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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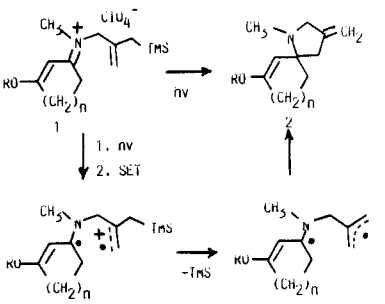
Exploratory studies have been conducted to test features of two strategies established for synthesis of members of the harringtonine alkaloid family. In order to assess the feasibility of synthetic approaches in which the spirocyclic CD-ring portions of these substances are fabricated by allyliminium 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.

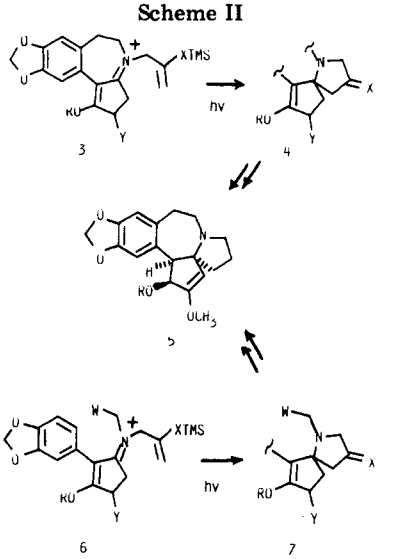
In the two preceding publications[1,2] we have shown how the electron-transfer photochemistry of allylsilane–iminium salt systems can serve as useful carbon–carbon bond forming methodologies. In particular, the results from model studies with the [2-[(trimethylsilyl)methyl]allyl]-iminium perchlorates **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



(1) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.*, first of three papers in this issue.
(2) Ullrich, J. W.; Chiu, F. T.; Tiner-Harding, T.; Mariano, P. S., *J. Org. Chem.*, preceding paper in this issue.
(3) (a) Kariyouonu, T.; Takahashi, M.; Nitta, A.; Tsunehisa, M. *J. Pharm. Soc. Jpn.* **1950**, *76*, 611. (b) Powell, R. G.; Weisleder, D.; Smith, G. R.; Wolff, J. A. *Tetrahedron Lett.* **1969**, 4081. Arora, S. K.; Bates, R. B.; Grady, R. A.; Powell, R. G. *J. Org. Chem.* **1974**, *39*, 1269.
(4) Powell, R. G.; Weisleder, D.; Smith, C. R. *J. Pharm. Sci.* **1972**, *61*, 1227. Huang, M. T. *Mol. Pharmacol.* **1975**, *11*, 511. Smith, C. R.; Mikolajczak, K. L.; Powell, R. G. "Medicinal Chemistry. Anticancer Agents Based on Natural Product Models"; Cassady, J. M., Duros, J. D., Eds.; Academic Press: New York, 1980; Vol. 16, p 392.

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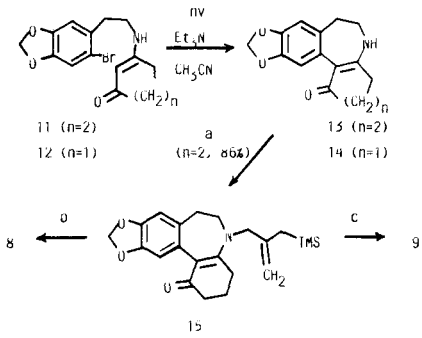
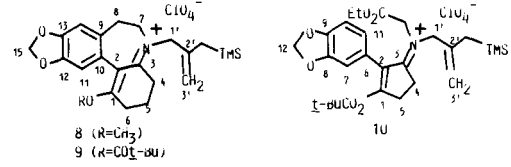
Scheme III[a]



[a] (a) NaH, THF, $CH_2=C(CH_2SiMe_3)CH_2OSO_2Me$, 2 h; (b) CH_3I, $AgClO_4$, CH_3CN, 25 °C; (c) *t*-BuCOCl, $AgClO_4$, CH_3CN, 0 °C.

