoquinolinium perchlorate	quant mmol	solvent (100 mL)	irrad time, min	spirocycl product	% yield
5	0.44	MeCN	90	**25**	45
6	0.12	MeCN	60	**26**	88
6	0.12	MeOH	15	**26**	87
7	0.39	MeCN	80	**27**	70
8	0.25	MeCN	30	**31**	33
9	0.11	MeCN	60	**28**	17
9	0.12	MeOH	22	**28**	39
10	0.17	MeCN	60	**29**	41
10	0.20	MeOH	25	**29**	71
11	0.10	MeCN	180	**30**	36
11	0.11	MeOH	22	**30**	66



25 (R=H)
26 (R=Me)
27 (R=CH_2CO_2Et)



28 (R=Me)
29 (R=CH_2CO_2Et)



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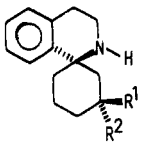
Photoproduct structures were assigned on the basis of their characteristic spectroscopic properties and elemental compositions. Especially diagnostic were resonances in the ^1H NMR spectra indicative of the exocyclic methylene protons and in the ^{13}C NMR spectra for the spirocyclic quaternary carbons (ca. 60–68 ppm) the exocyclic olefinic methylene carbons (ca. 106–113 ppm) and the quaternary vinyl carbons (ca. 142–144 ppm).

Irradiation of the [[(trimethylsilyl)methyl]pentenyl]-dihydroisoquinolinium perchlorate **8**, generated in situ by protonation of the isoquinoline **17** with 70% $HClO_4$, leads to production of the spirocyclic alcohol derivative **31**. The



31a (R^1=Me, R^2=OH)
31b (R^1=OH, R^2=Me)

structure of **31** is evidenced by the existence of a methyl singlet in the ^1H NMR spectrum at 0.81 ppm and of the methyl, spirocyclic quaternary (48 ppm) and carbinol quaternary (77 ppm) carbons in the ^{13}C NMR spectrum. In this case, the initially formed photoproduct **32** arising by the electron-transfer–desilylation pathway, and containing a methylene–cyclohexane grouping, must undergo catalyzed hydration to produce the tertiary alcohol **31** under the acidic condition present during its formation. In contrast, the homologue **25** appears to be stable under these conditions. This comparative behavior can be at-

(8) Johnson, W. S., Werthemann, L.; Bartlett, W. R.; Brocksom, T. J., Li, T.; Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.
(9) Trost, B. M.; Chen, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315.
(10) (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Chen, S. F.; Mariano, P. S. *Tetrahedron Lett.* **1985**, *26*, 47.

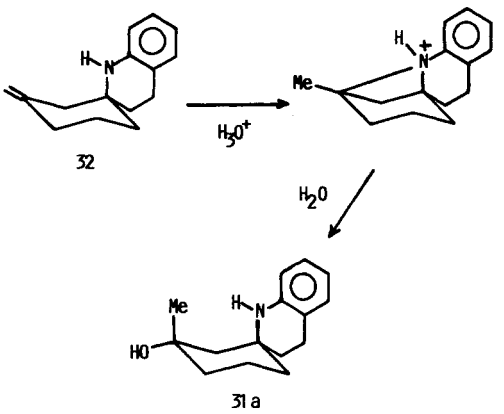
Table II. Fluorescence and Reaction Quantum Yields for Selected 1-(Silylalkenyl)-3,4-dihydroisoquinolinium Perchlorates

dihydroisoquinolinium perchlorate	redn pot. $E_{1/2}(-)$,[a] V	fluoresc quantum yields[b]	photoprod formn quantum yields MeOH	MeCN
5	−1.04			
6	−1.06	0.000[c]	0.0300	0.0038
7	−0.92	0.000[c]	0.0150	0.0024
9		0.084	0.0096	0.0008
10		0.027	0.0150	0.0037
11		0.013	0.0045	0.0005
35	−1.08			

[a] Measured in 5% H_2O–MeCN at 25 °C vs. Ag/AgCl with n-Bu_4NClO_4 (0.1 M) on 6×10^{-3} M solutions. [b] Measured in MeCN at 25 °C on nondegassed solutions using naphthalene ($\phi_f = 0.21$) as a standard. [c] $\phi_f < 0.0009$.

tributed to the well-known reactivity differences that exist between methylene–cyclopentane and methylene–cyclohexane systems and related ketones.

Only one stereoisomer of the spirocyclic alcohol **31** was detected in the photoproduct mixture arising from irradiation of **8**. The available spectroscopic data are not sufficiently diagnostic to allow assignment of stereochemistry (i.e., **31a** or **31b**) to this photoproduct. However, the high probability for neighboring group participation by the amine function in the hydration process suggests that the tertiary alcohol if it is formed under kinetic control might be the epimer **31a** in which a trans relationship exists between the NH and OH functions.

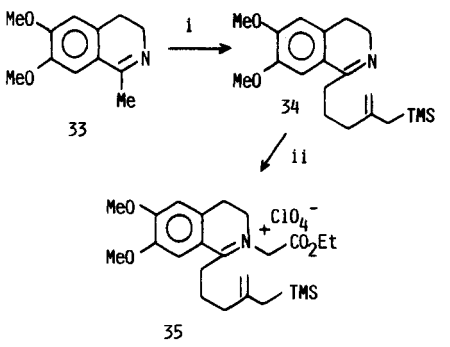


Fluorescence and Reaction Quantum Efficiencies. The data presented in Table I clearly show that the chemical yields of the 1-(silylalkenyl)-3,4-dihydroisoquinolinium salt photocyclization processes are a sensitive function of the nature of the nitrogen substituent, the solvent, and the chain length separating the iminium salt acceptor and allylsilane donor moieties. In an attempt to uncover the source of this control, we have conducted further studies with these salts.

Fluorescence efficiencies for the N-Me perchlorate salts **6**, **9**, and **11** and related systems **7** and **10** with the nitrogen-appended acetic ester residues were measured with acetonitrile solutions of these substances at 25 °C. Quantum yields for fluorescence, determined relative to naphthalene,[11] are recorded in Table II. Also included in Table II are reduction potentials, measured for the three dihydroisoquinolinium perchlorates **5–7** having the same (silylmethyl)butenyl side chain and varying (NH, N-Me, N-CH_2CO_2Et) substituents. The cyclic voltamagrams for these substances are nonreversible. The reduction potentials were obtained by measurement of the half-wave potentials vs. Ag/AgCl.

(11) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251.
(12) Spath, E. *Monatsh. Chem.* **1921**, *42*, 97.

Scheme VII[a]

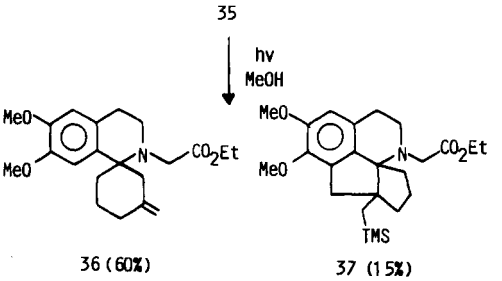


[a] Key: (i) n-BuLi, TMEDA, THF; **15** (54%); (ii) ICH_2CO_2Et, MeCN; ClO_4^- ion exchange, Florisil chromatography (69%).

A qualitative indication of the relative quantum efficiencies for formation of the spirocyclic products can be gleaned by inspection of the reaction yield vs. irradiation time data provided in Table I. A more quantitative evaluation of the relative efficiencies of spirocyclic product formation from the 3,4-dihydroisoquinolinium perchlorates **6**, **7**, and **9–11** was made. Quantum yields for photoproduct formation in MeCN and MeOH solvents were accurately measured at low (1–10%) conversion. The results are recorded in Table II.

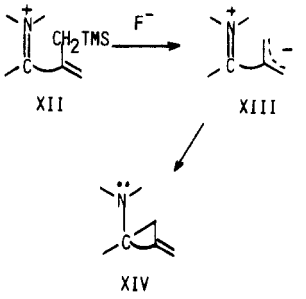
Preparation and Photochemistry of the 6,7-Dimethoxy-3,4-dihydroisoquinolinium Perchlorate 35. The applicability of the diradical cyclization methodology described above in synthetic approaches to members of the erythrina alkaloid family is dependent upon the success of photocyclization processes of 3,4-dihydroisoquinolinium salts containing alkoxy functionality on the aromatic ring. This feature along with questions about the nature of the chain length, N-substituent, and solvent effects on reaction efficiency, summarized above, encouraged a study of the photochemistry of the 6,7-dimethoxyhydroisoquinolinium perchlorate **35**. This material was prepared starting with the known 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline (**33**) by a sequence (Scheme VII) similar to that employed for generation of the desmethoxy analogue.

Irradiation of a methanol solution of **35** followed by basic



workup and chromatographic separation led to isolation of two products, the spirocyclic amino ester **36** (60%) and the silicon-containing, tetracyclic substance **37** (15%). The key spectroscopic parameters of **36** are similar to those previously recorded for the desmethoxy analogue **29**. The structure of **37** was assigned on the basis of spectroscopic data. Important features in the ^1H NMR spectrum include a Si methyl singlet at 0.01 ppm and a Si methylene AB quartet at 0.75 ppm. The ^{13}C NMR spectrum of **37** is consistent with its structure; the presence of a single aromatic methine carbon resonance at 109.5 ppm and of

Scheme VIII



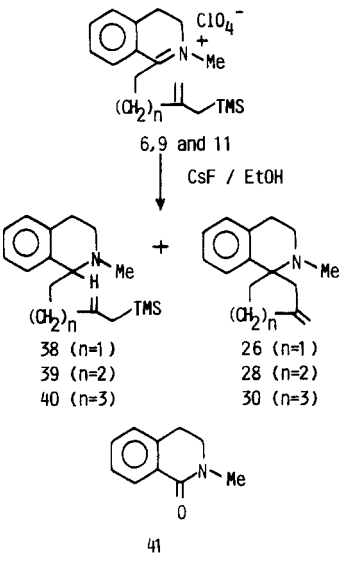
two sp^3-hybridized quaternary carbon signals at 78.0 and 63.1 ppm is particularly significant. While these data along with mechanistic precedent (see below) are highly suggestive of the tetracyclic structure of this minor photoproduct, information about the relative stereochemistry at the adjacent chiral, quaternary centers in **37** is currently unavailable. Arguments based upon ring strain, however, could be used to argue that **37** possesses the cis-fused bicyclopentanoid stereochemistry shown. Interestingly, photoreaction of the dihydroisoquinolinium perchlorate **35** in acetonitrile leads to formation of the tricyclic and tetracyclic products **36** and **37** in respective yields of 23% and 24%.

