Electron-Transfer-Initiated Photospirocyclization Reactions of β-Enaminone-Derived Allyliminium Salts[1]

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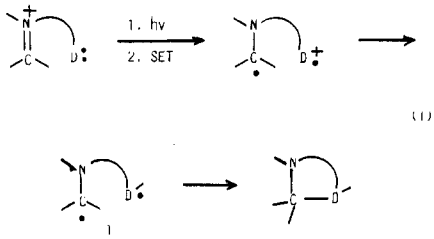
Model studies have been conducted to test several features of spirocyclization methodologies based upon excited-state reactions of allyliminium salts. Results from investigations of the photocyclization reactions of the β-enaminone-derived prenyliminium perchlorates **4–8** suggest that spirocyclic amine forming reactions, induced by intramolecular electron transfer and leading to 2-aza-1,5-diradicals by methanol addition to precursor diradical cations, are inefficient. In contrast, spirocyclic amine formation occurs with exceptionally high efficiency when the *N*-[[(trimethylsilyl)methyl]allyl]-substituted iminium perchlorates **32–35** are irradiated. The comparative efficiencies of these reactions are addressed in discussions about photospirocyclization reaction mechanisms and the effect of cation diradical desilylation. In addition, methods for preparation of the β-enaminone-derived *o*-methyl and *o*-pivaloyl iminium salts are described.

In recent years, our studies have focused on the electron-transfer-initiated, excited-state reactions of compounds containing the iminium cation ($R_2C{=}NR_2^+$) grouping. With the aim of uncovering new and synthetically useful excited-state processes and of developing an understanding of the underlying mechanistic fabric, we have explored a number of different photochemical reactions of electron donor–iminium cation systems. Through these efforts we have demonstrated that the excited states of substances containing the iminium cation chromophore in cyclic, acyclic, and N-heteroaromatic environments participate in reaction pathways induced by electron transfer from a variety of neutral donors including olefins,[3] ethers and alcohols,[4] and aromatic hydrocarbons.[5,6] In the cases investigated, the nature of the pathways followed appears to be controlled by secondary transformations of donor-derived, cation radical intermediates including nucleophilic addition,[3] deprotonation,[4,5] and desilylation.[5,7] These transformations compete with reverse electron transfer and convert the cation radical pairs to radical precursors of photoproducts.

Sequential, intramolecular electron transfer and diradical cation transformations of donor–iminium salt systems can serve as the route for generation of 2-aza-1, *n*-diradical intermediates (1) and as a key step in photocyclization reaction pathways (eq 1). Prior studies of allyliminium



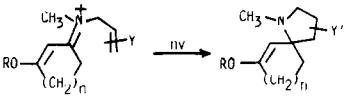
(1)

salts have uncovered examples of reactions proceeding by pathways patterned after those shown in eq 1 which serve as useful methods for construction of pyrrolidine-ring-containing heterocycles.[3b,c] The unique structural outcomes and modest yields of these transformations suggested that photocyclization processes based upon this strategy might be applied in the construction of complex molecular systems. Recent studies designed to test this hypothesis have been guided by our desire to develop general excited-state, spirocyclization methods which can be employed in synthetic routes to members of the harringtonine alkaloid family.[8]

Prior to launching into the synthetic routes which follow this strategy, we have designed and executed model studies with structurally less elaborates allyliminium salts **2** in order to probe several key aspects of these processes. The results of these investigations and of studies with more complex systems outlined in the following paper[9] have shown that this photochemical methodology can be used to efficiently construct spirocyclic amine systems and, as a result, is adaptable to synthetic approaches to harringtonine alkaloids.

Results and Discussion

Preparation and Photocyclization of Prenyliminium Salt Systems. Our initial studies were designed to explore two key features of the photospirocyclization methodologies (**2** → **3**) discussed above. First, general



2 3

methods were required for the preparation of allyliminium salts of general structure **2** and formally derived by O-protonation (R = H), O-alkylation (R = alkyl), or O-acylation (R = acyl) of β-aminocycloalk-2-en-1-one precursors. Second, we wanted to determine if the oxyvinyl-substituted iminium cation chromophore found in these salts would participate in electron-transfer-induced photocyclization reactions like those observed earlier with phenyl-conjugated[3b] and N-heteroaromatic[3c] systems. The prenyliminium perchlorates **4–8** were selected for the initial

(1) For a preliminary communication of a portion of these studies see: Tiner-Harding, T.; Ullrich, J. W.; Chiu, F. T.; Chen, S. F.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 3360.

(2) A portion of the initial phases of these studies was conducted at Texas A&M University.

(3) (a) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136. (b) Stavinoha, J. L.; Mariano, P. S.; Leone, A. S.; Swanson, R. *Ibid.* **1981**, *103*, 3148. (c) Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinoha, J. L.; Bay, E. *Ibid.* **1983**, *105*, 1204.

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

(5) Unpublished results of S. Quillen, A. Lan, R. Heuckeroth, P. S. Mariano, and L. Klingler.

(6) For a recent review summarizing results in this area see: Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130.

(7) (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.*, preceding paper in this issue.

(8) For a review a several aspects of harringtonine alkaloid chemistry see: Smith, C. R.; Mikoljczak, K. L.; Powell, R. G. "Medicinal Chemistry. Anticancer Agents Based on Natural Product Models"; Carrady, J. M., Douros, J. D., Eds.; Academic Press: New York, 1980; Vol. 16, p 392.

(9) Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *J. Org. Chem.*, following paper in this issue.

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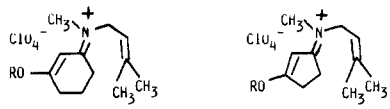
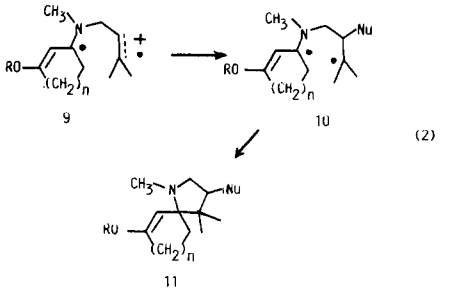


4 (R= CO-t-Bu)
5 (R= CH_3)
6 (R= H)

7 (R= CO-t-Bu)
8 (R= CH_3)

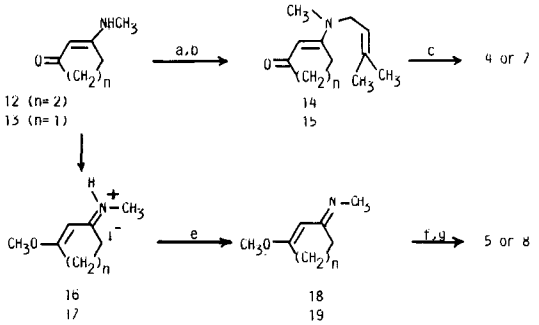
investigation of these issues. We reasoned that the presence of highly alkyl-substituted olefinic groupings in the allyl side chains of these substances would maximize the potential for electron transfer between the olefinic and photoexcited iminium cation moieties. This conclusion was reached by a consideration of electron transfer rates which are known to be dependent upon the donor–olefin oxidation potentials ($E_{1/2}$ (+)), the iminium cation–acceptor reduction potentials ($E_{1/2}$ (−)), and singlet[10] excited-state energies ($\Delta E_{0,0}$).[11] On the basis of UV absorption spectroscopic data and known reduction potentials of analogous systems,[9,12] we estimate that the $\Delta E_{0,0}$ and $E_{1/2}$ (−) values for the oxyvinyliminium cation chromophores in these salts are ca. 90 kcal/mol and ca. −1.5 V, respectively. Thus, $E_{1/2}$ (+) values for the olefinic groups must be below ca. 2.4 V in order to make the free energies for electron transfer ($\Delta G_{et} = E_{1/2}$ (+) − $E_{1/2}$ (−) − $\Delta E_{0,0}$)[11] negative and, therefore, the electron transfer rates sufficiently large to compete with alternate modes of excited state decay.[13] Accordingly, the trialkyl-substituted olefinic moieties in **4–8** which have oxidation potentials in the region of ca. 1.8 V[14,15] should serve as ideal donors in intramolecular electron-transfer processes required to initiate the photospirocyclization processes. Furthermore, the intermediate cation diradicals (e.g., **9**) should be precursors for spirocyclic amines (e.g., **11**) through pathways involving regiocontrolled[3] nucleophilic addition to produce 2-aza-1,5-diradicals **10** followed by carbon–carbon bond formation (eq 2).



9 10 11 (2)

Preparative routes to the prenyliminium perchlorates followed the two basic designs outlined in Scheme I. The *O*-methyl perchlorates **5** and **8** were synthesized by starting with the known (**12**)[16] or easily prepared (**13**) β-(methylamino)cycloalkenones via sequences involving alkylation with methyl iodide to produce the corresponding iminium iodides **16** (mp 145–146 °C) and **17** (mp 123–124 °C). These salts were deprotonated under basic conditions to afford the respective imines **18** and **19**, which owing to their lability were used directly in ensuing reactions with 3-methylbut-2-enyl bromide. The alkylation reactions gave the desired prenyliminium salts **5** and **8** after perchlorate ion exchange as 1:1 mixtures of C=N bond *E*/*Z* isomers. Slightly different procedures were employed to prepare the *O*-pivaloyl perchlorates **4** and **7**. Accordingly, N-prenylation of the *N*-methyl enaminones **12** and **13** via the corresponding lithiated anions gave the tertiary vinylogous amides **14** and **15** which were acylated by reaction with pivaloyl chloride and silver perchlorate in acetonitrile solution. Importantly, these O-acylation processes are exceptionally efficient (96%) and are not complicated by competitive C_α-acylation, a process observed for related β-enaminones when acetyl chloride is used without activation by silver ion.[17] Lastly, these sequences also produce ca. 1:1 *E*/*Z* isomeric mixtures of the iminium salts.

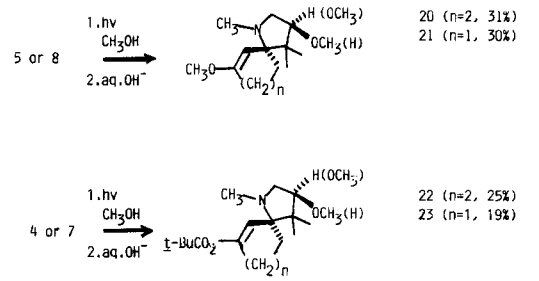
Scheme I[a]



12 (n= 2)
13 (n= 1)
14
15
4 or 7
16
17
18
19
5 or 8

[a] (a) *n*-BuLi, THF, −78 °C; (b) $(CH_3)_2C{=}CHCH_2Br$, 25 °C; (c) $AgClO_4$, *t*-BuCOCl, CH_3CN, 0 °C; (d) CH_3I, THF, 60 °C, (e) eqeous NaOH, $CHCl_3$; (f) $(CH_3)_2C{=}CHCH_2Br$, $CHCl_3$, 25 °C; (g) Dowex X-2, ClO_4^-.