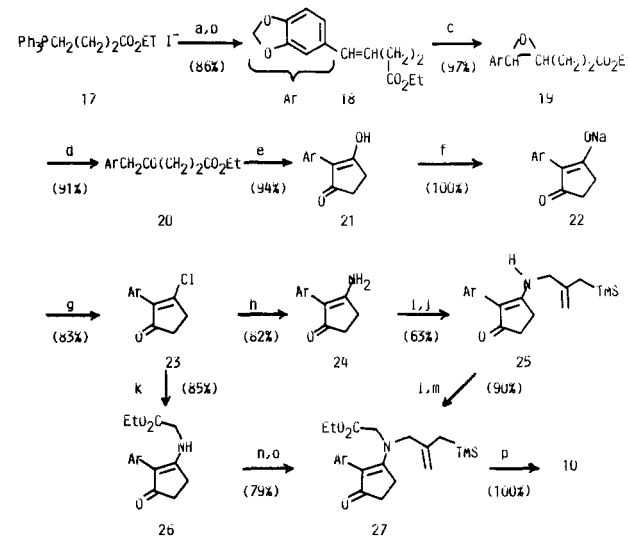
ficult conversion of the naturally more abundant cephalotaxine to its biologically active esters have been disclosed.[6]

Our exploratory studies in this area have been guided by two basic and related strategies for synthesis of members of the harringtonine alkaloid family in which the spirocyclic CD-ring portions of these molecules are fabricated by allyliminium salt photocyclizations (**3** → **4** and **6** → **7**) as depicted in Scheme II. The major difference between routes based upon these designs resides in the timing of steps used to construct the benzazepine and spirocyclic units. As will be seen, this difference is not a trivial one but rather serves as an important determinant in governing the success of approaches employing electron-transfer-initiated photospirocyclization processes. In order to assess the feasibility of these harringtonine alkaloid synthetic approaches and, more importantly, to determine if the electron-transfer-initiated photocyclization methodology uncovered in earlier studies[2] is applicable to the more highly conjugated systems represented by **3** and **6**, we have investigated methods for preparation of the tricyclic allyliminium perchlorates **8** and **9** and a B-ring-incomplete analogue, **10**, and conducted a detailed photochemical study of these systems.



Preparation of the [[(Trimethylsilyl)methyl]allyl]iminium Perchlorates 8 and 9. The ready availability of the tricyclic β-aminocyclohexenone **13** via intramolecular photoarylation of the bromoarene precursor **11**[7] made this substance a logical choice as a starting material for construction of the [[(trimethylsilyl)methyl]allyl]-iminium perchlorates **8** and **9** by the routes outlined in Scheme III. It is important to note that the cyclopentanone homologue **14** can be prepared by similar

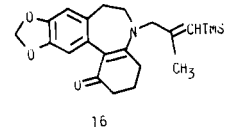
Scheme IV[a]



[a] (a) NaOEt, DMF, 25 °C, 0.5 h; (b) piperonal, 25 °C, 12 h; (c) MCPBA, K_2HPO_4, CH_2Cl_2, 12 h, 25 °C; (d) $BF_3 \cdot Et_2O$, C_6H_6, 25 °C, 1 h; (e) NaH, THF, 3 h; (f) 1 equiv of aqueous NaOH; (g) ClCOCOCl, C_6H_6, 12 h; (h) NH_3, NH_4OH, 25 °C, 3 days; (i) *n*-BuLi, THF, −78 °C; (j) $CH_2=C(CH_2SiMe_3)CH_2OSO_2Me$, 3 h; (k) $EtO_2CCH_2NH_3Cl$, Et_3N, K_2CO_3, C_6H_6, 2 d; (l) NaH, C_6H_6, 4 h; (m) EtO_2CCH_2Br, 12 h, 60 °C; (n) IDA, THF, −78-0 °C; (o) $CH_2=C(CH_2SiMe_3)CH_2OSO_2Me$, 0-25 °C, 12 h; (p) $AgClO_4$, *t*-BuCOCl, CH_3CN, 0 °C, 1 h.

technology. However, the greatly diminished yield of this process (**12** → **14**, 50% vs. **11** → **13**, 80%) coupled with the fact that 1,3-cyclopentadione, the precursor of **12**, is less accessible than 1,3-cyclohexandione made choice of the six-membered-ring salts in initial model studies more reasonable. In addition, previous efforts have shown that the quantum efficiencies for photospirocyclization of the cyclohexylidene salts **1** ($n = 2$) are greater than for the five-membered-ring counterparts.[2] Thus, results from photochemical studies with **8** and **9** should shed light on the viability of harringtonine alkaloid synthetic routes which depend upon the efficiencies of photocyclization allyliminium salt systems.