Attempts at Fluoride Ion Induced Cyclizations of the Dihydroisoquinolinium Perchlorates 6, 9, and 11. An alternative to the "diradical strategy" for conversion of (silylalkenyl)iminium salts XII to their corresponding carbocyclic products XIV involves an ionic cyclization methodology (Scheme VIII). Dipolar intermediates XIII generated by fluoride ion induced desilylation of XII should be capable of undergoing cyclization by addition of the nucleophilic allyl anionic function to the iminium cation grouping. The feasibility of this alternative pathway for cyclization was tested with the *N*-methyldihydroisoquinolinium perchlorates **6**, **9**, and **11**.

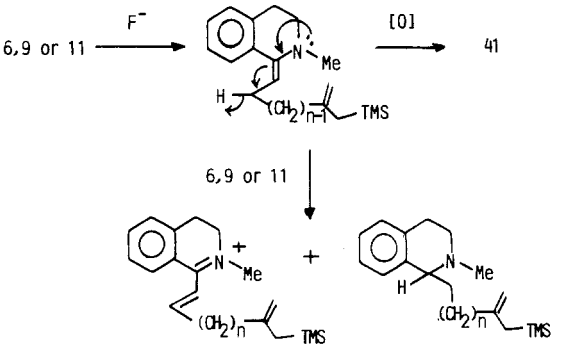
Optimal conditions for reaction of the hydroisoquinolinium salts with CsF were uncovered through an investigation probing a variety of solvents and reaction temperatures. Highest yields of cyclization products were obtained when ethanol was used as solvent and reactions are run at 70 °C. This observation is similar to that noted earlier by Takano and his co-workers[13] in studies of the fluoride ion induced cyclization of *N*-xylyldihydroisoquinolinium salts. Thus, treatment of the (silylbutenyl)-3,4-dihydroisoquinolinium perchlorate **6** with CsF in anhydrous ethanol at 70 °C resulted in the low-yielding production of the spirocyclic amine **26** (7%) along with the tetrahydroisoquinoline **38** (21%) and hydroisoquinolone **41** (21%) (Scheme IX). Similar results were obtained from studies with the homologous hydroisoquinolinium perchlorates **9** and **11** (Scheme IX). The structures of the tetrahydroisoquinolines **38–40** were initially assigned by use of spectroscopic methods and then confirmed by independent synthesis via $NaBH_4$ reduction of the respective hydroisoquinolinium perchlorates **6**, **9**, and **11**.

The observations suggest that the fluoride method for spirocyclic ring formation is generally less efficient than the photochemical process via diradical intermediates. The low yields for the former reactions can be attributed to alternate pathways open to the fluoride–hydroisoquinolinium salt systems. Thus, along with nucleophilic attack on silicon, leading to generation of the dipolar intermediate, the fluoride ion can also participate in α-deprotonation of the iminium salt function (Scheme X). The enamines generated in this way can then undergo either disproportionation by hydride transfer to form the tetrahydroisoquinoline products or oxidation, yielding the hydroisoquinolone.

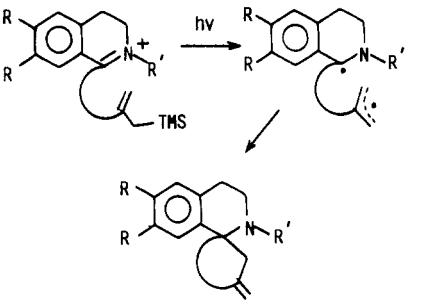
Scheme IX



Scheme X



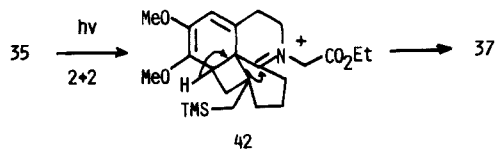
Scheme XI



Discussion of Photochemical Observations. Several features of the photocyclization reactions of the hydroisoquinolinium perchlorates described above warrant discussion. Irradiations, involving excitation of the phenyl-conjugated iminium salt functions in these substances, induce photocyclization processes leading to production of the corresponding spirocyclic products. Thus, as the precedent gained from earlier studies suggests,[1] excited states of these hydroisoquinolinium salts, which contain both electron-acceptor (iminium cations) and -donor (allylsilane) functions, participate in intramolecular electron transfer as part of pathways leading to generation of diradical intermediates (Scheme XI). Diradical collapse by carbon–carbon bond formation then leads to production of the spirocyclic products.

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

Scheme XII



In only one case, that of the 6,7-dimethoxy-3,4-dihydroisoquinolinium perchlorate **35**, is an identifiable product other than the corresponding spirocyclic amine generated upon irradiation. Photolysis of **35** in methanol results in low-yielding production of the tetracyclic substance **37** along with the spirocyclic amino ester **36**. A possible mechanism for conversion of **35** to **37** involves intramolecular 2+2 cycloaddition of the olefinic function of **35** across the 8,10 π-bond of the aromatic ring giving the polycyclic diene **42** (Scheme XII). Migration of the (trimethylsilyl)methyl-substituted cyclobutane σ-bond to the carbinyl cation center followed by deprotonation would then provide **37**. Precedent for this sequence is found in our earlier observations of photoaddition of olefins to 2-aryl-1-pyrrolinium salts.[14] In those efforts, we noted that 2+2 cycloaddition dominates single-electron-transfer processes when the olefin partner is substituted by electron-withdrawing groups. Thus, when olefin oxidation potentials are sufficiently high to make excited-state electron transfer thermodynamically unfavorable, olefin–iminium salt cycloaddition becomes a competitive reaction pathway.

The electron-donating, methoxy groups on the phenyl-conjugated iminium cation chromophore of **35** may have a similar effect upon the relative rates of excited-state cycloaddition and electron transfer. The more negative reduction potential of **35** ($E_{1/2}(-)$ = −1.08 V) and its lower singlet energy ($E_{0,0}^{S1}$ = 67.5 kcal/mol) could combine to reduce the efficiency (rate) of electron transfer.[15] The dramatic changes in the yields of the spirocyclic and tetracyclic products **36** and **37** noted on changing the solvent for photoreaction from methanol to acetonitrile support this speculation. Accordingly, the yield of **36** arising by the electron-transfer pathway falls dramatically at the expense of that for the intramolecular photocycloadduct when the solvent is varied from the more polar methanol to acetonitrile. This is the expected result (see below) for processes that proceed via the intermediacy of a common intramolecular exciplex where collapse by cycloaddition to form **42** is competitive with diradical cation generation. An increase in solvent polarity would cause the rate of exciplex to diradical cation conversion to increase. Finally, products of intramolecular cycloaddition like **37** have not been detected in reaction mixtures resulting from irradiation of the desmethoxy salts.

Perhaps of greater interest are the trends observed in the chemical and quantum yields for spirocyclic product formation. The quantum yield data, which generally parallel chemical yields within each series, are summarized in Table III. Inspection of this data reveals an inverse relationship between the photocyclization quantum efficiencies and the chain length connecting the electron-donor and -acceptor groups. For example, a ca. 6-fold decrease in product formation quantum yields occurs when the number of intervening methylene units within the hydroisoquinolinium salts is increased from 2 to 4. Likewise, solvent appears to have a pronounced influence on these processes. Quantum efficiencies are ca. 4–9 times larger for photoreactions conducted in methanol vs. acetonitrile. Fewer data are currently available on the effects of nitrogen substituents. However, the reaction and quantum yield results for (silylalkenyl)dihydroisoquinolinium salts **8–10** indicate that photocyclization becomes increasingly more facile in the series CH_3 < H < CH_2CO_2Et.

Table III. Summary of Quantum Yield Data for Spirocyclic Product Formation from Irradiation of the 3,4-Dihydroisoquinolinium Perchlorates

compd	nitrogen subst	no. of interven CH_2 units	rel ϕ MeCN	rel ϕ MeOH
6	CH_3	2	0.13	1.00
7	CH_2CO_2Et	2	0.08	0.50
9	CH_3	3	0.03	0.32
10	CH_2CO_2Et	3	0.12	0.50
11	CH_3	4	0.02	0.17

Initial thoughts about these results focus on a unified rationale to explain the effects of chain length, solvent, and N substituent on reaction efficiencies. The observed trends appear to correlate with those anticipated for the effects of electron donor–acceptor separation,[16] medium polarity,[17] and iminium salt reduction potential[15] on the rates of intramolecular electron transfer. For example, the hydroisoquinolinium salt **5–7** reduction potentials vary, albeit slightly, as a function of N substituent in a manner similar to reaction efficiencies. In addition, since intramolecular electron transfer in these systems transforms a stabilized, iminium cation into a higher energy olefin-centered radical cation, its facility should be enhanced in a more polar medium. Thus, higher quantum yields based upon more favorable electron transfer would be expected in the more polar methanol vs. acetonitrile solutions (Z values of 83.6 vs. 55.5 and E_T values of 71.3 vs. 46.0, respectively).[18]

The varying efficiencies for photocyclization might well be related to effects upon the relative rates of diradical formation via electron transfer vs. other processes open to the excited hydroisoquinolinium salts. Unfortunately, the inabilityy to isolate other identifiable products from these reactions despite attempts to do so hinders efforts to draw definite conclusions about the nature of factors controlling reaction efficiencies. In addition, the high yield for photocyclization of the 6,7-dimethoxyhydroisoquinolinium salt **35** does not appear to fit the pattern outlined. The singlet energy ($E_{0,0}^{S1}$ = 67.5 kcal/mol) and ground-state reduction potential ($E_{1/2}(-)$ = −1.08 V) of the iminium cation chromophore in **35** translate into a calculated excited-state reduction of potential of ($E_{1/2}^{S1}(-)$ = +1.79 V) that is ca. 0.62 V less positive than that for the desmethoxy analogue **10** ($E_{0,0}^{S1}$ = 77.9 kcal/mol; $E_{1/2}(-)$ = −0.92 V). Yet the yields for photocyclization reactions of these salts are nearly equal (60 vs. 71% in methanol). A much smaller difference in excited-state reduction potentials exists between the N-CH_3- and N-CH_2CO_2Et-substituted dihydroisoquinolinium salts **9** and **10**

(14) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136. Mariano, P. S.; Leone-Bay, A. *Tetrahedron Lett.* **1980**, 4581.