Having uncovered two general methods for preparation of the prenyliminium perchlorates, our attention next turned to the photochemistry of these substances. As discussed above, we anticipated that photocyclization reactions would follow the pathways outlined in eq 2 and provide spirocyclic amines related to **11**. Indeed, irradiation of methanolic solutions of the *O*-methyl (**5** and **8**) and



5 or 8 — 1.hv, CH_3OH, 2.aq.OH^- — 20 (n=2, 31%), 21 (n=1, 30%)

4 or 7 — 1.hv, CH_3OH, 2.aq.OH^-, t-$BuCO_2$ — 22 (n=2, 25%), 23 (n=1, 19%)

O-pivaloyl (**4** and **7**) perchlorates conducted in a preparative apparatus with light of λ > 240 nm, followed by aqueous base treatment of the crude photolysates and chromatographic purification on alumina or silica gel, affords the enol ether and ester containing spirocyclic amines **20–23**, respectively, as mixtures of C-8 or C-9 epimers in low yields ranging from 19% to 31%. In the cases of the enol pivalates **22** and **23**, separation of the pyrrolidine ring isomers occurs during purification by preparative TLC on silica gel, a procedure which fails to resolve the

(10) We assume that the singlet excited states of these iminium salts will be involved in photocyclization on the basis of results obtained with other systems.[3,7]

(11) (a) The free energy and, thus, the rate constants for electron transfer in the excited state manifold are directly related to the oxidation potentials of the donor systems as seen in he familiar Weller relationship:[11b] $\Delta G_{et} = E_{1/2}(+) - E_{1/2}(-) - \Delta E_{0,0}$. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(12) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1970**, *26*, 223.

(13) Iminium salts related to **2** and closely related substances lacking *N*-allyl side chains do not fluoresce. Thus, the fluorescence quenching experiments needed to experimentally determine the validity of these predictions are not possible.

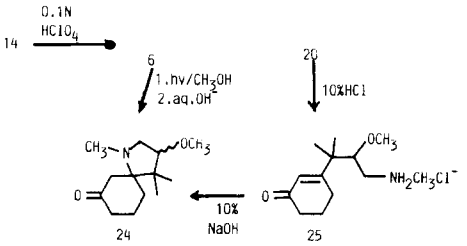
(14) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937. Watanabe, K. W. *J. Chem. Phys.* **1957**, *26*, 542.

(15) Miller, L. L.; Mordblam, G. D.; Mageda, E. A. *J. Org. Chem.* **1972**, *37*, 916.

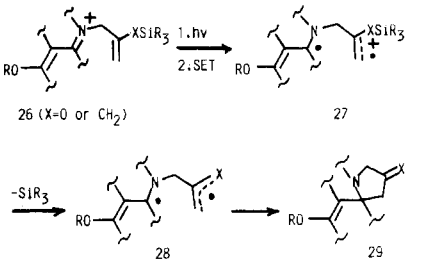
(16) Chen, Y. L.; Mariano, P. S.; Little, G. M.; O'Brien, D.; Huesmann, P. L. *J. Org. Chem.* **1981**, *46*, 4643.

(17) Det, G. H.; Speziale, A. J. *J. Org. Chem.* **1964**, *29*, 798.

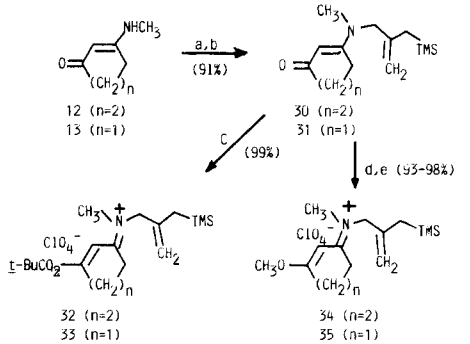
Scheme II



Scheme III



Scheme IV[a]



[a] (a) NaH, THF, reflux, 1 h; (b) CH_2=C(CH_2Si-(CH_3)$_3$)CH_2OSiMe_3, 25 °C, 24 h; (c) $AgClO_4$ *t*-BuCOCl, CH_3CN, 0 °C, 1 h; (d) $AgClO_4$, CH_3I, CH_3CN, 25 °C, 24 h; (e) flash chromatography (silica gel, 4% MeOH-$CHCl_3$).

enol ether isomers of **20** and **21**. Structural assignments to the photoproducts are made on the basis of characteristic spectroscopic data which in each instance verifies the presence in these substances of enol ether and ester functions, spirocyclic and adjacent *gem*-dimethyl substituted quaternary centers, and *N*-methyl-3-methoxy-substituted pyrrolidine rings.

The O-protonated prenyliminium salt **6** (λ_{max} 280 nm), prepared in situ by dissolution of the β-enaminone **14** in methanol containing 0.1 N $HClO_4$, is transformed to the spirocyclic amino ketones **24** (6%) by irradiation with Vycor-filtered light (Scheme II). These substances can also be prepared by treatment of the six-membered-ring enol ethers **20** first with 10% aqueous HCl to produce the ring-opened enone **25** (detected by UV spectroscopic methods) and then with 10% aqueous NaOH to liberate the free amine which spontaneously cyclizes to form **24**.[18]

The low chemical efficiencies of these photocyclization reactions can be attributed in part to competitive, photoinduced, heterolytic cleavage processes, signaled by detection of 3-methoxycyclopent-2-en-1-one and 3-methoxycyclohex-2-en-1-one in the crude photolysates after base treatment. Thus, photodeprenylation reactions of the perchlorate salts following pathways analogous to those detected earlier in N-heteroaromatic systems[9c] must be responsible for production of imine precursors of these enones. In addition, the steric conjestion attending carbon–carbon bond formation between two quaternary centers in the 2-aza-1,5-diradical cyclization could also contribute to the low efficiencies of these processes by allowing intervention of other yield-diminishing reaction pathways (e.g., disproportionation). However, no products characteristic of these alternate processes have been isolated. In any event, these preliminary results indicate that cyclic β-enaminone-derived prenyliminium salts can participate in electron-transfer-induced photocyclizations leading to generation of products containing azaspirocyclic ring systems.

Preparation and Photocyclization of [[(Trimethylsilyl)methyl]allyl]iminium Salts. Alternate approaches to photospirocyclization were next explored in order to address the questions concerning reaction efficiency and pyrrolidine ring functionality. Previous studies in our laboratory[7] concerned with allylsilane–iminium salt photoaddition reactions suggested that trialkylsilyl substitution on the allyl groupings of iminium salts related to **26** might be as effective as multiple alkyl substituents in enhancing electron-transfer efficiencies through an effect on olefin oxidation potential.[19] In addition, rapid desilylation of the intermediate cation diradicals **27** should compete effectively with alternate modes of reaction including C–N bond cleavage and, thus, provide 2-aza-1,5-diradicals **28** (Scheme III). Finally, we hypothesized that diradical cyclization would occur smoothly to generate the spirocyclic amines **29** with the synthetically attractive exocyclic olefin or ketone functionality in the pyrrolidine rings. We have published elsewhere the results of an effort probing a related photospirocyclization design which is based upon *C*-vinylazomethine ylide formation by photoinduced electron transfer.[20] The details of our successful investigations with [[(trimethylsilyl)methyl]-allyl]iminium perchlorates **32–35**, outlined below and in the following paper,[9] illustrate the unique synthetic potential of strategies which follow sequences shown in Scheme III (X = CH_2).

The *O*-methyl- and *O*-pivaloyl [[(trimethylsilyl)-methyl]allyl]iminium perchlorates **32–35** are prepared in a straightforward, efficient fashion from the corresponding β-(methylamino)cycloalkenones **12** and **13** through sequences (Scheme IV) involving N-allylation of the derived sodiated anions with the mesylate of [(trimethylsilyl)-methyl]allyl alcohol[21] followed by silver ion induced methylation or pivaloylation. In each case, the perchlorate salts are obtained as mixtures of C=N bond *E*/*Z* isomers, have spectroscopic properties fully consistent with assigned structures, and are stable substances which resist cyclization (see below) under a variety of "dark" reaction conditions.

As predicted, the trimethylsilyl-substituted allyliminium salts undergo exceedingly clean photocyclization reactions to produce the corresponding 3-methylenepyrrolidine-containing spirocyclic amines in *exceptionally* high chemical yields. Accordingly, preparative irradiations of acetonitrile solutions of **32–35** with light of λ > 280 nm afford,

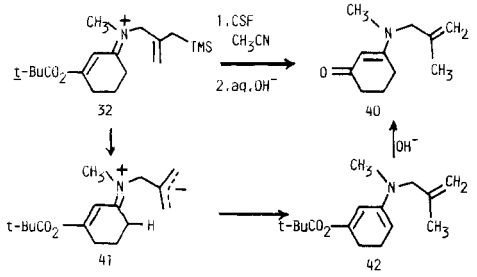
(18) (a) UV spectroscopic monitoring of the hydrolysis of **20** shows that the open-chain enone **25** exists in HCl solution and that it rapidly cyclizes to the spirocyclic ketone **20** upon basification in a fashion analogous to that of related systems.[18b] (b) Corey, E. J.; Balanson, R. D. *Heterocycles* **1976**, *5*, 445. Venit, J. J.; Magnus, P. *Tetrahedron Lett.* **1980**, *21*, 4815.

(19) Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *15*, 9; *J. Am. Chem. Soc.* **1980**, *102*, 4429. Bock, H.; Kaim, W.; Rohwer, H. F. *J. Organomet. Chem.* **1977**, 135. Bock, H.; Kaim, W. *Tetrahedron Lett.* **1977**, 2343.

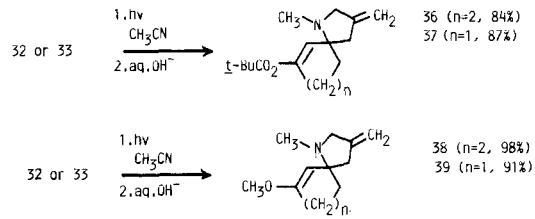
(20) Chen, S. F., Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1983**, *105*, 6160.

(21) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6492.

Scheme V

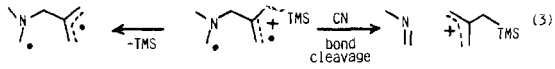


after an aqueous base workup and chromatography on Florisil or silica gel, the spirocyclic amino enol esters and ethers **42–45** in yields of 84–95%. It should be noted that the yields of these processes are essentially quantitative as judged by ^{1}H NMR spectroscopic analyses of the crude photolysates obtained after base treatment and solvent removal. Thus, the slightly lower isolated yields are due to losses incurred during chromatographic purifications. Finally, the quantum efficiencies measured for photospirocyclizations of the *O*-pivaloyl six- and five-membered-ring iminium salts **32** and **33** in CH_3CN at low conversions (ca 3–12%) are 0.210 and 0.034, respectively.