(15) (a) The free energy for excited-state electron transfer is related to the hydroisoquinolinium salt reduction potential ($E_{1/2}(-)$) and singlet energy ($E_{0,0}^{S1}$) and the olefin oxidation potential ($E_{1/2}(+)$) by the following relationship: $\Delta G_{SET} = E_{1/2}(+) - E_{1/2}(-) - E_{0,0}^{S1}$.[15b] (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(16) Chandross, E.; Thomas, H. *Chem. Phys. Lett.* **1971**, *9*, 393. LaBlanche-Combier, A. *Bull. Chim. Soc. Fr.* **1972**, *12*, 4805.

(17) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunseges. Phys. Chem.* **1968**, *72*, 257. Ware, W. R.; Richter, H. P. *J. Chem. Phys.* **1968**, *48*, 1595. Knibbe, H.; Rollig, K.; Schafer, F. P.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1184.

(18) (a) Observations made in a study of allene–iminium salt photoaddition reactions[18b] reflect a dramatic effect on the rates of electron transfer vs. cycloaddition reaction pathways induced by changes in solvent from acetonitrile to methanol. (b) Somekawa, K.; Haddaway, K.; Fleming, P.; Mariano, P. S., unpublished results.

($\Delta E_{1/2}^{S1}(-) \approx 0.14$ V), yet the photocyclization yields are greatly different (39 vs. 71% in methanol).

The studies described above have demonstrated that the "diradical cyclization" route based upon photoinduced sequential electron-transfer–desilylation processes can be applied as a spirocyclic ring-forming method in synthetic designs for erythrina alkaloid synthesis. Interesting dependencies of photocyclization reaction yields on chain length, solvent, and N substituent have been uncovered. However, the exact nature of these effects has not as yet been unveiled.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded on $CDCl_3$ solutions by using a Varian EM-360 or IBM WP-200 (FT) spectrometers. Chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. For compounds containing trimethylsilyl groupings, $CHCl_3$ was employed as an internal standard. ^{13}C NMR spectra were recorded on $CDCl_3$ solutions with the IBM WP-200 spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane or $CHCl_3$ as internal standards. Multiplicities are assigned on the basis of INEPT results. Infrared spectra were taken on a Perkin-Elmer spectrometer. A GCA McPherson EU-700-56 spectrometer was used to record ultraviolet spectra.

Drying of organic layers obtained by workup of reaction mixtures was by treatment with anhydrous sodium sulfate. Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer 44-B fluorimeter with a DCSU-1 differential corrected spectral unit and an LDC 308 digital integrator. Column chromatography was performed with Florisil (Fisher, 100–200 mesh) as absorbent. Molecular distillations were performed at reduced pressure with a Kugelrohr apparatus. Perchlorate anion exchange was performed on a 2.5 × 20 cm Dowex-1 column (50–100 mesh) with methanol as the eluant. All reactions were carried out under a N_2 atmosphere. Mass spectrometric analysis was accomplished by using a low-resolution Hitachi RMU-6E and a high-resolution VG-7700 instrument.

1-[3-[(Trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinoline (16). To a cooled solution (−78 °C) of 1-methyl-3,4-dihydroisoquinoline[19b] (513 mg, 3.54 mmol) in 2 mL of anhydrous THF was added slowly 4.25 mmol of *n*-butyllithium in hexane and tetramethylethylenediamine (493 mg, 4.25 mmol). The resulting mixture was stirred for 3.5 h at 0 °C. After cooling to −78 °C, 3-[(trimethylsilyl)methyl]-2-propenyl iodide[7] (1.077 g, 4.24 mmol) in 6 mL of THF was added dropwise over a period of 2–3 min. The reaction mixture was then stirred for 24 h at 25 °C, poured into water, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried, concentrated in vacuo, and subjected to Florisil column chromatography (2.5% MeOH–97.5% $CHCl_3$) to yield 777 mg (81%) of the desired dihydroisoquinoline **16**: ^{1}H NMR δ 0.01 (s, 9 H, $Si(CH_3)_3$), 1.50 (s, 2 H, CH_2Si), 2.20 (t, 2 H, allylic CH_2), 2.55 (t, 2 H, C-4 CH_2), 2.80 (t, 2 H, homoallylic CH_2), 3.55 (t, 2 H, C-3 CH_2), 4.50 (d, 2 H, vinyl CH_2), 7.00–7.50 (m, 4 H); ^{13}C NMR δ −1.8 (q, $Si(CH_3)_3$), 25.7 (t, CH_2Si), 26.4 (t, C-4), 33.8 (t, allylic CH_2), 34.9 (t, homoallylic CH_2), 46.4 (t, C-3), 106.7 (t, vinyl CH_2), 124.3 (d, C-5), 126.3 (d, C-7), 127.0 (d, C-8), 128.5 (s, C-10), 129.8 (d, C-6), 137.2 (s, C-9), 146.4 (s, vinyl), 166.0 (s, C-1); IR ($CHCl_3$) 2940, 1620, 1245, 845 cm^{-1}; mass spectrum, *m/e* (relative intensity) 271 (M^+, 13), 270 (M^+, 16), 198 ($M^+ - Si(CH_3)_3$, 100), 184 (24), 158(11), 73(30); high-resolution mass spectrum, *m/e* 198.1281 ($M^+ - Si(CH_3)_3$, $C_{14}H_{16}N$ requires 198.1282).

***N*-Methyl-1-[3-[(trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinolinium Perchlorate (6).** A solution of 1-[3-[(trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinoline (**16**; 699 mg, 2.6 mmol) and methyl iodide (3.66 g, 26 mmol) in 10 mL of anhydrous ether was stirred at 40 °C for 48 h, giving 1.00 g of the isoquinolinium iodide that was subject to perchlorate anion-exchange chromatography. The eluant was concentrated in vacuo, giving a residue which was subjected to column chromatography on Florisil (3% MeOH–97% $CHCl_3$) to yield 752 mg (75% overall) of the desired perchlorate salt 6: ^{1}H NMR δ 0.01 (s, 9 H, $Si(CH_3)_3$), 1.50 (s, 2 H, CH_2Si), 2.30 (t, 2 H, allylic CH_2), 3.20 (t, 2 H, C-4 CH_2), 3.35 (t, 2 H, homoallylic CH_2), 3.87 (s, 3 H, CH_3), 4.12 (t, 2 H, C-3 CH_2), 4.60 (d, 2 H, vinyl), 7.30–7.83 (m, 4 H); ^{13}C NMR δ −1.8 (q, $Si(CH_3)_3$), 25.1 (t, CH_2Si), 26.1 (t, C-4), 29.5 (t, homoallylic CH_2), 35.0 (t, allylic CH_2), 44.5 (q, CH_3), 52.7 (t, C-3), 109.0 (t, vinyl CH_2) 125.9 (s, C-10), 127.9 (d, C-5), 128.2 (d, C-7), 129.4 (d, C-8), 136.0 (d, C-6), 137.1 (s, C-9), 143.8 (s, vinyl), 178.5 (s, C-1); IR ($CHCl_3$) 2950, 1635, 1345, 1250, 1090, 850 cm^{-1}; mass spectrum, *m/e* (relative intensity) 286 (M^+, 3), 285 ($M^+ - H$, 17), 213 ($M^+ - Si(CH_3)_3$, 21), 212 (66), 198 (17), 181 (48), 169 (45), 147 (100), 131 (62), 119 (76), 73 (83); high-resolution mass spectrum, *m/e* 286.1917 ($M - ClO_4^-$, $C_{18}H_{28}NSi$ requires 286.1991); UV (CH_3CN) λ_{max} 279 nm (ϵ 12 000).

***N*-(Carbethoxymethyl)-1-[3-[(trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinolinium Perchlorate (7).** A solution of 1-[3-[(trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinoline (**16**; 554 mg, 2.04 mmol) and ethyl iodoacetate (560 mg, 2.62 mmol) in 10 mL of anhydrous ether was stirred at 25 °C for 7 days, producing the iodide salt (877 mg). This salt was subjected to perchlorate anion-exchange chromatography. The eluant was concentrated in vacuo and subjected to column chromatography on Florisil (2.5% MeOH–97.5% $CHCl_3$), yielding 602 mg (65%) of the desired perchlorate salt **7**: ^{1}H NMR δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.33 (t, 3 H, CH_3), 1.50 (s, 2 H, CH_2Si), 2.20 (t, 2 H, allylic CH_2), 3.15–3.34 (m, 4 H, C-4 CH_2 and homoallylic CH_2), 4.10 (t, 2 H, C-3 CH_2), 4.27 (q, 2 H, OCH_2CH_3), 4.58 (d, 2 H, vinyl CH_2), 5.09 (s, CH_2CO_2Et), 7.10–7.70 (m, 4 H); ^{13}C NMR δ −1.7 (q, $Si(CH_3)_3$), 13.8 (q, OCH_2CH_3), 25.7 (t, CH_2Si), 26.3 (t, C-4), 30.3 (t, homoallylic CH_2), 35.9 (t, allylic CH_2), 52.9 (t, C-3), 58.0 (t, OCH_2CH_3), 63.1 (t, CH_2CO_2Et), 109.3 (t, vinyl CH_2), 126.0 (s, C-10), 128.4 (d, C-5), 128.6 (d, C-7), 130.4 (d, C-8), 137.2 (d, C-6), 138.1 (s, C-9), 143.7 (s, vinyl C), 165.5 (s, carbonyl C), 183.0 (s, C-1); IR ($CHCl_3$) 2950, 1745, 1625, 1245, 1100, 850 cm^{-1}; mass spectrum, *m/e* (relative intensity) 358 (M^+, 10), 357 ($M^+ - H$, 25), 329 ($M^+ - Et$, 10), 285 ($M^+ - CO_2Et$ or $M^+ - Si(CH_3)_3$, 50), 270 (70), 256 (75), 212 (70), 73 (100); high-resolution mass spectrum, *m/e* 358.2183 ($M - ClO_4^-$, $C_{21}H_{32}NO_2Si$ requires 385.2202); UV (CH_3CN) λ_{max} 285 nm (ϵ 9220).