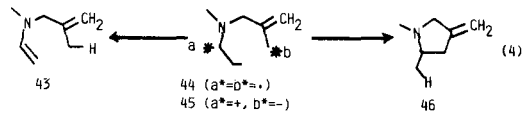
Structural assignments to the photoproducts were aided by comparisons of important spectroscopic parameters with those obtained earlier for the prenyliminium salt derived photospirocyclization products which share common acyloxy and alkoxycycloalkene ring systems.

Interpretive Discussion. The results of the photospirocyclization reactions outlined above demonstrate the importance of trialkylsilylmethyl substitution in enhancing the chemical efficiencies of allyliminium salt photocyclization reactions. One of the major reasons for this appears to be that desilylation of the cation diradical intermediates effectively competes with alternative reaction pathways including C–N bond cleavage (eq 3). The latter



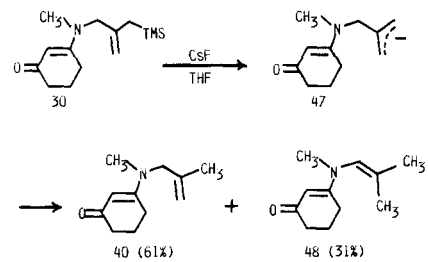
process is an important contributor to the low efficiencies for reactions of other allyliminium salt systems. In addition, cyclization of the 2-aza-1,5-diradicals produced by desilylation appears to be a praticularly efficient reaction, occurring to the complete exclusion of other processes such as disproportionation by hydrogen atom transfer. This is an important feature of these allyliminium cation photocyclizations activated by sequential electron transfer and desilylation. In contrast, attempts at inducing spirocyclization of the six-membered-ring *O*-pivaloyl perchlorate **32** through fluoride ion initiated desilylation via the intermediate zwitterion are unsuccessful. Specifically, the *N*-methallyl β-enaminone **40** is produced by treatment of **32** with cesium fluoride in anhydrous acetonitrile followed by an aqueous base workup (Scheme V). Thus, it appears that the zwitterion **41** resists a disfavored, 5-endo-trig cyclization[22] and rather undergoes inter- or, more likely, intramolecular proton transfer. The latter process would generate the cyclohexadiene **42** which would be transformed to **40** by aqueous base hydrolysis during workup.[23]

These results suggest the tentative conclusion that 2-aza-1,5-diradicals **44** favor cyclization while their zwitterionic analogues **45** participate in disproportionation via proton shifts (eq 4). While a more thorough investigation



of these differences is needed before more firm conclusions can be drawn, it is reasonable to assume at this point that the comparative cyclization reactivity of the diradical and zwitterionic intermediates would be reflective of the different stereoelectronic requirements for cyclization of these systems, perhaps resulting from the lower C–N π-bond order in the radical vs. the cationic systems.

Finally, it is worthwhile to mention the results from attempts at fluoride ion induced cyclization of the *N*-trimethylsilylmethyl β-enaminone **30** since they appear relevant to the question of uniqueness of the photochemically based spirocyclization methodology. The desilylated β-enaminones **40** and **48**, which come from inter- or intramolecular proton transfers to the aminoallyl anion intermediate **47** are generated in excellent yields from reaction of **30** with cesium fluoride in anhydrous THF.



In conclusion, the ease of formation and exceptionally high chemical efficiencies for photocyclization of *N*-[[(trimethylsilyl)methyl]allyl]-substituted iminium salts indicate that this methodology for N heterocycle ring formation will have general synthetic utility. Indeed, our continuing studies in this area, described in the following paper[7b] and elsewhere,[20] appear to confirm this conclusion.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded by using Varian EM-360, EM-390, XL-100 FT, and XL-200 spectrometers. ^{13}C NMR spectra were recorded by using a Varian XL-100, a Bruker WP-200, or a JEOL PS-100 spectrometer at an operating frequency of 25.0345 MHz. All ^{13}C NMR spectra were obtained in deuteriochloroform as the solvent, and the chemical shifts are recorded in parts per million relative to tetramethylsilane as an internal standard. High-resolution mass spectra were obtained at the Pennsylvania State University Mass Spectrometry Center. Low-resolution mass spectra were recorded by using a Du Pont 492 spectrometer. UV absorption spectra were measured on G. C. A. McPherson EV-700-56 and Beckman ACTA III spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer. Elemental analyses were performed by Galbraith Inc., Knoxville, TN, or by Dr. F. Kassler at the University of Maryland. Melting points were taken on a Griffen Mel-Temp or Thomas-Hoover Capillary melting point apparatus and are reported uncorrected. Preparative chromatographic separations were accomplished by using the following absorbents:

(22) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734, 736, 738.

(23) An analogous reaction pathway is followed by similarly structured cyclic dienes.[20]

thin-layer chromatography, Merck-EM Type 60 GF-254 silica gel; flash column chromatography, Merck-EM Type 60 (230–400 mesh) silica gel. Column chromatography was performed with either Fisher silica gel (100–200 mesh), Florisil (100–200 mesh), or MCB alumina (Type F-20). Gas chromatographic analyses and separations were performed on a Varian Series 2700 GLC instrument with thermal-conductivity detection and a Varian 940 GLC instrument with a flame-ionization detector. Unless otherwise mentioned, drying during workup of crude reaction mixtures involved washing with brine and drying with Na_2SO_4. Molecular distillations were performed by using a Kugelrohr apparatus at the recorded temperatures and pressures.

Preparative irradiations were performed by using an apparatus consisting of a 450-W Hanovia medium-pressure lamp surrounded by the indicated glass filter all within a water-cooled quartz immersion well placed in the solution being irradiated under a nitrogen atmosphere. Progress of the photoreactions were followed by UV monitoring of aliquots.

3-(Methylamino)-2-cyclopenten-1-one (13). To a cooled solution (0 °C) of 1.47 g (15 mmol) of cyclopentane-1,3-dione in 50 mL of CH_2Cl_2 was slowly added 3.84 g (2.6 mL, 30 mmol) of oxalyl chloride in 20 mL of CH_2Cl_2. The reaction mixture was allowed to slowly warm to 25 °C and slowly poured into cold, saturated aqueous $NaHCO_3$. After gas evolution ceased, the mixture was extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo, giving 3-chloro-2-cyclopenten-1-one as a yellow oil which was immediately converted to the desired enaminone. To a solution of the chloroenone in CH_2Cl_2 at 0 °C was added 3 mL of a 40% aqueous solution of methylamine (1.2 g, 39 mmol). The mixture was stirred for 1 h and then extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo to yield the desired *N*-methyl enaminone **13** as a brown solid. Recrystallization from toluene gave 1.16 g (70%) of **13** as a tan crystalline solid: mp 125–127 °C; UV max (CH_3OH) 278 nm (ϵ 36 900); ^1H NMR ($CDCl_3$) δ 2.5 (m, 4 H, methylene H's), 2.9 (d, 3 H, NCH_3), 5.05 (s, 1 H, vinyl), 6.15 (br s, 1 H, NH); ^{13}C NMR 27.50 (t, C-4), 31.1 (q, NCH_3), 33.6 (t, C-5), 97.3 (d, C-2), 178.6 (s, C-3), 204.10 (s, C-1); IR ($CHCl_3$) 3450, 3275, 3075, 2950, 1700, 1650, 1560, 1425, 1380, 1150 cm^{-1}. Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.99; H, 8.35; N, 12.32.

3-[Methyl(3-methyl-2-butenyl)amino]-2-cyclohexen-1-one (14). To a cooled solution (−78 °C) of 10.0 g (80 mmol) 3-(methylamino)-2-cyclohexen-1-one (**12**)[16] in 420 mL of anhydrous THF was added 60 mL of a 1.56 M solution (94 mmol) of *n*-butyllithium in hexane over a 30-min period. The resulting suspension was stirred at −78 °C for 1 h, allowed to warm to 25 °C, and stirred for an additional 1 h. The reaction mixture was cooled to −78 °C, and 14.0 g (94 mmol) 3-methyl-2-butenyl bromide in 20 mL of THF was added. The reaction mixture was again warmed to 25 °C, stirred for 5 h, poured into 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo, giving after flash column chromatography (5% MeOH–CH_2Cl_2) 13.5 g (87%) of the desired enaminone **14** as pale yellow crystals: mp 45.0–45.6 °C; UV max (MeOH) 300 nm (ϵ 31 200); ^1H NMR ($CDCl_3$) δ 1.69, 1.77 (s, 6 H, *gem*-dimethyl), 2.00 (q, 2 H), 2.27 (t, 2 H), 2.45 (t, 2 H), 2.92 (s, 3 H, NCH_3), 3.83 (d, 2 H, N–CH_2), 5.08 (br m, 1 H, $(CH_3)_2CCH$), 5.13 (s, 1 H, COCHCN); ^{13}C NMR 22.2 (t, C-5), 25.7 (q, C-3′ CH_3's), 26.8 (t, C-4), 35.5 (t, C-6), 37.5 (q, NCH_3), 49.8 (t, N–CH_2), 98.4 (d, C-2), 118.7 (d, C-2′), 136.2 (s, C-3′), 165.5 (s, C-3), 196.5 (s, C=O); IR (neat) 3000, 1600, 1560, 1250, 1175, 800 cm^{-1}; high-resolution mass spectrum, *m/e* 193.1465 ($C_{12}H_{19}NO^+$ requires 193.1466).

3-[Methyl(3-methyl-2-butenyl)amino]-2-cyclopenten-1-one (15). To a cooled solution (−78 °C) of 1.64 g (14.8 mmol) of **13** in 100 mL of anhydrous THF was slowly added 11.1 mL of a 1.56 M solution 17.3 mmol) of *n*-butyllithium in hexane. The resulting solution was allowed to warm to 25 °C and stirred for an additional 2 h. The reaction mixture was cooled to 25 °C, and 2.57 g (17.3 mmol) 3-methyl-2-butenyl bromide in 10 mL THF was added. The reaction mixture was refluxed for 20 min, cooled to 25 °C, and concentrated in vacuo. The residue was diluted with H_2O and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo, giving after flash column chromatography (silica gel, 3% MeOH–CH_2Cl_2) 2.02 g (77%) of the desired enaminone **15** as a crystalline substance: mp 62.1–62.8 °C, UV max (MeOH) 278 nm (ϵ 36 900); ^1H NMR ($CDCl_3$) δ 1.74, 1.79 (2 s, 6 H, *gem*-dimethyl), 2.30–2.46 (m, 2 H), 2.61–2.78 (m, 2 H), 2.93 (br s, 3 H, NCH_3), 3.82 (br d, 2 H, N–CH_2), 4.98 (s, 1 H, COCH=C), 5.10 (m, 1 H, $(CH_3)_2C$=C*H*); ^{13}C NMR 17.3 (q, C-3′ CH_3), 25.1 (q, C-3′ CH_3), 37.2 (q, NCH_3), 33.6 (t, C-5), 27.2 (t, C-4), 50.4 (t, C-1′), 99.3 (d, C-2), 117.5 (d, C-2′), 136.1 (s, C-3′), 176.3 (s, C-3), 202.3 (s, C-1); IR ($CHCl_3$) 3020, 2980, 2930, 1650, 1220, 760, 665 cm^{-1}; high-resolution mass spectrum, *m/e* 179.1317 ($C_{11}H_{17}NO^+$ requires 179.1310). Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.78; H, 9.76; N, 7.88.

***N*-[3-[(*tert*-Butylacyl)oxy]cyclohex-2-enylidene]-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (4).** To a cooled solution (0 °C) of 3.9 g (20.2 mmol) of **14** in 20 mL of CH_3CN was added slowly 2.74 mL (2.68 g, 22.2 mmol) of pivaloyl chloride. The resulting solution was stirred at 0 °C for 20 min. To this solution was added 4.19 g (20.2 mmol) of silver perchlorate in 20 mL of CH_3CN slowly over a 20-min period. The resulting heterogeneous mixture was stirred at 0 °C for an additional 20 min after which silver chloride was removed by rapid filtration. TThe filtrate was concentrated in vacuo, giving an oil which was washed with anhydrous ether to remove traces of pivaloyl chloride. Volatile components were removed under high vacuum, resulting in 7.33 g (96%) of the desired O-pivaloylated iminium salt **4** as a ca. 1:1 mixture of *E,Z* isomers: UV max (MeOH) 287 nm (ϵ 19 000); ^1H NMR ($CDCl_3$) δ 1.30 (s, 9 H, $(CH_3)_3CCO$), 1.77 (br s, 6 H, *gem*-dimethyl), 1.90–2.30 (m, 2 H), 2.50–2.70 (m, 2 H), 2.80–3.10 (m, 2 H), 3.44, 3.52 (2 s, 3 H, NCH_3), 4.22–4.55 (m, 2 H, N–CH_2), 5.03–5.28 (m, 1 H, $(CH_3)_2C$=C*H*), 6.7 (br s, 1 H, OC=OH); IR ($CHCl_3$) 3020, 2980, 1760, 1600, 1220, 1090, 750, 675 cm^{-1}; high-resolution mass spectrum, *m/e* 278.2129 ($C_{17}H_{28}NO_2^+$ requires 278.2120).

***N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclopent-2-enylidene]-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (7).** To a cooled solution (−78 °C) of 0.3 g (1.7 mmol) of **15** in 10 mL CH_3CN was added 0.23 mL (225 mg, 1.84 mmol) of pivaloyl chloride in 50 mL of CH_3CN. After 10 min, 0.35 g (1.7 mmol) silver perchlorate in 3.0 mL of CH_3CN was added over a 10-min period. The reaction mixture was stirred at 0 °C for 30 min then filtered. The filtrate was concentrated in vacuo to give an oil which was washed with three 10-mL portions of anhydrous ether. Evaporation of the volatile components yielded 0.59 g (97%) of the desired O-pivaloylated iminium salt **7** as a 1:1 mixture of *E,Z* isomers: UV max (MeOH) 275 nm (ϵ 2500); ^1H NMR ($CDCl_3$) δ 1.33 (s, 9 H, $(CH_3)_3CO$), 1.80 (br s, 6 H, $(CH_3)_2C$=C), 3.13 (m, 4 H, methylene H's), 3.37, 3.44 (s, 3 H, NCH_3), 4.30 (m, 2 H, N–CH_2), 5.22 (m, 1 H, $(CH_3)_2C$=C*H*), 6.70, 6.77, (s, 1 H, vinyl); IR ($CHCl_3$) 3020, 2980, 2940, 1785, 1650, 1570, 1220, 1080, 760 cm^{-1}; high-resolution mass spectrum, *m/e* 263.1861 ($C_{16}H_{25}NO_2^+$ requires 263.1951).

***N*-(3-Methoxycyclohex-2-enylidene)-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (5).** This material was prepared by starting with the known 3-(methylamino)cyclohex-2-enone (**12**)[16] via the intermediate *N*-(3-methoxycyclohex-2-enylidene)methylammonium iodide (**16**), and *N*-(3-methoxycyclohex-2-enylidene)methanimine (**18**) by the following procedure. A mixture of 3.40 g (27 mmol) of 3-(methylamino)cyclohex-2-enone and 17.5 mL (0.28 mol) of iodomethane in 15 mL of THF was heated at 60 °C for 15 h. The crystals formed on cooling the solution were removed by filtration, washed with ether, and dried under vacuum to yield 6.44 g (88%) of the desired immonium salt **16**: mp 145–146 °C; UV max (CH_3OH) 274 nm (ϵ 22 400); ^1H NMR ($CDCl_3$) δ 1.80–3.40 (m, 6 H), 3.25 (d, 3 H, NCH_3), 4.10 (s, 3 H, OCH_3), 5.78 (s, 1 H, vinyl H). Due to its hygroscopic nature, this material was used without further purification.

A solution of 2.50 g (9.0 mmol) of **16** in 25 mL of $CHCl_3$ was washed with 25 mL of 10% aqueous NaOH. The $CHCl_3$ layer was dried and concentrated in vacuo, giving the labile imine **18** as an oil: UV max (CH_3OH) 277 nm; ^1H NMR ($CDCl_3$) δ 1.70–2.60 (m, 6 H), 3.10 (d, 3 H, NCH_3), 3.60 (d, 3 H, OCH_3), 5.50 (d, 1 H, vinyl H).

A solution of the imine **18** (1.13 g, 8.1 mmol) and 1.65 mL (14.2 mmol) of 1-bromo-3-methyl-2-butene was stirred at 25 °C for 4 h. Concentration in vacuo gave an oil which was subjected to ion exchange on Dowex X-8 (ClO_4^- form), eluting with methanol. Concentration of the eluant gave 2.70 g (98%) of the desired imminium perchlorate **5** as a 1:1 mixture of *E,Z* isomers: UV max (CH_3OH) 285 nm (ϵ 20 800); ^1H NMR ($CDCl_3$) δ 1.85 (q, 6 H,

gem-dimethyl), 2.10 (m, 2 H, H-5), 2.55 (t, 2 H), 2.88 (t, 2 H) 3.45 (s, 3 H, NCH_3), 3.97, 4.05 (2 s, 3 H, OCH_3), 4.35 (br d, 2 H, CH_2–N), 5.15 (br s, 1 H, $(CH_3)_2C{=}CH$), 5.85 (d, 1 H, $CH_3OC{=}CH$); IR ($CHCl_3$) 3020, 1580, 1220, 1090, 760 cm^{-1}; high-resolution mass spectrum, *m/e* 278.2129 ($C_{17}H_{28}NO_2^+$ requires 279.2120).

***N*-(3-Methoxycyclopent-2-enylidene)-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (8).** This material was prepared by starting with 3-(methylamino)cyclopent-2-en-1-one (**13**) via the intermediate *N*-(3-methoxycyclopent-2-enylidene)-methylimminium iodide (**17**) and *N*-(3-methoxycyclopent-2-enylidene)methanimine (**19**) by the following procedure. A solution of the enaminone **13** (500 mg, 4.5 mmol) and CH_3I (5 mL, 11.35 g, 80.0 mmol) in 5 mL of THF was stirred at 60 °C for 12 h. The crystalline salt, formed on cooling the reaction mixture to 0 °C, was separated by filtration, washed with THF, and recrystallized (CH_3OH–EtOAc), giving 406 mg (30%) of the desired hydroiodide salt **17**: mp 123–124 °C; ^1H NMR ($CDCl_3$) δ 3.00 (m, 2 H, ring CH_2), 3.25 (m, 2 H, ring CH_2) 3.26 (s, 3 H, NCH_3), 4.21 (s, 3 H, OCH_3), 6.25 (s, 1 H, vinyl). This material was used immediately in the following reaction sequence.

A solution of 400 mg (1.58 mmol) of **17** in 5 mL of $CHCl_3$ was washed with 2 N aqueous NaOH, dried, and concentrated in vacuo, yielding the desired imine **19** as an oil: ^1H NMR ($CDCl_3$) δ 2.50 (m, 4 H, ring CH_2), 3.08 (s, 3 H, NCH_3), 3.72 and 3.77 (s, 3 H, OCH_3), 5.35 and 5.50 (s, 1 H, vinyl). A solution of the labile imine **19** and 256 mg (1.72 mmol) of 1-bromo-3-methyl-2-butene in 10 mL of CH_2Cl_2 was stirred at 25 °C for 5 h. Concentration in vacuo gave an oil which was subjected to anion exchange with Dowex X-2 (ClO_4^- form), eluting with methanol. Concentration of the eluaent gave 243 mg (52%) of the desired iminium salt **8** as a ca. 1:1 mixture of *E,Z* isomers: UV max (CH_3OH) 270 nm (ε 26 500); ^1H NMR ($CDCl_3$) δ 1.80 (m, 6 H, *gem*-dimethyl), 2.80–3.17 (m, 4 H, ring methylene H's), 3.30, 3.33 (2 s, 3 H, NCH_3), 4.10 (s, 3 H, OCH_3), 4.10–4.25 (m, 2 H, N–CH_2), 5.13 (m, 1 H, $(CH_3)_2C{=}CH$), 5.97, 6.04 (2 s, 1 H, $CH_3OC{=}CH$); IR ($CHCl_3$) 3020, 1640, 1560, 1220, 1080, 760, 665 cm^{-1}; high-resolution mass spectrum, *m/e* 194.1538 ($C_{12}H_{20}NO^+$ requires 194.1545).