3-[(Trimethylsilyl)methyl]-3-buten-1-ol (24). This compound was prepared by use of the general procedure of Trost.[9a] The starting alcohol used was 3-methyl-3-buten-1-ol[19] (17.1 g, 199 mmol) and purification of the product by vacuum distillation (70 °C (4 mmHg)) yielded 19.3 g (67%) of the desired silyl alkenol **24**: ^{1}H NMR δ 0.04 (s, 9 H, $Si(CH_3)_3$), 1.55 (s, 2 H, CH_2Si), 2.12 (t, 2 H, CH_2CH_2OH), 2.13 (s, 1 H, OH), 3.59 (t, 2 H, CH_2OH), 4.56 (s, 2 H, vinyl); ^{13}C NMR δ −1.6 (q, $Si(CH_3)_3$), 26.7 (t, CH_2Si), 41.1 (t, CH_2CH_2OH), 60.3 (t, allylic CH_2), 108.6 (t, vinyl CH_2), 143.8 (s, vinyl); IR ($CHCl_3$) 3450, 2950, 1635, 1250, 850 cm^{-1}; high-resolution mass spectrum, *m/e* 158.1120 ($C_8H_{18}OSi$ requires 158.1113).

1-[4-[(Trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinoline (17). To a −78 °C solution of 1-methyl-3,4-dihydroisoquinoline (306 mg, 2.11 mmol) in 2 mL of anhydrous THF was added slowly 2.53 mmol of *n*-butyllithium in hexane solution and tetramethylethylenediamine (293 mg, 2.52 mmol). The reaction mixture was warmed to 0 °C and stirred for 3.5 h. This solution was then added via a canula to a −78 °C solution of 4-[(trimethylsilyl)methyl]-3-butenyl benzenesulfonate (**14**), which was prepared immediately prior to its use by the following procedure. *n*-Butyllithium (2.74 mmol) in hexane solution was added to a −78 °C solution of 4-[(trimethylsilyl)methyl]-3-butenyl alcohol (**24**; 434 mg, 2.74 mmol) in 3 mL of anhydrous THF. The mixture was stirred for 0.5 h before adding benzenesulfonyl chloride (484 mg, 2.74 mmol). The reaction mixture was warmed to 25 °C, stirred for 2.5 h, and cooled to −78 °C prior to addition of the methyldihydroisoquinoline anion. After addition, the solution was brought to a total volume of 15 mL by the addition of THF, warmed to 60 °C, stirred for 1 day, poured into water, and extracted with $CHCl_3$. The chloroform extracts were dried and concentrated in vacuo, and the residue were subjected to column chromatography on Florisil (1% MeOH–99% $CHCl_3$) to yield 300 mg (50%) of the desired dihydroisoquinoline **17**: ^{1}H NMR δ −0.01 (s, 9 H, $Si(CH_3)_3$), 1.51 (s, 2 H, CH_2Si), 1.79 (m, 2 H, homoallylic CH_2), 2.04 (t, 2 H, allylic CH_2), 2.64–2.76 (m, 4 H, C-4 CH_2 and $CH_2C{=}N$), 3.65 (t, 2 H, C-3 CH_2), 4.55 (d, 2 H, vinyl CH_2),

(19) (a) This substance is commercially available from Aldrich Chemical Co. (b) Wehrli, P. A.; Schaer, B. *Synthesis* **1974**, 288.

7.16–7.45 (m, 4 H); ^{13}C NMR δ –1.4 (q, $Si(CH_3)_3$), 25.3 (t, CH_2Si), 26.2 (t, C-4) 26.7 (t, homoallylic CH_2), 35.4 (t, $CH_2C{=}N$), 38.0 (t, allylic CH_2), 46.7 (t, C-3), 107.3 (t, vinyl CH_2), 125.1 (d, C-5), 126.9 (d, C-7), 127.5 (d, C-8), 129.0 (s, C-10), 130.4 (d, C-6), 137.9 (s, C-9), 147.1 (s, vinyl), 167.4 (s, C-1); IR ($CHCl_3$) 3000, 2970, 1620, 1210, 850, 740 cm^{-1}; mass spectrum, *m/e* (relative intensity) 285 (M^+, 13), 212 (M^+ – $Si(CH_3)_3$, 75), 198 (26), 158 (71), 145 (100), 73 (63); high-resolution mass spectrum, *m/e* 285.1895 ($C_{18}H_{27}NSi$ requires 285.1914).

***N*-Methyl-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinolinium Perchlorate (9).** A solution of 1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinoline (**17**; 278 mg, 0.975 mmol) and methyl iodide (1.368 g, 9.63 mmol) in 10 mL of anhydrous ether was stirred at 40 °C for 2 days, producing the iodide salt (340 g, 0.796 mmol), which was subjected to perchlorate anion exchange. Concentration of the eluant in vacuo followed by column chromatography on Florisil (2.5% MeOH–97.5% $CHCl_3$) gave 307 mg (79% overall) of the desired perchlorate salt **9**: ^{1}H NMR δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.50 (s, 2 H, CH_2Si), 1.89 (m, 2 H, homoallylic CH_2), 2.12 (t, 2 H, allylic CH_2), 3.03–3.27 (m, 4 H, C-4 CH_2 and $CH_2C{=}N$), 3.84 (s, 3 H, CH_3), 4.09 (t, 2 H, C-3 CH_2), 4.61 (s, 2 H, vinyl CH_2), 7.27–7.85 (m, 4 H); ^{13}C NMR δ –1.4 (q, $Si(CH_3)_3$), 25.3 (t, CH_2Si), 25.6 (t, homoallylic CH_2), 26.4 (t, C-4), 30.6 (t, $CH_2C{=}N$), 37.7 (t, allylic CH_2), 44.8 (q, CH_3), 53.0 (t, C-3), 109.3 (t, vinyl CH_2), 126.2 (s, C-10), 128.4 (d, C-5), 128.6 (d, C-7), 129.8 (d, C-8) 136.5 (d, C-6), 137.4 (s, C-9), 145.2 (s, vinyl), 178.9 (s, C-1); IR ($CHCl_3$) 2955, 1640, 1250, 1190, 1100, 860 cm^{-1}; mass spectrum, *m/e* (relative intensity) 300 (M^+, 1), 299 (2), 227 (13), 226 (14), 172 (100), 73 (38); high-resolution mass spectrum, *m/e* 300.2085 (M – ClO_4^-, $C_{19}H_{30}NSi$ requires 300,2090); UV (CH_3CN) λ_{max} 280 nm (ϵ 8500).

***N*-(Carbethoxymethyl)-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinolinium Perchlorate (10).** A solution of 1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinoline (**17**; 227 mg, 0.796 mmol) and ethyl iodoacetate (235 mg, 1.098 mmol) in 10 mL of anhydrous ether was stirred at 25 °C for 7 days, producing the iodide salt (302 mg), which was subjected to perchlorate anion exchange. Concentration of the eluant gave a residue that was subjected to column chromatography on Florisil (2.5% MeOH–97.5% $CHCl_3$), yielding 250 mg (67%) of the perchlorate salt **10**: ^{1}H NMR δ –0.01 (s, 9 H, $SiCH_3)_3$), 1.34 (t, 3 H, CH_3), 1.47 (s, 2 H, CH_2Si), 1.77 (m, 2 H, homoallylic CH_2), 2.10 (t, 2 H, allylic CH_2), 3.10 (t, 2 H, C-4 CH_2), 3.27 (t, 2 H, $CH_2C{=}N$), 4.14 (t, 2 H, C-3 CH_2), 4.30 (q, 2 H, $CO_2CH_2CH_3$), 4.62 (d, 2 H, vinyl CH_2), 5.07 (s, 2 H, CH_2CO_2Et), 7.38–7.86 (m, 4 H); ^{13}C NMR δ –1.7 (q, $Si(CH_3)_3$), 13.7 (q, CH_3), 25.4 (t, homoallylic CH_2), 25.8 (t, CH_2Si), 25.9 (t, C-4), 30.5 (t, $CH_2C{=}N$), 37.2 (t, allylic CH_2), 52.6 (t, C-3), 57.7 (t, $CO_2CH_2CH_3$), 63.0 (t, CH_2CO_2Et), 109.1 (t, vinyl CH_2), 125.8 (s, C-10), 128.4 (d, C-5), 128.5 (d, C-7), 130.4 (d, C-8), 137.1 (d, C-6), 137.9 (s, C-9), 144.9 (s, vinyl), 165.4 (s, carbonyl), 181.8 (s, C-1); IR ($CHCl_3$) 2960, 1750, 1635, 1350, 1250, 1195, 1100, 860 cm^{-1}; mass spectrum, *m/e* (relative intensity) 299 (15), 259 (2), 245 (10), 226 (16), 147 (100), 73 (20); high-resolution mass spectrum, *m/e* 299.1899 (M – ClO_4^- and $(CH_3)_3)Si$ requires 299.1895); UV (CH_3CN) λ_{max} 285 nm (ϵ 10 090).

4-[(Trimethylsilyl)methyl]-4-penten-1-ol (21). This alcohol was prepared from the corresponding ethyl ester **20** by reduction. The ester **20** was derived by use of the modified Claisen rearrangement process suggested by Johnson.[8] A mixture of 2-(trimethylsilyl)-2-propen-1-ol (**19**; 4.094 g, 28.4 mmol), triethyl orthoacetate (31.86 g, 196 mmol), and propionic acid (126 mg, 1.70 mmol) was heated, in an apparatus appropriate for the distillative removal of ethanol, at 145 °C for 3 h. The reaction mixture was then poured into aqueous $NaHCO_3$ and extracted with ether. The ethereal extracts were dried and concentrated in vacuo. Molecular distillation (25 °C (1 mmHg), trapped at –78 °C) was used to remove the excess triethyl orthoacetate and isolate the desired ester **20** (contaminated with triethylorthoacetate), which was used directly for the reduction reaction. Spectroscopic data for **20**: ^{1}H NMR δ 0.00 (s, 9 H, $SiMe_3$), 1.23 (t, 3 H, OCH_2CH_3), 1.51 (s, 2 H, CH_2Si), 2.29 (t, 2 H, allylic CH_2), 2.42 (t, 2 H, CH_2CO_2Et), 4.10 (q, 2 H, $CO_2CH_2CH_3$), 4.56 (d, 2 H, vinyl CH_2); ^{13}C NMR δ –1.9 (q, $Si(CH_3)_3$), 13.8 (q, $CO_2CH_2CH_3$), 26.6 (t, CH_2Si), 32.3 (t, allylic CH_2), 32.6 (t, CH_2COEt), 59.5 (t, OCH_2CH_3), 106.7 (t, vinyl CH_2), 145.4 (s, vinyl), 172.3 (s, carbonyl); IR ($CHCl_3$) 2960, 1730, 1640, 1375, 1250, 1160, 860 cm^{-1}; mass spectrum, *m/e* (relative intensity) 214 (20), 169 (85), 73 (100); high-resolution mass spectrum, *m/e* 214.1386 ($C_{11}H_{22}O_2Si$ requires 214.1385).