Irradiation of *N*-(3-[(*tert*-Butylcarbonyl)oxy]cyclohex-2-enylidene)-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (4). Preparation of 2-[(*tert*-Butylcarbonyl)-oxy]-7,10,10-trimethyl-9-methoxy-7-azaspiro[5.4]dec-1-ene (22). A solution of 500 mg (1.32 mmol) of **4** in 400 mL of absolute methanol was irradiated (Vycor) for 6.0 h. The photolysate was mixed with 1.0 g of $NaCHO_3$ and concentrated in vacuo. The crude residue was diluted with 5% aqueous $NaHCO_3$ and extracted with ether. The ethereal extracts were washed with H_2O, dried, and concentrated in vacuo to give an oil which was subjected to separation by preparative thin-layer chromatography (silica gel, 50% petroleum ether–ether) to afford 39 mg of **22a** (R_f 0.51) and 21 mg of **22b** (R_f 0.39) in a total yield of 25.2%. **22a**: ^1H NMR ($CDCl_3$) δ 1.01 (s, 6 H, $(CH_3)_2C$), 1.24 (s, 3 H, $(CH_3)_3CCO$), 1.71 (m, 4 H, H-4 and H-5 methylenes), 2.03 (m, 2 H, H-3 methylene), 2.26 (s, 3 H, NCH_3), 2.92 (m, 2 H, N–CH_2), 3.32 (s, 3 H, CH_3OC), 3.44 (m, 1 H, H-9 methine), 5.01 (br s, H-1 vinyl); ^{13}C NMR 18.0 (q, C-10 CH_3), 20.4 (t, C-4), 24.3 (q, C-10 CH_3), 26.2 (t, C-5), 26.7 (t, C-3), 27.1 (q, $(CH_3)_3$), 29.7 (s, $(CH_3)_3C$), 36.5 (q, NCH_3), 48.2 (s, C-10), 57.8 (q, OCH_3), 58.1 (t, C-8), 67.6 (s, C-6), 86.4 (d, C-9), 115.1 (d, C-1), 151.5 (s, C-2), 176.8 (s, C=O); IR (neat) 2950, 1747, 1680, 1455, 1360, 1280, 1135 cm^{-1}; high-resolution mass spectrum *m/e* 309.2318 ($C_{18}H_{30}NO_3^+$ requires 309.2364). **22b**: ^1H NMR ($CDCl_3$) δ 0.95 (s, 6 H, $(CH_3)_2C$), 1.24 (s, 9 H, $(CH_3)_3C$), 1.41–2.13 (m, 6 H, H-3 and H-5 methylenes), 2.27 (s, 3 H, NCh_3), 2.50 (m, 2 H, N–CH_2), 3.23 (s, 3 H, OCH_3), 3.35 (m, 1 H, H-9), 5.27 (br s, 1 H, vinyl H); ^{13}C NMR 19.2 (q, C-10 CH_3), 20.5 (t, C-4), 25.1 (q, C-10 CH_3), 26.6 (t, C-5), 27.5 (t, C-3), 27.1 (q, $(CH_3)_3C$), 30.2 (s, $(CH_3)_3C$), 36.9 (q, NCH_3), 48.8 (s, C-10), 58.0 (q, OCH_3), 59.0 (t, C-8), 66.7 (s, C-6), 87.8 (d, C-9), 115.2 (d, C-1), 150.8 (s, C-2), 177.0 (s, C=O); IR (neat) 2950, 1747, 1680, 1455, 1360, 1280, 1135 cm^{-1}; high-resolution mass spectrum, *m/e* 309.2295 ($C_{18}H_{30}NO_3^+$ requires 309.2267).

Irradiation of *N*-(3-Methoxycyclohex-2-enylidene)-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (5). Preparation of 7,10,10-Trimethyl-2,9-dimethoxy-7-azaspiro[5.4]dec-1-ene (20). A solution of 200 mg (0.65 mmol) of **5** in 200 mL of methanol (3.25 mM) was irradiated (Vycor) for 8 h. The photolysate was poured into 200 mL of 5% aqueous $NaHCO_3$. The mixture was extracted with ether. The ethereal extracts were washed with water, dried, and concentrated in vacuo to yield 85 mg of a viscous oil. Column chromatography on alumina (50% etther/hexane, 200 mL/h) yielded 49 mg (31%) of an oil consisting of a 1:1 mixture of diastereomeric azaspirodecenes **20**: ^1H NMR ($CDCl_3$) δ 0.91, 0.95, 1.00 (3 s, 1:1:2, 6 H, *gem*-dimethyl), 1.69 (m, 4 H), 220 (m, 2 H), 2.19, 2.23 (2 s, 1:1, 3 H NCH_3), 2.47–3.21 (m, 3 H), 3.30, 3.32 (2 s, 1:1, 3 H, $CHOCH_3$), 3.56 (s, 3 H, $CH{=}COCH_3$), 4.26, 4.61 (2 s, 1:1, 1 H, $CH{=}COCH_3$); ^{13}C NMR, 18.3, 19.3, 25.0 (q, C-10 CH_3's), 20.6 (t, C-4), 26.4 (t, C-5), 27.6 (t, C-3), 36.3 (q, NCH_3), 48.3, 48.5 (s, C-10), 53.9, 56.6 (q, OCH_3's), 58.0, 58.8 (t, C-8), 67.0, 67.5 (s, C-6), 87.0, 87.8 (d, C-9), 94.4 (d, C-1), 158.2, 159.0 (s, C-2); IR ($CHCl_3$) 3020, 2940, 1660, 1220, 750, 670 cm^{-1}; high-resolution mass spectrum, *m/e* 239.1877 ($C_{14}H_{25}NO_2^+$ requires 239.1885).

Irradiation of *N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclopent-2-enylidene]-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (7). Preparation of 2-[(*tert*-Butylcarbonyl)-oxy]-6,9,9-trimethyl-8-methoxy-6-azaspiro[4.4]non-1-ene (23). A solution of 592 mg (1.63 mmol) of **7** in 400 mL of absolute methanol was irradiated (Vycor) for 3.0 h. The photolysate was mixed with 1.0 g of $NaHCO_3$ concentrated in vacuo. The crude residue was diluted with 5% aqueous $NaHCO_3$ and extracted wth Et_2O and CH_2Cl_2. The combined organic extracts were washed with H_2O, dried, and concentrated in vacuo to give an oil which was subjected to preparative thin-layer chromatography (silica gel, 50% petroleum ether-ether) to afford 28 mg **23a** (R_f 0.49) and 21 mg **23b** (R_f 0.33) in a total yield of 19%. **23a**: ^1H NMR ($CDCl_3$) δ 0.94 (s, 6 H, $(CH_3)_2C$), 1.23 (s, 9 H, $(CH_3)_3C$), 1.46–2.45 (m, 4 H, H-3 and H-4 methylenes), 2.21 (s, 3 H, NCH_3), 2.79 (m, 2 H, N–CH_2), 3.31 (s, 3 H, OCH_3), 3.53 (m, 1 H, H-9 methine), 5.17 (br s, 1 H, vinyl H); ^{13}C NMR 16.4 (q, C-9 CH_3), 22.5 (q, C-9 CH_3), 23.8 (t, C-3), 24.7 (s, $(CH_3)_3C$), 25.8 (q, $(CH_3)_3C$), 29.1 (t, C-4), 34.3 (q, NCH_3), 45.6 (s, C-9), 56.4 (q, OCH_3), 56.9 (t, C-7), 78.8 (s, C-5), 85.5 (d, C-8), 112.1 (d, C-1), 150.6 (s, C-2), 174.6 (s, C=O); IR (neat) 2985, 1750, 1665, 1470, 1355, 1280, 1155, 1100, 1040 cm^{-1}; high-resolution mass spectrum, *m/e* 295.2162 ($C_{17}H_{29}NO_3^+$ requires 295.2147). **23b**: ^1H NMR ($CDCl_3$) δ 0.92 (s, 6 H, $(CH_3)_2C$), 1.29 (s, 9 H, $(CH_3)_3C$), 1.57–2.10 (m, 4 H, H-3 and H-4 methylenes), 2.24 (s, 3 H, NCH_3), 2.72 (m, 2 H, N–CH_2), 3.24 (s, 3 H, OCH_3), 3.55 (m, 1 H, H-9 methine), 5.36 (br s, 1 H, H-1); ^{13}C NMR 18.6 (q, C-9 CH_3), 24.3 (q, C-9 CH_3), 25.1 (s, $(CH_3)_3C$), 26.6 (t, C-3), 27.1 (q, $(CH_3)_3C$), 30.1 (t, C-4), 35.6 (q, NMe), 47.1 (s, C-9), 57.6 (t, C-7), 58.7 (q, OCH_3), 79.2 (s, C-5), 87.4 (d, C-8), 114.5 (d, C-1), 151.3 (s, C-2), 175.4 (s, C=O); IR (neat) 2985, 1750, 1665, 1470, 1355, 1280, 1155, 1100, 1040 cm^{-1}; high-resolution mass spectrum, *m/e* 295.2140 ($C_{17}H_{29}NO_3^+$ requires 295.2115).

Irradiation of *N*-(3-Methoxycyclopent-2-enylidene)-*N*-(3-methyl-2-butenyl)methylammonium Perchlorate (8). Preparation of 6,9,9-Trimethyl-2,8-dimethoxy-6-azaspiro-[4.4]non-1-ene (21). A solution of 110 mg (0.37 mmol) of the iminium salt **8** in 250 mL of CH_3OH was irradiated (Vycor) for 5 h. The photolysate was diluted with 5% aqueous $NaHCO_3$ and extracted with Et_2O. The ethereal extracts were dried, concentrated in vacuo to ca. 50 mL, diluted with water, and extracted with CH_2Cl_2. The methylene chloride extracts were dried and concentrated in vacuo, giving 42 mg of an oil which was subjected to chromatographic purification on alumina (50% Et_2O–hexane) to give 25 mg (30%) of a 1:1 mixture of the diastereomeric azaspirononenes **21**: ^1H NMR ($CDCl_3$) δ 0.86, 0.89, 0.95 (3 s, 6 H, $(CH_3)_2C{=}CH$), 1.24 (m, 2 H), 1.65 (m, 2 H), 2.12, 2.15 (2 s, 3 H, NCH_3), 3.10 (m, 1 H, methine), 3.28, 3.30 (2 s, 3 H, $CHOCH_3$), 3.63 (s, 3 H, $CH_3OC{=}C$), 4.19, 4.45 (s, 1 H, vinyl H); ^{13}C NMR (selected resonances) 17.7, 18.7 (C-10 CH_3's), 29.5, 29.6 (C-3), 30.5 (C-4), 35.3 (NCH_3), 46.7, 48.3 (C-9), 56.8, 57.7 (OCH_3), 57.7, 58.4 (C-7), 66.1, 66.2 (C-5), 86.9, 87.4 (C-8), 94.3, 94.0 (C-1), 163.0, 165.0 (C-2); high-resolution mass spectrum, *m/e* 225.1742 ($C_{13}H_{23}NO_2$ requires 225.1728).

7,10,10-Trimethyl-9-methoxy-7-azaspiro[5.2]decan-2-one (24) by Irradiation on in Situ Prepared *N*-(3-Hydroxycyclohex-2-enylidene)-*N*-(3-methylbut-2-enyl)methylammonium Perchlorate (6). A solution of 200 mg (1.04 mmol) of the enaminone **14** in 200 mL of 0.1 M methanolic perchloric acid was irradiated (Vycor) for 31 h. The photolysate was concentrated and diluted with ether and saturated aqueous $NaHCO_3$. The organic layer was separated, dried, and concentrated in vacuo

to yield 182 mg of a brown oil. Gas chromatographic and NMR analysis indicated the presence of the spiro ketone **24** in addition to other unidentified products. The yield of spiro ketone **24** was found to be 6% by GC analysis (2% OV-101 on Chromosorb, 150 °C, xanthone as internal standard).