A solution of ester **20** (ca, 6.1 g, 28 mmol) in 200 mL of ether was added to a solution of $LiAlH_4$ in 200 mL of ether at 0 °C. After addition, the reaction mixture was stirred at 25 °C for 2 h, cooled to 0 °C, and quenched with aqueous Na_2SO_4. Filtration of the formed crystalline precipitate through Celite gave an ethereal filtrate that was washed with water and aqueous NaCl, dried, and concentrated in vacuo. The residue obtained was subjected to Florisil column chromatography ($CHCl_3$) to yield 3.7 g (75% overall from **19**) of the desired alcohol **21**: ^{1}H NMR δ 0.04 (s, 9 H, $Si(CH_3)_3$), 1.52 (s, 2 H, CH_2Si), 2.0 (m, 5 H, $CH_2CH_2CH_2OH$), 3.59 (t, 2 H, CH_2OH), 4.53 (d, 2 H, vinyl CH_2); ^{13}C NMR δ –1.5 (q, $Si(CH_3)_3$), 26.7 (t, CH_2Si), 30.8 (t, allylic CH_2), 34.5 (t, CH_2CH_2OH), 62.5 (t, CH_2OH), 107.2 (t, vinyl CH_2), 147.1 (s, vinyl C); IR ($CHCl_3$) 3440, 3070, 2940, 1630, 1245, 845 cm^{-1}; mass spectrum, *m/e* (relative intensity) 172 (5), 157 (6), 128 (100); high-resolution mass spectrum, *m/e* 172.1287 ($C_9H_{20}OSi$ requires 172.1291).

1-[5-[(Trimethylsilyl)methyl]-5-hexenyl]-3,4-dihydroisoquinoline (18). To a solution of 1-methyl-3,4-dihydroisoquinoline (406 mg, 2.8 mmol) in 2 mL of anhydrous THF at –78 °C was added slowly 3.36 mmol of *n*-butyllithium in hexane and tetramethylethylenediamine (393 mg, 3.38 mmol). The reaction mixture was warmed to 0 °C and stirred for 3.5 h. The anion was then added, via a canula, to a –78 °C solution of 4-[(trimethylsilyl)methyl]-4-pentenylbenzenesulfonate (**15**; 1.048 g, 3.36 mmol) which was freshly prepared immediately prior to its use by the following procedure. *n*-Butyllithium (3.64 mmol) in hexane was added to a –78 °C solution of 4-[(trimethylsilyl)methyl]-4-penten-1-ol (**21**; 579 mg, 3.36 mmol) in 3 mL of anhydrous THF. The mixture was stirred for 0.5 h. Benzenesulfonyl chloride (650 mg, 3.68 mmol) was added, and the mixture was stirred at 25 °C for 2.5 h, cooled to –78 °C, and then reacted with the methylisoquinoline anion. After addition, the solution was brought to a total volume of 15 mL by the addition of THF, warmed to 60 °C, stirred for 1 day, poured into water, and extracted with chloroform. The chloroform extracts were dried, concentrated in vacuo, and subjected to Florisil column chromatography (1% MeOH–99% $CHCl_3$), yielding 370 mg (41%) of the desired dihydroisoquinoline (**18**): ^{1}H NMR δ –0.01 (s, 9 H, $Si(CH_3)_3$, 1.49 (s, 2 H, CH_2Si), 1.50–1.98 (m, 6 H, homoallylic CH_2, allylic CH_2, and $CH_2CH_2C{=}N$), 2.63–2.77 (m, 4 H, C-4 CH_2 and $CH_2C{=}N$), 3.65 (t, 2 H, C-3 CH_2), 4.53 (d, 2 H, vinyl CH_2), 7.16–7.50 (m, 4 H); ^{13}C NMR δ –1.3 (q, $Si(CH_3)_3$), 26.2 (t, CH_2Si), 26.8 (t, C-4), 27.0 (t, homoallylic CH_2), 27.8 (t, $CH_2CH_2C{=}N$), 35.8 ($CH_2C{=}N$), 38.0 (t, allylic CH_2), 46.8 (t, C-3), 106.9 (t, vinyl CH_2), 125.0 (d, C-5), 126.8 (d, C-7), 127.5 (d, C-8), 129.0 (s, C-10), 130.3 (d, C-6), 137.9 (s, C-9), 147.5 (s, vinyl), 167.4 (s, C-1); IR ($CHCl_3$) 2950, 1630, 1250, 1190, 1120, 860 cm^{-1}; mass spectrum, *m/e* (relative intensity) 299 (M^+, 5), 284 (12), 226 (36), 145 (100), 73 (58); high-resolution mass spectrum, *m/e* 299.2095 ($C_{19}H_{29}NSi$ requires 299.2069).

***N*-Methyl-1-[5-[(trimethylsilyl)methyl]-5-hexenyl]-3,4-dihydroisoquinolinium Perchlorate (11).** A solution of 1-[5-[(trimethylsilyl)methyl]-5-hexenyl]-3,4-dihydroisoquinoline (**18**; 512 mg, 1.71 mmol) and methyl iodide (2.96 g, 20.8 mmol) in 10 mL of anhydrous ether was stirred at 40 °C for 2 days, producing the iodide salt (570 mg, 1.29 mmol). The iodide salt was subjected to perchlorate anion exchange. The eluant was concentrated in vacuo, giving a residue that was subjected to Florisil column chromatography (2.5% MeOH–97.5% $CHCl_3$), yielding 504 mg (71% overall) of the desired perchlorate salt **11**: ^{1}H NMR δ 0.01 (s, 9 H, $Si(CH_3)_3$), 1.48 (s, 2 H, CH_2Si), 1.62–1.76 (m, 4 H, homoallylic CH_2 and $CH_2CH_2C{=}N$), 2.00 (t, 2 H, allylic CH_2), 3.12–3.24 (m, 4 H, C-4 CH_2 and $CH_2C{=}N$), 3.86 (s, 3 H, CH_3), 4.09 (t, 2 H, C-3 CH_2), 4.56 (d, 2 H, vinyl CH_2), 7.33–7.82 (m, 4 H); ^{13}C NMR δ –1.4 (q, $Si(CH_3)_3$), 25.5 (t, CH_2Si), 26.3 (t, C-4), 26.7 (t, homoallylic CH_2), 27.5 (t, $CH_2CH_2C{=}N$), 31.1 (t, $CH_2C{=}N$), 37.2 (t, allylic CH_2), 44.7 (q, CH_3), 52.9 (t, C-3), 107.9 (t, vinyl CH_2), 126.2 (s, C-10), 128.3 (d, C-5), 128.5 (d, C-7), 129.7 (d, C-8), 136.4 (d, C-6), 137.3 (s, C-9), 146.3 (s, vinyl C), 178.8 (s, C-1); IR ($CHCl_3$) 2950, 1640, 1350, 1250, 1100, 850 cm^{-1}; mass spectrum, *m/e* (relative intensity), 314 (1), 313 (5), 298 (7), 240 (18), 173 (16), 172 (100), 159 (9), 73 (22); high-resolution mass

spectrum, m/e 314.228 ($M - ClO_4^-$, $C_{20}H_{32}NSi$ requires 314.2293); UV (CH_3CN) λ_{max} 280 nm (ϵ 13 000).

General Procedure for Photolysis of the 3,4-Dihydroisoquinolinium Perchlorates. Irradiations were conducted on N_2-purged solutions of the dihydroisoquinolinium perchlorates (concentrations and solvents given in Table I) by using an apparatus consisting of a 450-W Hanovia, medium-pressure lamp surrounded by a Corex glass ($\lambda > 280$ nm) filter in a quartz immersion well. Reaction progress was followed by UV spectrophotometric monitoring, and irradiations were terminated (times given in Table I) when decreases in the absorbance due to the starting perchlorate salt ceased. The crude photolysates were concentrated in vacuo, made basic by the addition of saturated aqueous $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving residues that were subjected to chromatographic separations on Florisil ($CHCl_3$ to 3% MeOH–$CHCl_3$ as eluant). The *N*-H-substituted dihydroisoquinolinium perchlorates were generated in situ by addition of 1 equiv of 70% aqueous $HClO_4$ to solutions of the corresponding dihydroisoquinoline at 0 °C. This was followed by irradiation, workup, and purification as described above.

The spectrometric data for the spirocyclic photoproducts are as follows.

25: ^1H NMR δ 1.98–3.30 (m, 11 H), 5.00 (s, vinyl CH_2), 7.06–7.33 (m, 4 H); ^{13}C NMR δ 30.7 (m, C-4 and C-5′), 39.5 (t, C-4′), 41.5 (t, C-1′), 49.8 (t, C-3), 63.8 (s, C-1), 106.8 (t, vinyl CH_2), 125.7 (d, C-5), 125.8 (d, C-6), 126.0 (d, C-7), 129.2 (d, C-8), 135.5 (s, C-9), 141.9 (s, vinyl), 151.2 (s, C-10); IR ($CHCl_3$) 3400, 3250, 2940, 1660, 1495, 1450, 1430, 1190, 1110, 890 cm^{-1}; mass spectrum, m/e (relative intensity) 199 (M^+, 75), 198 (100), 184 (66), 144 (16); high-resolution mass spectrum, m/e 199.1325 ($C_{14}H_{17}N$ requires 199.1323).

26: ^1H NMR δ 1.95–3.40 (m, 13 H), 2.35 (s, 3 H, CH_3), 4.93 (d, 2 H, vinyl CH_2), 7.00–7.25 (m, 4 H); ^{13}C NMR δ 23.9 (t, C-5′), 31.5 (t, C-4), 37.3 (q, $-CH_3$), 39.4 (t, C-4′), 46.6 (t, C-3), 47.5 (t, C-1′), 68.2 (s, C-1), 105.9 (t, vinyl CH_2), 126.1 (m, C's-6, 7, and 8); 128.8 (d, C-5), 132.9 (s, C-9), 141.6 (s, vinyl), 151.4 (s, C-10); IR ($CHCl_3$) 2940, 1660, 1100, 880 cm^{-1}; mass spectrum, m/e (relative intensity) 213 (M^+, 63), 212 ($M^+ - H$, 100), 198 ($M^+ - CH_3$, 73), 184 (88); high-resolution mass spectrum, m/e 213.1508 ($C_{15}H_{19}N$ requires 213.1598).

27: ^1H NMR 1.20 (t, 2 H, OCH_2CH_3), 2.00–3.50 (m, 12 H), 32.0 (s, 2 H, CH_2CO_2Et), 4.20 (q, 2 H, $CO_2CH_2CH_3$), 4.90 (s, 2 H, vinyl), 7.0–7.25 (m, 4 H); ^{13}C NMR δ 14.1 (q, $CO_2CH_2CH_3$), 24.4 (t, C-5′), 31.7 (t, C-4), 39.9 (t, C-4′), 45.1 (t, C-3), 46.6 (C-1′), 51.9 (t, CH_2CO_2Et), 60.5 (t, $CO_2CH_2CH_3$), 68.1 (s, C-1), 105.8 (t, vinyl CH_2), 125.9 (m, C's-6, 7, and 8), 128.8 (d, C-5), 133.2 (s, C-9), 142.0 (s, vinyl), 151.4 (s, C-10), 171.7 (s, carbonyl); IR ($CHCl_3$) 2950, 1745, 1665, 1210, 740, 660 cm^{-1}; mass spectrum, m/e (relative intensity) 285 (M^+, 2), 284 ($M^+ - H$, 2), 256 ($M^+ - CO_2CH_3$, 3), 212 ($M^+ - CH_2CH_2CH_3$, 9), 198 ($M^+ - CH_2CO_3Et$, 2), 184 (4); high-resolution mass spectrum, m/e 285.1730 ($C_{18}H_{23}NO_2$ requires 285.1729).

31: ^1H NMR δ 0.76 (s, 3 H, CH_3), 1.50–3.45 (m, 14 H), 7.17–7.25 (m, 4 H); ^{13}C NMR δ 22.9 (q, CH_3), 24.3 (t, C-5′), 25.1 (t, C-6′), 39.8 (t, C-4), 40.6 (t, C-4′), 46.0 (s, C-3), 47.8 (t, C-1), 59.1 (s, C-1′), 76.7 (s, C-2′), 126.1 (d, C-6 and C-7), 126.4 (d, C-8), 128.7 (d, C-5), 135.7 (s, C-9), 136.4 (s, C-10); IR ($CHCl_3$) 3600–3200, 2940, 1495, 1450, 1430, 1190, 1120 cm^{-1}; mass spectrum, m/e (relative intensity) 213 ($M^+ - H_2O$, 100), 212 (99), 199 (36), 198 (95), 158 (46), 145 (96), 144 (95); high-resolution mass spectrum, m/e 213.1520 ($M - H_2O$, $C_{15}H_{19}N$ requires 213.1519).

28: ^1H NMR δ 1.56–2.73 (m, 11 H, 2.35 (s, 3 H, CH_3), 2.80–2.86 (t, 2 H, C-3 CH_2), 3.22–3.29 (t, 2 H, C-4 CH_2), 4.75–4.87 (d, 2 H, vinyl CH_2), 7.03–7.34 (m, 4 H); ^{13}C NMR δ 22.2 (t, C-5′), 22.5 (t, C-6′), 34.0 (t, C-4), 35.6 (q, CH_3), 36.0 (t, C-4′), 45.1 (m, C-3 and C-1′), 60.7 (s, C-1), 109.4 (t, vinyl CH_2), 126.0–126.2 (m, C's-5, 6, and 7), 129.3 (d, C-5), 133.6 (s, C-9), 141.6 (s, vinyl) 146.4 (s, C-10); IR ($CHCl_3$) 2940, 1650, 1450, 1190, 1120, 890 cm^{-1}; mass spectrum, m/e (relative intensity) 227 (M^+, 13), 226 ($M^+ - H$, 20), 198 (10), 184 (13), 172 (100); high-resolution mass spectrum, m/e 227.1647 ($C_{16}H_{21}N$ requires 227.1659).

29: ^1H NMR δ 1.20 (t, 3 H, OCH_2CH_3), 1.45–3.48 (m, 14 H), 4.18 (q, 2 H, OCH_2CH_3), 4.73 (d, 2 H, vinyl CH_2), 7.00–7.42 (m, 4 H); ^{13}C NMR δ 14.1 (q, $CO_2CH_2CH_3$), 22.0 (t, C-6′), 22.5 (t, C-5′), 34.1 (t, C-4), 36.0, (t, C-4′), 41.7 (t, C-1′), 44.5 (t, C-3), 49.4 (t, CH_2CO_2Et), 59.8 (s, C-1), 60.3 (t, $CO_2CH_2CH_3$), 109.1 (t, vinyl CH_2), 125.4 (d, C-6), 125.8 (d, C-7), 126.1 (d, C-8), 129.4 (d, C-5), 134.2 (s, C-9), 142.7 (s, vinyl), 146.5 (s, C-10), 172.2 (s, carbonyl); IR ($CHCl_3$) 2945, 1750, 1655, 1195, 1140 cm^{-1}; mass spectrum, m/e (relative intensity) 299 (M^+, 18), 298 ($M^+ - H$, 22), 245 (18), 244 (100), 226 (28); high-resolution mass spectrum, m/e 299.1873 ($C_{19}H_{25}NO_2$ requires 299.1885).

30: ^1H NMR δ 1.38–2.14 (m, 6 H), 2.34 (s, 3 H, CH_3), 2.50 (m, 2 H), 2.58–3.40 (m, 6 H), 4.70 (d, 2 H vinyl CH_2), 7.00–7.29 (m, 4 H); ^{13}C NMR δ 22.6 (t, C-7′), 24.5 (t, C-6′), 28.0 (t, C-5′), 36.3 (q, CH_3), 37.3 (t, C-4), 39.9 (t, C-4′), 45.6 (t, C-3), 49.0 (t, C-1′), 61.3 (s, C-1), 112.6 (t, vinyl CH_2), 125.7 (d, C-6), 125.9 (d, C-7), 126.0 (d, C-8), 129.3 (d, C-5), 132.7 (s, C-9), 143.8 (s, vinyl), 148.5 (s, C-10); IR ($CHCl_3$) 2930, 1640, 1450, 1190, 1125, 910, 890 cm^{-1}; mass spectrum, m/e (relative intensity) 241 (M^+, 14), 240 ($M^+ - H$, 39), 226 ($M^+ - CH_3$, 4), 186 (44), 172 (100), 159 (18); high-resolution mass spectrum, m/e 241.1834 ($C_{17}H_{23}N$ requires 241.1830).

Reaction of *N*-Methyl-1-[3-[(trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinolinium Perchlorate (6) with Cesium Fluoride. A solution of dihydroisoquinoline perchlorate **6** (180 mg, 0.467 mmol) and cesium fluoride (200 mg, 1.32 mmol) in 10 mL of anhydrous ethanol was stirred at 70 °C for 40 h. The reaction mixture was cooled to 25 °C, washed with water, and extracted with chloroform. The chloroform extracts were dried, concentrated in vacuo, and subjected to Florisil column chromatography (3% MeOH–97% $CHCl_3$), yielding 11 mg (15%) of 1-oxo-2-methyl-3,4-dihydroisoquinoline (**41**),[20] 28 mg (21%) of *N*-methyl-1-[3-[(trimethylsilyl)methyl]-3-butenyl]-1,2,3,4-tetrahydroisoquinoline (**38**), and 7 mg (7%) of the spirocyclic product **26**. Spectroscopic data for **41**: ^1H NMR δ 2.97 (t, 2 H, C-4 CH_2), 3.11 (s, 3 H, CH_3), 3.54 (t, 2 H, C-3 CH_2), 7.0–8.1 (m, 4 H); ^{13}C NMR ($CDCl_3$) 28.0 (t, C-4), 35.1 (q, CH_3), 48.2 (t, C-3), 126.8 (d, C-7), 127.0 (d, C-6), 128.2 (d, C-8), 129.5 (s, C-10), 131.5 (d, C-5), 137.9 (s, C-9), 164.8 (s, C-1); IR ($CHCl_3$) 2940, 1640, 850 cm^{-1}; mass spectrum, m/e (relative intensity) 161 (M^+, 74), 160 (11), 118 (100); high-resolution mass spectrum, m/e 161.0847 ($C_{10}H_{11}NO$ requires 161.0846).

Spectroscopic data for **38**: ^1H NMR δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.50 (s, 2 H, CH_2Si), 1.62–2.19 (m, 4 H, allylic and homoallylic CH_2s), 2.41 (s, 3 H, CH_3), 2.50–3.20 (m, 4 H, C-3 and C-4 CH_2s), 3.44 (t, 1 H, C-1 CH), 4.49 (d, 2 H, vinyl CH_2), 7.00–7.17 (m, 4 H); ^{13}C NMR δ −1.4 (q, $Si(CH_3)_3$), 26.4 (t, CH_2Si), 27.1 (t, C-4), 33.0 (t, homoallylic CH_2), 33.7 (t, allylic CH_2), 42.8 (q, CH_3), 48.5 (t, C-3), 63.3 (d, C-1), 106.5 (t, vinyl CH_2), 125.7 (m, C-6 and C-7), 127.0 (d, C-8), 128.6 (d, C-5), 134.8 (s, C-9), 138.3 (s, C-10), 148.1 (s, vinyl C); IR ($CHCl_3$) 2940, 1630, 1245, 1090, 850 cm^{-1}; mass spectrum, m/e (relative intensity) 287 (M^+, 0.2), 272 ($M^+ - CH_3$, 3), 161 (4), 147 (11), 146 (100), 145 (2), 73 (5); high-resolution mass spectrum, m/e 287.2071 ($C_{18}H_{29}NSi$ requires 287.2069).

Reaction of *N*-Methyl-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinolinium Perchlorate (9) with Cesium Fluoride. A solution of the dihydroisoquinolinium perchlorate **9** (68 mg, 0.170 mmol) and cesium fluoride (200 mg, 1.3 mmol) in 10 mL of anhydrous ethanol was stirred at 70 °C for 3 days. The reaction mixture was washed with water and extracted with chloroform. The chloroform extracts were dried, concentrated in vacuo, and purified by Florisil column chromatography (3% MeOH–97% $CHCl_3$), yielding 15 mg (29%) of *N*-methyl-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-1,2,3,4-tetrahydroisoquinoline (**39**) and 12 mg (31%) of the spirocyclic product **28**. Spectroscopic data for **39**: ^1H NMR δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.32–2.21 (m, 6 H), 2.48 (s, 3 H, CH_3), 2.58–3.23 (m, 4 H), 3.46 (t, 1 H, C-1 CH), 4.51 (d, 2 H, vinyl CH_2), 7.00–7.18 (m, 4 H); ^{13}C NMR δ −1.3 (q, $Si(CH_3)_3$, 23.5 (t, homoallylic CH_2), 26.3 (t, CH_2Si), 26.6 (t, C-4), 34.4 (t, CH_2CHNCH_3), 38.4 (t, allylic CH_2), 42.9 (q, CH_3), 48.4 (t, C-3), 63.7 (d, C-1), 107.1 (t, vinyl CH_2), 125.7 (m, C-6 and C-7), 127.1 (d, C-8), 128.6 (d, C-5), 134.7 (s, C-9), 138.5 (s, C-10), 147.5 (s, vinyl C); IR ($CHCl_3$) 2940, 1260, 1190, 1120, 860, 730 cm^{-1}; mass spectrum, m/e (relative intensity) 301

(20) (a) Spectroscopic data for this substance matched those for the known compound.[20b] (b) Gramain, J. C.; Simonet, N.; Vermeersch, G.; Febuay-Garot, N.; Caplain, S.; LaBlanche-Combier, A. *Tetrahedron* **1982**, *38*, 539 and references therein.