7,10,10-Trimethyl-9-methoxy-7-azaspiro[5.4]decan-2-one (24) from Hydrolysis of Enol Ether 20. A solution of 50 mg (0.21 mmol) of **20** in 20 mL of 10% aqueous HCl was stirred at 25 °C for 11 h, neutralized with 10% aqueous NaOH, and extracted with chloroform. The chloroform extracts were dried and concentrated in vacuo to yield 35 mg (74%) of a 1:1 diastereromeric mixture of azaspiro ketones **24**: ^{1}H NMR ($CDCl_3$) characteristic resonances δ 0.89, 0.91, 0.97, (1:1.2, 3 s, $(CH_3)_2C$), 2.29, 2.30, (2 s, NCH_3), 3.25, 3.30, (2 s, OCH_3); ^{13}C NMR 17.9, 19.5, 24.6 (q, C-10 CH_3's), 20.2, 20.3 (t, C-4), 29.3, 30.0 (t, C-5), 40.1, 40.2 (t, C-3), 35.6, 35.8 (q, NCH_3), 48.2, 48.7 (s, C-10), 57.3, 57.8 (q, OCH_3), 58.2, 58.4 (t, C-8), 68.8, 69.2 (s, C-6), 86.4, 86.9 (d, C-9), 43.9 (t, C-1), 212.9 (s, C-2); IR ($CHCl_3$) 2950, 1700, 1650, 1460, 1205, 1100 cm^{-1}; high-resolution mass spectrum, *m/e* 225.1733 ($C_{13}H_{23}NO_2^+$ requires 225.1706).

3-[Methyl[2-[(trimethylsilyl)methyl]-2-propenyl]amino]cyclohex-2-enone (30). A solution of 1.35 g (28 mmol) of NaH and 1.15 g (9.1 mmol) of 3-(methylamino)cyclohex-2-enone (**12**)[16] in 70 mL of THF was stirred at reflux for 1 h and cooled to 0 °C. To this solution was added 2.02 g (9.1 mmol) of 2-[(trimethylsilyl)methyl]-2-propenyl methanesulfonate.[21] The resulting mixture was stirred at 25 °C for 24 h, poured into ice–water and extracted with $CHCl_3$. The chloroform extracts were dried and concentrated in vacuo giving an oil which was purified by flash chromatography on silica gel (2% CH_3OH–$CHCl_3$) to yield 2.08 g (91%) of the desired trimethylsilyl enaminone **30** as an oil: UV max (CH_3CN) 290 nm (ϵ 30 400); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.22 (s, 2 H, CH_2–Si), 1.45–2.40 (m, 6 H, methylene H's), 2.70 (s, 3 H, NCH_3), 3.60 (s, 2 H, N–CH_2), 4.30 (s, 1 H, vinyl), 4.50 (s, 1 H, vinyl), 4.90 (s, 1 H, vinyl); ^{13}C NMR ($CDCl_3$) –1.27 (q, $Si(CH_3)_3$), 22.3 (t, C-5), 23.9 (t, $SiCH_2$), 26.4 (t, C-4), 35.6 (t, C-6), 38.6 (q, NCH_3), 57.9 (t, N–CH_2), 98.6 (d, C-2), 107.3 (t, $=CH_2$), 141.2 (s, C-2′), 165.4 (s, C-3), 196.6 (s, C_1, C=O); IR ($CHCl_3$) 2950, 1600, 1550, 1250, 1180, 840 cm^{-1}; high-resolution mass spectrum, *m/e* 251.1699 ($C_{14}H_{25}NOSi^+$ requires 251.1702).

3-[Methyl[2-[(trimethylsilyl)methyl]-2-propenyl]amino]cyclopent-2-enone (31). A solution of 0.200 g (4.17 mmol) of NaH and 0.185 g (1.66 mmol) of the 2-(methylamino)cyclopent-2-enone (**13**) in 70 mL of THF was stirred at reflux for 1 h, cooled to 25 °C, and quenched with 0.369 g (1.66 mmol) of 2-[(trimethylsilyl)methyl]prop-2-enyl methanesulfonate.[21] The resulting mixture was stirred at 25 °C for 24 h and poured into ice–H_2O. The $CHCl_3$ extracts of this solution were dried and concentrated in vacuo, yielding an oil which was subjected to flash chromatography on silica gel (2% CH_3OH–$CHCl_3$) which provided 0.359 g (91%) of the pure enaminone **31** as an oil: UV max (CH_3CN) 273 nm (ϵ 31 800); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $Si(CH_3)_3$, 1.35 (s, 2 H, CH_2–Si), 1.95–2.75 (m, 4 H, CH_2's), 2.90 (s, 3 H, NCH_3), 3.65 (s, 2 H, N–CH_2), 4.50, 4.65 (s, $=CH_2$), 4.95 (s, 1 H, H-2); ^{13}C NMR –1.4 (q, $Si(CH_3)_3$), 23.7 (t, Si–CH_2), 26.8 (t, C-4), 34.2 (t, C-5), 38.9 (q, NCH_3), 57.5 (t, N–CH_2), 100.1 (d, C-2), 107.6 (t, C-3′), 141.8 (s, C-2′), 178.9 (s, C-3), 204.6 (s, C-1); IR ($CHCl_3$) 3080, 2950, 1640, 1550, 1400, 1250, 1180, 870, 850, 840 cm^{-1}; high-resolution mass spectrum, *m/e* 237.1546 ($C_{13}H_{23}NOSi^+$ requires 237.1532).

***N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclohex-2-enylidene]-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (32).** To a solution of 3-[*N*-methyl[[2-(trimethylsilyl)methyl]prop-2-enyl]amino]cyclohex-2-enone (**30**; 122 mg, 0.49 mmol) and 100 mg (0.49 mmol) of $AgClO_4$ in 20 mL of CH_3CN at 0 °C was slowly added 1.3 mL (0.54 mmol) of a 0.5 mL/10 mL solution of pivaloyl chloride in CH_3CN. The reaction mixture was stirred at 0 °C for 1 h and filtered to remove the formed AgCl. Concentration of the filtrate in vacuo gave an oil which was washed with Et_2O and dried in vacuo producing 0.21 g (99%) of the desired *O-tert*-butylcarbonyloxy iminium perchlorate **32** as a 1:1 mixture of *E,Z* isomers: UV max (CH_3CN) 300 nm (ϵ 23 200); ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H, $Si(CH_3)_3$), 1.26, 1.30 (s, 9 H, $(CH_3)_3C$), 1.53 (s, 2 H, CH_2–Si), 2.19 (t, J = 5.9 Hz, 2 H, H-5), 2.50–3.20 (m, 4 H, H-4 and H-6), 3.49, 3.58 (s, 3 H, NCH_3), 4.22, 4.30 (br s, N–CH_2), 4.46, 4.54 (br s, 1 H, *gem*-vinyl), 4.82 (br s, 1 H, *gem*-vinyl), 6.50, 6.81 (s, 1 H, vinyl); ^{13}C NMR ($CDCl_3$) –1.3 (q, Si-$(CH_3)_3$), 20.1 (t, CH_2–Si), 20.6 (t, C-5), 24.2 (t, C-6), 26.7 (q, $(CH_3)_3$), 27.9 (t, C-4), 39.9 (s, $(CH_3)_3C$), 42.4, 42.9 (q, NCH_3), 61.6, 62.0 (t, C-1), 107.0 (d, C-2), 108.3, 109.7 (t, C-3′), 137.3, 138.1 (s, C-2′), 173.9 (s, C=O), 176.7, 177.3 (s, C-1), 179.2, 179.6 (s, C-3); IR ($CHCl_3$) 3050, 2980, 2970, 1770, 1650, 1610, 1250, 1100, 910, 850, 840 cm^{-1}; high-resolution mass spectrum, 236.1471 (p^+ – 100) ($C_{13}H_{22}NOSi^+$ requires 236.1472).

***N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclopent-2-enylidene]-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (33).** To a solution of 114 mg (0.48 mmol) of the enaminone **31** and 98 mg (0.48 mmol) of $AgClO_4$ in 20 mL of CH_3CN at 0 °C was added a CH_3CN solution of pivaloyl chloride [1.3 mL (0.54 mmol) of a 0.5 mL/10 mL solution]. After being stirred for 0.75 h at 0 °C, the reaction mixture was filtered and concentrated in vacuo to give 20 mg (99%) of an oil characterized as the iminium salt **33** as a 3:2 mixture of *E,Z* isomers: UV max (CH_3CN) 273 nm (ϵ 28 000); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.30 (s, 9 H, $C(CH_3)_3$), 1.50, 1.70 (s, 2 H, CH_2Si), 2.85–3.30 (m, 4 H, CH_2's), 3.35, 3.40 (s, 3 H, NCH_3), 4.11 (br s, 2 H, N–CH_2), 4.6, 4.85 (br s, 2 H, $=CH_2$), 6.60, 6.80 (s, 1 H, H-2); ^{13}C NMR –0.1 (q, $Si(CH_3)_3$), 25.3 (t, C-5), 27.8 (q, $(CH_3)_3$), 29.0, 29.6 (t, C-4), 33.2 (t, CH_2Si), 41.1 (s, $C(CH_3)_3$), 42.9, 43.2 (q, NCH_3), 62.8, 63.4 (t, NCH_2), 109.4 (d, C-2), 111.0 (t, $=CH_2$), 139.3 (s, C-2′), 174.1 (s, C=O), 185.1, 184.5 (s, C-1), 190.4, 191.1 (s, C-3); IR ($CHCl_3$) 2960, 1790, 1650, 1560, 1100, 850 cm^{-1}; high-resolution mass spectrum, *m/e* 165.1151 (p^+ – 159) ($C_{10}H_{15}NO^+$ requires 165.1149).