(M^+, 1), 286 ($M^+ - CH_3$, 2), 161 (6), 146 (100), 73 (10); high-resolution mass spectrum, m/e 301.2249 ($C_{19}H_{31}NSi$ requires 301.2226).

Reaction of *N*-Methyl-1-[5-[(trimethylsilyl)methyl]-5-hexenyl]-3,4-dihydroisoquinolinium Perchlorate (11) with Cesium Fluoride. A solution of the dihydroisoquinolinium perchlorate **11** (69 mg, 0.17 mmol) and cesium fluoride (200 mg, 1.80 mmol) in 10 mL of anhydrous ethanol was stirred at 70 °C for 3 days, cooled to 25 °C, washed with water, and extracted with chloroform. The chloroform extracts were dried, concentrated in vacuo, and subjected to Florisil column chromatography (3% MeOH–97% $CHCl_3$), yielding 19 mg (36%) of *N*-methyl-1-[5-[(trimethylsilyl)methyl]-5-hexenyl]-1,2,3,4-tetrahydroisoquinoline **40**: ^1H NMR δ −0.96 (s, 9 H, $Si(CH_3)_3$), 1.10–2.18 (m, 8 H), 2.45 (s, 3 H, CH_3), 2.58–3.23 (m, 4 H), 3.45 (t, 2 H, C-1 CH), 4.51 (d, 2 H, vinyl CH_2), 7.00–7.16 (m, 4 H); ^{13}C NMR δ −1.3 (q, $Si(CH_3)_3$), 25.5 (t, $CH_2CH_2CHNCH_3$), 26.2 (t, CH_2Si), 26.8 (t, C-4), 28.3 (t, homoallylic CH_2), 34.8 (t, CH_2CHN), 38.2 (t, allylic CH_2), 42.8 (q, CH_3), 48.3 (t, C-3), 63.8 (d, C-1), 106.7 (t, vinyl CH_2), 125.7 (m, C-6 and C-7), 127.2 (d, C-8), 128.6 (d, C-5), 134.6 (s, C-9), 138.5 (s, C-10), 147.9 (s, vinyl); IR ($CHCl_3$) 2930, 1630, 1240, 1180, 1120, 850 cm^{-1}; mass spectrum, m/e (relative intensity) 315 (M^+, 1), 300 ($M^+ - CH_3$, 3), 242 ($M^+ - Si(CH_3)_3$, 1), 146 (100), 73 (16); high-resolution mass spectrum, m/e 315.2336 ($C_{20}H_{33}NSi$) requires 315.2382).

***N*-Methyl-1-[3-[(trimethylsilyl)methyl]-3-butenyl]-1,2,3,4-tetrahydroisoquinoline (38).** Solid $NaBH_4$ (20 mg, 0.43 mmol) was added to a solution of the dihydroisoquinoline perchlorate **6** (32 mg, 0.08 mmol) in 5 mL of ethanol, and the resulting solution was stirred at 0 °C for 0.5 h and at 25 °C for 5 h. Water was added, and the resulting mixture was extracted with chloroform. The chloroform extracts were dried and concentrated in vacuo, giving a residue that was subjected to Florisil column chromatography (2.5% MeOH–97.5% $CHCl_3$), yielding 16 mg (67%) of the tetrahydroisoquinoline **38**. The tetrahydroisoquinolines **39** and **40** were prepared in the same fashion starting with the hydroisoquinolinium salts **9** and **11** in respective yields of 82% and 67%. The spectroscopic and TLC properties of these substances matched those of materials generated in the CsF induced processes.

Fluorescence Measurements. Fluorescence spectra were recorded at 25 °C on nondegassed acetonitrile solutions. Excitation was at 275 nm in all cases. Emission scans were run in the range of 310–500 nm with excitation and emission band passes of 3 and 5 nm, respectively. Concentrations of fluorescing species ($(4–5 \times 10^{-5}$ M) were adjusted to ensure identical absorbances at the excitation wavelength. Fluorescence quantum yields of the iminium salts were measured by use of naphthalene (ϕ = 0.21)[11] as a fluorescence standard. The data obtained are summarized in Table II.

Reduction Potential Measurements. Reduction potentials of the dihydroisoquinolinium perchlorates **5–7** and **35** were measured on 5×10^{-3} M solutions in 5% H_2O–CH_3CN with 0.1 M n-Bu_4NClO_4 as supporting electrolyte and mercury (working), Ag/AgCl (reference), and platinum wire (auxiliary) electrodes. The scan rate was 100 mV/s with currents of 5–10 μA. Cyclic voltamograms were nonreversible. The $E_{1/2}(-)$ values were obtained by half-wave measurements and are recorded in Table II.

Quantum Yield Measurements. Quantum yields were measured by using a "linear optical bench" apparatus described earlier.[14] Product analyses were performed by GLC (6 ft × 1/8 in., 10% OV-101 on Chromosorb W, flow rate 30 mL/min). Reaction mixtures were worked up as in the preparative runs and then subjected to $NaBH_4$ in EtOH reduction to remove unreacted iminium salts. The reduction step was required since the iminium salts interfered with GLC analysis of photoproducts. Internal standards employed in the GLC analyses of photoproducts were either bibenzyl, benzophenone, or 2,6-dimethoxynaphthalene.

Irradiations were conducted on 133-mL solutions at 15 °C by using light in the 260–300-nm region. The quantum yield data listed below are as follows: iminium salt (solvent, mmol of iminium salt) light absorbed, product (mmol), quantum yield of formation, percent conversion, internal standard for GLC, GLC column temperature.

***N*-Methyl-1-[3-[(trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinolinium Perchlorate (6)**: (CH_3OH, 0.180 mmol) 0.44 mEinstein, 26 (0.0131 mmol), ϕ = 0.0300, 7.3% conversion, bibenzyl, 160 °C; (CH_3OH, 0.169 mmol) 0.68 mEinstein, 26 (0.0201 mmol), ϕ = 0.0290, 11.9% conversion, bibenzyl, 160 °C; (CH_3CN, 0.172 mmol) 0.70 mEinstein, 26 (0.0027 mmol), ϕ = 0.0038; 1.6% conversion, bibenzyl, 160 °C; (CH_3CN, 0.179 mmol) 2.66 mEinstein, 26 (0.0100 mmol), ϕ = 0.0038, 5.6% conversion, bibenzyl, 160 °C.

***N*-(Carbethoxymethyl)-1-[3-[(trimethylsilyl)methyl]-3-butenyl]-3,4-dihydroisoquinolinium Perchlorate (7)**: (CH_3OH, 0.142 mmol) 0.91 mEinstein, 27 (0.0120 mmol), ϕ = 0.0130, 8.4% conversion, benzophenone, 155 °C; (CH_3OH, 0.144 mmol) 0.72 mEinstein, 27 (0.0114 mmol), ϕ = 0.0160, 7.9% conversion, benzophenone, 155 °C; (CH_3CN, 0.138 mmol) 2.58 mEinstein, 27 (0.0059 mmol), ϕ = 0.0023, 4.3% conversion, benzophenone, 155 °C; (CH_3CN, 0.135 mmol) 2.37 mEinstein, 27 (0.0060 mmol), ϕ = 0.0025, 4.4% conversion, benzophenone, 155 °C.

***N*-Methyl-1-[4-(trimethylsilyl)-4-pentenyl]-3,4-dihydroisoquinolinium Perchlorate (9)**: (CH_3OH, 0.163 mmol) 0.407 mEinstein, 28 (0.0039 mmol), ϕ = 0.0096, 2.4% conversion, benzophenone, 150 °C; (CH_3OH, 0.0826 mmol) 0.24 mEinstein, 28 (0.0023 mmol), ϕ = 0.0096, 2.8% conversion, benzophenone, 150 °C, (CH_3CN, 0.154 mmol) 2.09 mEinstein, 28 (0.0016 mmol), ϕ = 0.0008, 1.0% conversion, benzophenone, 150 °C.

***N*-(Carbethoxymethyl)-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinolinium Perchlorate (10)**: (CH_3OH, 0.110 mmol) 1.00 mEinstein, 29 (0.0153 mmol), ϕ = 0.0150, 13.9% conversion, 2,6-dimethoxynaphthalene, 160 °C; (CH_3OH, 0.110 mmol) 0.713 mEinstein, 29 (0.00818 mmol), ϕ = 0.0150, 7.4% conversion, 2,6-dimethoxynaphthalene, 160 °C; (CH_3CN, 0.110 mmol) 0.719 mEinstein, 29 (0.0027 mmol), ϕ = 0.0037, 2.4% conversion, 2,6-dimethoxynaphthalene, 160 °C; (CH_3CN, 0.110 mmol) 1.418 mEinstein; 29 (0.00531 mmol), ϕ = 0.0037, 4.8% conversion, 2,6-dimethoxynaphthalene, 160 °C.

***N*-Methyl-1-[5-[(trimethylsilyl)methyl]-5-hexenyl]-3,4-dihydroisoquinolinium Perchlorate (11)**: (CH_3OH, 0.175 mmol) 0.30 mEinsteins, 30 (0.0014 mmol), ϕ = 0.0045, 0.8% conversion, benzophenone, 150 °C; (CH_3OH, 0.175 mmol) 0.80 mEinstein, 30 (0.0034 mmol), ϕ = 0.0043, 2.0% conversion, benzophenone, 150 °C; (CH_3CN, 0.175 mmol) 1.39 mEinstein, 30 (0.0007 mmol), ϕ = 0.0005, 0.4% conversion, benzophenone, 150 °C; (CH_3CN, 0.175 mmol) 1.52 mEinstein, 30 (0.0008 mmol), ϕ = 0.0006, 0.5% conversion, benzophenone, 150 °C.

6,7-Dimethoxy-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinoline (34). To a −78 °C solution of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (**33**;[12] 567 mg, 2.76 mmol) in 3 mL of anhydrous THF was added slowly 5.53 mmol of *n*-dibutyllithium in hexane and tetramethylethylenediamine (643 mg, 5.53 mmol). The reaction mixture was stirred at 0 °C for 1.5 h and at 25 °C for 2 h. The solution was then added, via a cannula, to a −78 °C solution of the benzenesulfonate **15** that was freshly prepared as follows: 3.87 mmol of *n*-butyllithium in hexane solution was added to a −78 °C solution of the silyl alcohol **21** (590 mg, 3.73 mmol) in 4 mL of anhydrous THF. The mixture was warmed to 0 °C and stirred for 0.5 h. It was again cooled to −78 °C, and benzenesulfonyl chloride (684 mg, 3.87 mmol) was then added. The reaction mixture was warmed to 25 °C and stirred for 12 h. After addition, the solution was brought to a total volume of 24 mL by the addition of anhydrous THF, warmed to 60 °C, and stirred for 1 day. The reaction mixture was poured into water and extracted with chloroform. The chloroform extracts were dried and concentrated in vacuo, and the residue was subjected to column chromatography on Florisil (2.5% MeOH–97.5% $CHCl_3$), yielding 513 mg (54%) of the desired dihydroisoquinoline **34**: ^1H NMR δ −0.03 (s, 9 H, $Si(CH_3)_3$), 1.51 (s, 2 H, $-CH_2Si$), 1.74–1.82 (m, 2 H, homoallylic CH_2), 2.04 (t, 2 H, allylic CH_2), 2.55–2.71 (m, 4 H, C-4 and $CH_2C{=}N$), 3.61 (t, 2 H, C-3 CH_2), 4.55 (d, 2 H, vinyl CH_2), 6.67 (s, 1 H, C-5 CH), 7.00 (s, 1 H, C-8 CH); ^{13}C NMR δ −1.6 (q, $Si(CH_3)_3$), 25.0 (t, C-4), 25.6 (t, CH_2Si), 26.5 (t, homoallylic CH_2), 35.2 (t, $CH_2C{=}N$), 37.6 (t, allylic CH_2), 55.6 (q, C-6 OCH_3), 56.0 (q, C-7 OCH_3), 107.0 (t, vinyl CH_2), 108.7 (d, C-5), 110.2 (d, C-8), 121.6 (s, C-10), 131.3 (s, C-9), 146.7 (s, C-7), 147.2 (s, vinyl), 150.5 (s, C-6), 166.5 (s, C-1); IR ($CHCl_3$) 2940, 1630, 1270, 860 cm^{-1}; mass spectrum, m/e (relative intensity) 345 (M^+, 17), 330 (13), 272 (52), 218 (26), 205 (100), 204 (25), 73 (31); high-resolution mass spectrum, m/e

345.2149 ($C_{20}H_{31}NO_2Si$ requires 345.2141).

***N*-(Carbethoxymethyl)-6,7-dimethoxy-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinolinium Perchlorate (35).** A solution of 6,7-dimethoxy-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinoline (**34**; 470 mg, 1.328 mmol) and ethyl iodoacetate (416 mg, 1.943 mmol) in 10 mL of anhydrous ether was stirred at 25 °C for 9 days to produce the iodide salt. A methanol solution of the iodide salt was then eluted through a perchlorate anion-exchange column. The product fraction was concentrated in vacuo and purified by column chromatography on Florisil (1% MeOH–99% $CHCl_3$), yielding 500 mg (69% overall) of the perchlorate salt **35**: ^1H NMR δ –0.01 (s, 9 H, $Si(CH_3)_3$), 1.33 (t, 3 H, CH_3), 1.47 (s, 2 H, CH_2Si), 1.75 (m, 2 H, homoallylic CH_2), 2.10 (t, 2 H, allylic CH_2), 3.06 (t, 2 H, $CH_2C{=}N$), 3.21 (t, 2 H, C-4 CH_2), 3.90 (s, 3 H, C-7 OCH_3), 4.01 (s, 3 H, C-6 OCH_3), 4.05 (t, 2 H, C-3 CH_2), 4.29 (q, 2 H, $CO_2CH_2CH_3$), 4.62 (s, 2 H, vinyl CH_2), 4.96 (s, 2 H, $CH_2CO_2CH_2CH_3$), 6.88 (s, 1 H, C-7 CH), 7.17 (s, 1 H, C-6 CH); ^{13}C NMR δ –1.8 (q, $Si(CH_3)_3$), 13.7 (q, CH_3), 25.4 (t, homoallylic CH_2), 25.8 (t, CH_2Si), 26.1 (t, C-4), 29.3 (t, $CH_2C{=}N$), 37.0 (t, allylic CH_2), 52.1 (t, C-3), 56.2 (q, C-7 OCH_3), 56.6 (q, C-6 OCH_3), 57.1 (t, $CO_2CH_2CH_3$), 62.8 (t, $CH_2CO_2CH_2CH_3$), 108.9 (t, vinyl CH_2), 110.9 (d, C-5), 112.0 (d, C-8), 118.1 (s, C-10), 134.8 (s, C-9), 145.1 (s, C-7), 148.5 (s, vinyl C), 156.9 (s, C-6), 165.7 (s, carbonyl), 179.2 (s, C-1); IR ($CHCl_3$) 2940, 1750, 1610, 1260, 860 cm^{-1}; UV (CH_3OH) λ_{max} 312 nm (10 000), 366 (10 200); mass spectrum, *m/e* (relative intensity) 431 (M – $HClO_4$, 1), 359 (30), 304 (100), 218 (30), 157 (41); high-resolution mass spectrum, *m/e* (for M – $HClO_4$) 431.2496 ($C_{24}H_{37}O_4NSi$ requires 431.2491).

Irradiation of *N*-(Carbethoxymethyl)-6,7-dimethoxy-1-[4-[(trimethylsilyl)methyl]-4-pentenyl]-3,4-dihydroisoquinolinium Perchlorate (35) in Methanol and Acetonitrile. A N_2-purged solution of iminium salt **35** (89 mg, 0.167 mmol) in 110 mL of methanol was irradiated for 0.5 h with a flint glass filter ($\lambda > 310$ nm). The photolysate was concentrated in vacuo and subjected to the normal workup procedure. The residue obtained was purified by column chromatography on Florisil (100% $CHCl_3$), yielding 38 mg (63%) of cyclized product **36** and 11 mg (15%) of the tetracyclic product **37**.

Spectroscopic data for **36**: ^1H NMR δ 1.22 (t, 3 H, OCH_2CH_3), 3.13–3.43 (q, 2 H, $CH_2CO_2CH_2CH_3$), 1.48–3.5 (m, 14 H including $CH_2CO_2CH_2CH_3$), 3.81 (s, 3 H, C-7 OCH_3), 3.84 (s, 3 H, C-6 OCH_3), 4.12 (q, 2 H, OCH_2CH_3), 4.75 (d, 2 H, vinyl CH_2), 6.54 (s, 1 H, C-5 CH), 6.90 (s, 1 H, C-8 CH); ^{13}C NMR δ 14.1 (q, $CO_2CH_2CH_3$), 22.1 (C-5′ and C-6′), 34.1 (t, C-4), 36.9 (t, C-4′), 42.1 (t, C-1′), 44.7 (t, C-3), 49.5 (t, $CH_2CO_2CH_2CH_3$), 55.7 (q, C-7-OCH_3), 56.0 (q, C-6-OCH_3), 59.6 (s, C-1), 60.3 (t, $CO_2CH_2CH_3$), 109.0 (t, vinyl CH_2), 109.6 (d, C-5), 111.9 (d, C-8), 126.1 (s, C-9), 134.6 (s, C-10), 146.8 (s, vinyl), 147.0 (s, C-7), 147.3 (s, C-6), 172.3 (s, carbonyl); IR ($CHCl_3$) 2940, 1750, 1655, 1250 cm^{-1}; mass spectrum, *m/e* (relative intensity) 359 (M^+, 28), 358 (16), 344 (8), 304 (100), 286 (25); high-resolution mass spectrum, *m/e* 359.2085 ($C_{21}H_{29}NO_4$ requires 359.2089).

Spectroscopic data for **37**: ^1H NMR δ 0.01 (s, 9 H, $Si(CH_3)_3$), 0.75 (q, 2 H, CH_2Si), 1.26 (t, 3 H, $CO_2CH_2CH_3$), 2.89–3.37 (q, 2 H, $CH_2CO_2CH_2CH_3$), 1.55–3.37 (m, 14 H including $CH_2CO_2CH_2CH_3$), 3.77 (s, 6 H, C-6 and C-7 OCH_3), 4.18 (q, 2 H, $CO_2CH_2CH_3$), 6.43 (s, 1 H, C-5 CH); ^{13}C NMR δ 0.09 (q, $Si(CH_3)_3$), 14.3 (q, $CO_2CH_2CH_3$), 20.4 (t, CH_2Si), 24.2 (t, C-2′), 27.0 (t, C-1′), 30.3 (t, C-4), 38.2 (t, C-3′), 41.9 (t, C-3), 48.3 (t, C-5′), 53.6 (t, $CH_2CO_2CH_2CH_3$), 56.1 (q, C-6-OCH_3), 60.4 (q, C-7-OCH_3), 60.6 (t, $-CO_2CH_2CH_3$), 63.1 (s, C-4′), 78.0 (s, C-1), 109.5 (d, C-5), 126.9 (s, C-9), 130.3 (s, C-8), 139.5 (s, C-10), 144.0 (s, C-6), 151.6 (s, C-7), 171.5 (s, carbonyl); IR ($CHCl_3$) 2950, 1750, 1250 cm^{-1}; mass spectrum, *m/e* (relative intensity) 431 (M^+, 35), 388 (65), 358 (65), 73 (100); high-resolution mass spectrum, *m/e* 431.2571 ($C_{24}H_{37}O_4NSi$ requires 431.2491).

A N_2-purged solution of iminium salt **35** (111 mg, 0.209 mmol) in 110 mL of acetonitrile was irradiated for 0.5 h with a flint glass filter ($\lambda > 310$ nm). The photolysate was concentrated in vacuo and subjected to the normal workup procedure. The residue obtained was purified by column chromatography on Florisil (100% $CHCl_3$), yielding 17 mg (23%) of cyclized product **36** and 22 mg (24%) of the tetracyclic product **37**.

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