***N*-(3-Methoxycyclohex-2-enylidene)-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (34).** To a solution of the enaminone **30** (1.78 g, 7.1 mmol) and $AgClO_4$ (1.62 g, 7.8 mmol) in 25 mL of acetonitrile at 0 °C was added 4.4 mL (71.0 mmol) of CH_3I. The resulting reaction mixture was stirred at 25 °C for 24 h and then filtered to remove the formed AgI. The filtrate was concentrated in vacuo, giving an oil which provided 2.4 g (93%) of the desired iminium salt **34** after flash chromatography on silica gel (4% CH_3OH–$CHCl_3$) as a 1:1 mixture of *E,Z* isomers: UV max (CH_3CN) 288 nm (ϵ 28 700); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.20, 1.60 (s, 2 H, CH_2–Si), 1.85–3.10 (m, 6 H, methylene H's), 3.50 (s, 3 H, NCH_3), 3.95, 4.05 (s, 3 H, OCH_3), 4.20 (br s, 2 H, N–CH_2), 4.50, 4.85 (2 s, 2 H, *gem*-vinyl), 5.70, 6.00 (s, 1 H, vinyl); ^{13}C NMR ($CDCl_3$) –1.5 (q, $Si(CH_3)_3$), 20.0, 20.6 (t, C-5), 23.9 (t, $SiCH_2$), 28.2 (t, C-6), 28.7 (t, C-4), 41.7 (q, NCH_3), 57.2, 57.9 (q, OCH_3), 60.7 (t, NCH_2), 94.0 (d, C-2), 108.0, 109.0 (t, C-3′), 137.0, 138.2 (s, C-2′), 177.4, 178.2 (s, C-1), 185.4, 185.9 (s, C-3); IR ($CHCl_3$) 2950, 2850, 1575, 1275, 1250, 1080, 870, 840 cm^{-1}; high-resolution mass spectrum, *m/e* 266.1921 ($C_{15}H_{28}NOSi^+$ requires 266.1848).

***N*-(3-Methoxycyclopent-2-enylidene)-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (35).** To a solution of 0.544 g (2.28 mmol) of the enaminone **31** and 0.522 g (2.51 mmol) of $AgClO_4$ in 30 mL of CH_3CN was added 1.42 mL (22.8 mmol) of CH_3I. The resulting mixture was stirred at 25 °C for 24 h and filtered to remove the AgI precipitate. The filtrate upon concentration in vacuo provided an oil which was subjected to flash chromatography (4% CH_3OH–$CHCl_3$), yielding 0.78 g (98%) of the desired iminium salt **35** as a 1:1 mixture of *E,Z* isomers: UV max (CH_3CN) 270 nm (ϵ 21 000); ^{1}H NMR ($CDCl_3$) δ –0.05 (s, 9 H, $Si(CH_3)_3$), 1.40, 1.45 (s, 2 H, CH_2–Si), 2.55–3.22 (m, 4 H, CH_2's), 3.258 3.21 (s, 3 H, NCH_3), 3.90 (br s, 2 H, N–CH_2), 3.95, 4.05 (s, 3 H, OCH_3), 4.50, 4.85 (br s, $=CH_2$), 5.85, 6.05 (s, 1 H, H-2); ^{13}C NMR –1.6 ($Si(CH_3)_3$, 23.6 ($SiCH_2$), 28.5 (C-4), 30.5 (C-5), 40.3, 41.3 (NCH_3), 60.3 (OCH_3), 61.2 (N–CH_2), 98.8, 99.2 (C-2), 108.8, 109.7 ($=CH_2$), 137.4, 137.8 ($C=CH_2$), 186.6, 187.2 (C-1), 194.5, 194.6 (C-3); IR ($CHCl_3$) 3090, 3050, 2950, 1700, 1575, 1450, 1425, 1400, 1300, 1250, 1100, 975, 850, 625 cm^{-1}; high-resolution mass spectrum, *m/e* 252.1775 (p^+, $C_{14}H_{26}NOSi^+$ requires 252.1741).

Irradiation of *N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclohex-2-enylidene]-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]-methylammonium Perchlorate (32). Preparation of 2-[(*tert*-Butylcarbonyl)oxy]-7-methyl-9-methylidene-7-azaspiro[5.4]dec-1-ene (36). A solution of 125 mg (0.29 mmol) of the iminium salt **32** in 250 mL of CH_3CN was irradiated (Corex) for 1.25 h. The photolysate was concentrated in vacuo, and the

resulting residue was diluted with saturated aqueous $NaHCO_3$ and then extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving an oil which was subjected to preparative thin-layer chromatography (silica gel, 50% petroleum, ether–ether, R_f 0.48) to give 63 mg (84%) of desired spirocyclic amine **36**: ^1H NMR ($CDCl_3$) δ 1.20 (s, 9 H, $(CH_3)_3$), 1.30–2.10 (m, 6 H, CH_2's), 2.20 (s, 3 H, NCH_3), 2.40 (br s, 2 H, H-10), 3.30 (br s, 2 H, N–CH_2), 4.70 (m, 2 H, =CH_2), 5.10 (s, 1 H, H-1); ^{13}C NMR 20.7 (t, C-4), 27.1 (q, $C(CH_3)_3$), 27.1 (t, C-5), 29.7 (q, C-3), 34.8 (q, NCH_3), 38.8 (s, $C(CH_3)_3$), 46.6 (t, C-10), 58.0 (t, C-8), 64.1 (s, C-6), 105.5 (t, =CH_2), 117.6 (d, C-1), 145.8 (s, C-9), 150.7 (s, C-2), 176.6 (s, C=O); IR ($CHCl_3$) 3075, 2950, 2875, 2800, 1740, 1675, 1475, 1360, 1275, 1140, 1010, 880 cm^{-1}; high-resolution mass spectrum, *m/e* 263.1876 ($C_{16}H_{25}NO_2^+$ requires 263.1842).

Irradiation of *N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclopent-2-enylidene]-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (33). Preparation of 2-[(*tert*-Butylcarbonyl)oxy]-7-methyl-9-methylidene-7-azaspiro[4.4]non-1-ene (37). A solution of 73 mg (0.17 mmol) of the iminium salt **33** in 250 mL of CH_3CN was irradiated (Cortex) for 1.25 h. The photolysate was concentrated in vacuo, giving a residue which was diluted with saturated aqueous $NaHCO_3$ and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving an oil which was subjected to chromatographic purification by preparative TLC (50% El_2O–petroleum ether, R_f 0.4) which yielded 38 mg (87%) of the spirocyclic amine **37**: ^1H NMR ($CDCl_3$) δ 1.10 (s, 9 H, $C(CH_3)_3$), 1.40–2.10 (m, 4 H, CH_2's), 2.20 (s, 3 H, NCH_3), 2.50 (m, 2 H, H-9), 3.35 (br s, 2 H, NCH_2), 4.85 (m, 2 H, =CH_2), 5.30 (s, 1 H, H-1); ^{13}C NMR 27.1 ($(CH_3)_3$), 27.7 (C-4), 30.6 (C-3), 34.6 (NCH_3), 38.9 ($C(CH_3)$), 46.5 (C-9), 58.5 (C-7), 74.8 (C-5), 105.6 (=CH_2), 114.5 (C-1), 145.5 (C-8), 152.9 (C-2), 165.8 (C=O); IR ($CHCl_3$) 3080, 2950, 2800, 1750, 1600, 1450, 1350, 1275, 1150, 1125, 875 cm^{-1}; high-resolution mass spectrum, *m/e* 249.1733 ($C_{15}H_{23}NO_2^+$ requires 249.1750).

Irradiation of *N*-(3-Methoxycyclohex-2-enylidene)-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (34). Preparation of 2-Methoxy-7-methyl-9-methylidene-7-azaspiro[5.4]dec-1-ene (38). A solution of 150 mg (0.41 mmol) of iminium salt **34** in 250 mL of anhydrous CH_3CN was irradiated (Corex) for 1 h. The photolysate was concentrated in vacuo. The resulting residue was diluted with saturated aqueous $NaHCO_3$ solution and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and coonnentrated in vacuo to yield an oil which was purified by column chromatography (Florisil, 95:5 $CHCl_3$–MeOH) to afford 75 mg (95%) of the desired azaspirodecene **38**: ^1H NMR ($CDCl_3$) δ 1.20–2.10 (m, 6 H, methylene H's), 2.20 (s, 3 H, NCH_3), 2.30 (m, 2 H, H-10), 3.35 (m, 2 H, H-8), 3.50 (s, 3 H, OCH_3), 4.35 (s, 1 H, vinyl), 4.80 (m, 2 H, =CH_2); ^{13}C NMR ($CDCl_3$) 20.5 (t, C-4), 26.4 (t, C-5), 27.9 (t, C-3), 34.50 (q, NCH_3), 47.40 (t, C-10), 54.10 (q, OCH_3), 57.9 (t, C-8), 64.7 (s, C-6), 97.9 (d, C-1), 105.4 (t, =CH_2), 146.0 (s, C_9), 158.3 (s, C-2); IR ($CHCl_3$) 3080, 2940, 2850, 2800, 1660, 1470, 1450, 1380, 1180, 1000, 900, 650 cm^{-1}; high-resolution mass spectrum, *m/e* 193.1460 ($C_{12}H_{19}NO^+$ requires 193.1424).

Irradiation of *N*-(3-Methoxycyclopent-2-enylidene)-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (35). Preparation of 2-Methoxy-7-methyl-9-methylidene-7-azaspiro[4.4]non-1-ene (39). A solution of 125 mg (0.36 mmol) of the iminium salt **35** in 250 mL of CH_3CN was irradiated (Corex) for 4.5 h. The photolysate was concentrated, yielding a residue which was diluted with saturated aqueous $NaCHO_3$. The $CHCl_3$ extracts of this solution were dried and concentrated in vacuo, giving an oil which was subjected to Florisil chromatography (5% CH_3OH–$CHCl_3$) to afford 58 mg (91%) of the spirocyclic amine **39**: ^1H NMR ($CDCl_3$) δ 1.30–2.25 (m, 4 H, CH's), 2.30 (s, 3 H, NCH_3), 2.60 (br s, 2 H, H-9), 3.45 (m, 2 H, N–CH_2), 2.80 (s, 3 H, OCH_3), 4.35 (s, 1 H, H-1), 4.90 (m, 2 H, =CH_2); ^{13}C NMR 27.5 (t, C-3), 31.0 (t, C-4), 34.0 (q, NCH_3), 46.2 (t, C-9), 57.2 (q, OCH_3), 57.9 (t, C-7), 77.7 (s, C-5), 94.5 (d, C-1), 106.8 (t, =CH_2), 143.4 (s, (C-8), 164.5 (s, C-2); IR ($CHCl_3$) 3040, 2950, 2850, 1650, 1450, 1350, 1150, 1040, 910 cm^{-1}; high-resolution mass spectrum, *m/e* 179.1314 ($C_{11}H_{17}NO^+$ requires 179.1335).

Attempted Fluoride Ion Induced Cyclization of the [[(Trimethylsilyl)methyl]allyl]iminium Salt 32. A solution of 91 mg (0.21 mmol) of the iminium salt **32** and 0.16 g (1.05 mmol) of cesium fluoride in 7 mL of CH_3CN was stirred at 25 °C for 24 h, poured into water, and extracted with $CHCl_3$. The organic extracts were dried and concentrated in vacuo, giving 45 mg of a residue which was shown by analytical TLC, ^1H NMR, and GLC to contain the enaminones **30** and **40**. GLC analysis (10% OV-101) indicates that the ratio of 36:46 is ca. 2:1. Spectroscopic datta for **40** are as follows: UV max (MeOH) 298 nm (ε 29900); ^1H NMR ($CDCl_3$) δ 1.7 (s, 3 H, CH_3), 1.8–3.6 (m, 6 H, methylene H's), 3.0 (s, 3 H, NCH_3), 3.7 (s, 2 H, N–CH_2), 4.7 (s, 1 H, *gem*-vinyl), 4.9 (s, 1 H, *gem*-vinyl), 5.2 (s, 1 H, vinyl); ^{13}C NMR 19.4 (q, CH_3), 21.9 (t, C-5), 26.2 (t, C-4), 35.3 (t, C-6), 37.9 (q, NCH_3), 57.1 (t, C-1′), 98.6 (d, C-2), 110.9 (t, C-3′), 139.6 (s, C-2′), 165.1 (s, C-3), 196.3 (s, C-1); IR ($CHCl_3$) 2960, 1600, 1550, 1420, 1380, 1180 cm^{-1}; high-resolution mass spectrum, *m/e* 179.1301 ($C_{11}H_{17}NO^+$ requires 179.1306).

Attempted Fluoride Ion Induced Cyclization of the *N*-[[(Trimethylsilyl)methyl]allyl]enaminone 30. A solution of 0.145 g (0.58 mmol) of the enaminone **30** and 2.89 mmol of tetra-*n*-butylammonium fluoride in 30 mL of THF was stirred at 25 °C for 14 h and at reflux for 12 h, poured into 20 mL of water, and extracted with $CHCl_3$. The organic layer was dried and concentrated in vacuo, giving a residue which was subjected to separation by preparative TLC (silica gel, 2% MeOH–$CHCl_3$) to produce 63 mg (61%) of 3-[*N*-methyl(2-methyl-2-propenyl)-amino]cyclohex-2-enone (**40**, R_f 0.1) and 32 mg (31%) of 3-[N-methyl(2-methyl-1-propenyl)amino]cyclohex-2-enone (**48**, R_f 0.32). Spectroscopic data for **48** are as follows: UV max (MeOH) 302 nm (ε 17200); ^1H NMR ($CDCl_3$) δ 1.5 (s, 3 H, CH_3), 1.7 (s, 3 H, CH_3), 1.8–2.4 (m, 6 H, methylene H's), 2.9 (s, 3 H, NCH_3), 52 (1 H, vinyl (ring), 5.8 (1 H, vinyl); ^{13}C NMR 17.4 (q, CH_3), 21.4 (q, C-3′), 22.2 (t, C-5), 27.2 (t, C-4), 36.0 (t, C-6), 38.6 (q, NCH_3), 99.3 (d, C-2), 126.6 (d, C-1′), 133.8 (s, C-2′), 165.2 (s, C-3), 196.9 (s, C-1); IR ($CHCl_3$) 2950, 2850, 1600, 1550, 1400, 1360 cm^{-1}; high-resolution mass spectrum, *m/e* 179.1309 ($C_{11}H_{17}NO^+$ requires 179.1269).

Quantum Yield Measurements for Photospirocyclization of [[(Trimethylsilyl)methyl]allyl]iminium Perchlorates 32 and 33. Quantum yields were measured by using a "linear optical bench" system described earlier[4] and employing a filter solution combination with three 1-cm compartments containing separately 2.0 M (525.72 g/L) nickel sulfate hexahydrate in 5% sulfuric acid, 0.8 M (224.88 g/L) cobalt sulfate heptahydrate in 5% sulfuric acid, and 0.0012 M (0.378 g/L) bismuth chloride in 2:3 hydrochloric acid/water. The UV transmission of this filter system was 240–310 nm with a maximum at 275 nm. Production analyses for spirocyclic amines **36** and **37** were performed by GLC (2.5 ft × $^1/_8$ in., 10% OV-101 on Variport 30, 20 mL/min flow rate) of reaction mixtures, which were subjected to the same workup procedures used in the preparative reactions; benzophenone and bibenzyl were employed as internal standards, respectively. The quantum yield data obtained are listed as follows: iminium salt; run number (millimoles of iminium sa); light absorbed; product (millimoles); quantum yield of formation; percent conversion; column temperature.

***N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclohex-2-enylidene]-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (32).** Run 1 (0.214 mmol); 0.1202 mEinstein; **36** **36** (0.256 mmol); φ 0.211; 11.7%; 120 °C. Run 3 (0.246 mmol); 0.078 mEinstein; **36** (0.016 mmo6); φ 0.199; 6%; 120 °C.

***N*-[3-[(*tert*-Butylcarbonyl)oxy]cyclopent-2-enylidene]-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]methylammonium Perchlorate (33).** Run 1 (0.189 mmol); 0.17 mEinstein; **37** (5.14 × 10^{-3} mmol); φ 0.031; 2.8%; 120 °C. Run 2 (0.223 mmol); 0.1721 mEinstein; **37** (6.27 × 10^{-3} mmol); φ 0.034; 3.6% 120 °C. Run 3 (0.2441 mmol); 0.1768 mEinstein;**37** (6.21 × 10^{-3} mmol); φ 0.035; 2.5%; 120 °C. Run 4 (.2062 mmol); 0.2134 7Einstein; **37** (7.5 × 10^{-3} mmol); φ 0.036; 3.7%; 120 °C.

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Registry No. (*E*)-**4**, 87883-54-3; (*Z*)-**4**, 87883-86-1; (*E*)-**5**, 87883-58-7; (*Z*)-**5**, 87883-90-7; **6**, 82444-60-8; (*E*)-**7**, 87883-56-5; (*Z*)-**7**, 87883-88-3; (*E*)-**8**, 87883-60-1; (*Z*)-**8**, 87883-92-9; **12**,

55998-74-8; **13**, 82444-46-0; **14**, 87883-51-0; **15**, 87883-52-1; **16**, 87883-61-2; **17**, 87883-62-3; **18**, 87883-63-4; **19**, 87883-64-5; **20a**, 82444-57-3; **20b**, 82444-58-4; **21a**, 82444-55-1; **21b**, 82444-56-2; **22a**, 82444-74-4; **22b**, 82444-75-5; **23a**, 82444-73-3; **23b**, 82456-18-6; **24a**, 87883-65-6; **24b**, 87883-66-7; **30**, 87883-67-8; **31**, 87883-68-9; (*E*)-**32**, 87883-70-3; (*Z*)-**32**, 87901-10-8; (*E*)-**33**, 87883-72-5; (*Z*)-**33**, 87883-74-7; (*E*)-**34**, 87883-76-9; (*Z*)-**34**, 87883-78-1; (*E*)-**35**, 87883-80-5; (*Z*)-**35**, 87883-82-7; **36**, 82444-72-2; **37**, 82444-71-1; **38**, 82444-70-0; **39**, 82444-69-7; **40**, 87883-83-8; **48**, 87883-84-9; cyclopentane-1,3-dione, 3859-41-4; oxalyl chloride, 79-37-8; 3-chloro-2-cyclopenten-1-one, 53102-14-0; methylamine, 74-89-5; 3-methyl-2-butenyl bromide, 870-63-3; pivaloyl chloride, 3282-30-2.

Model Studies Examining the Application of Allyliminium Salt Photospirocyclization Methodologies in Synthetic Approaches to the Harringtonine Alkaloids

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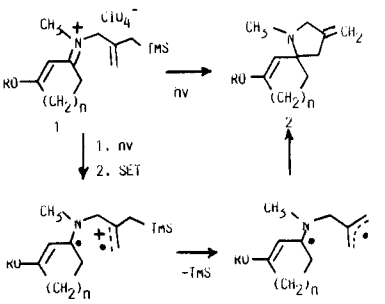
Exploratory studies have been conducted to test features of two strategies established for synthesis of members of the harringtonine alkaloid family. In order to assess the feasibility of synthetic approaches in which the spirocyclic CD-ring portions of these substances are fabricated by allyliminium salt photocyclizations, we prepared the tricyclic and B-ring-incomplete [[(trimethylsilyl)methyl]allyl]iminium perchlorates **8–10** and subjected them to photochemical investigations. While irradiation of the tricyclic salts **8** and **9** fails to induce cyclization reactions, photolysis of the B-ring-incomplete iminium perchlorate **10** leads to efficient formation of the spirocyclic amine **30**. Detailed mechanistic studies have shown that the source of these differences in excited-state reactivity is the ring constraints in **8** and **9**, but missing in **10**, which enforce conjugation of the electron-rich aryl ring and vinyliminium cation groupings. This causes reductions in both the singlet energies and reduction potentials of the iminium cation chromophores in **8** and **9** and results in inefficient, intramolecular electron transfer which serves as the obligatory step in photospirocyclization.

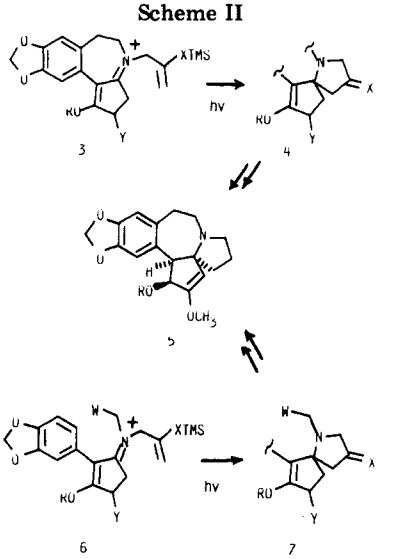
In the two preceding publications[1,2] we have shown how the electron-transfer photochemistry of allylsilane–iminium salt systems can serve as useful carbon–carbon bond forming methodologies. In particular, the results from model studies with the [2-[(trimethylsilyl)methyl]allyl]-iminium perchlorates **1** suggest that reaction pathways driven by sequential electron transfer–desilylation processes can lead to efficient formation of the spirocyclic amines **2**[2] (Scheme I). The last phase of our preliminary investigations in this area is focused on examination of the generality of this photochemical transformation and, specifically, its application to synthetic approaches for construction of members of the harringtonine alkaloid family.

Compounds in the harringtonine alkaloid family, exemplified by cephalotaxin (**5**, R = H), possess interesting tetracyclic skeletons comprised of benzazepine AB-ring systems stitched to intriguing 1-azaspiro[3.3]nonenone CD units.[3] Moreover, certain *O*-3-acyl derivatives of cephalotaxine (**5**, R = COR) display significant antileukemic activities.[4] The scarce availability of these substances, e.g., homoharringtonine, from natural sources and their interesting structural features and biological properties have encouraged a number of chemically oriented investigations of these systems. Two elegant total syntheses of the parent member of this alkaloid family, cephalotaxin, have been described,[5] and ingenious methods for the dif-

Scheme I



Scheme II



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