N-Allylation of the β-enaminone **13** is accomplished in a straightforward fashion through generation of the nitrogen anion by deprotonation with either NaH or *n*-BuLi followed by treatment with the mesylate derivative of [(trimethylsilyl)methyl]allyl alcohol.[8] Care must be exercised in this reaction since, over extended time periods under the strongly basic reaction conditions, the formed enaminone undergoes isomerization via a prototropic process to produce the vinylsilane derivative **16**. For



example, reaction of **13** with the allylic mesylate and NaH as the base for 12 h at reflux leads to formation of a mixture of **15** and **16** in which the latter predominates (e.g., 25% vs. 42%). The *O*-methyl and *O*-pivaloyl allyliminium perchlorates are then produced from **15** by tested methodologies[2] involving silver perchlorate promoted methylation and pivaloylation (Scheme III). The perchlorate salts **8** and **9** are obtained by these sequences starting with β-

(5) (a) Auerbach, J. A.; Weinreb, S. M. *J. Am. Chem. Soc.* **1972**, *94*, 7172. Semmelhack, M. F.; Chong, D. C.; Jones, L. D. *Ibid.* **1972**, *94*, 8629. Weinreb, S. M.; Semmelhack, M. F. *Acc. Chem. Res.* **1975**, *8*, 158. (b) See also the following references for synthetic approaches to the harringtonine alkaloids: Dolby, L. T.; Nelson, S. J., Senkovich, D. *J. Org. Chem.* **1972**, *37*, 3691. Tse, I.; Snieckus, V. *J. Chem. Soc., Chem. Commun.* **1976**, 505. Bryson, T. A.; Smith, D. C.; Krueger, S. A. *Tetrahedron Lett.* **1977**, 525.

(6) Abraham, D. J.; Rosenstein, R. D.; McGandy, E. L. *Tetrahedron Lett.* **1969**, 4081. Ipaktchi, T.; Weinreb, S. M. *Ibid.* **1973**, 3895. Kelley, T. R.; McKenna, J. C.; Christenson, P. A. *Ibid.* **1973**, 3501. Mikolajezak, K. L.; Smith, C. R.; Weisleder, D.; Kelley, T. R.; McKenna, J. C.; Christenson, P. A. *Ibid.* **1974**, 283. Hiranuma, S., Hudlicky, T. *Ibid.* **1982**, *23*, 3431.

(7) Tiner-Harding, T.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 482.

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

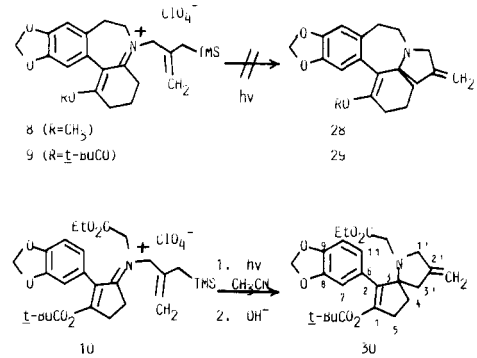
enaminone **13** in overall yields of ca. 77%. Spectroscopic data for **8** and **9** are in full accord with that expected for substances possessing the aryl–cross-conjugated oxyvinyliminium cation grouping and a [(trimethylsilyl)methyl]allyl nitrogen appendage.

Preparation of the (Arylcyclopentylidene)[[(trimethylsilyl)methyl]allyl]iminium Perchlorate 10. The routes employed for preparation of the B-ring-incomplete, [[(trimethylsilyl)methyl]allyl]iminium perchlorate **10** (Scheme IV) utilize the α-aryl-β-chlorocyclopentenone **23** as a key intermediate. This substance is efficiently synthesized via a sequence starting with the known[9] triphenylphosphonium salt **17**, formed by iodide ion catalyzed reaction of triphenylphosphine with ethyl γ-chlorobutyrate. Wittig reaction of the derived phosphorane with piperonal provides the styryl ester **18** which is then transformed to the oxirane **19** by epoxidation with MCPBA. Lewis acid (BF_3·Et_2O) catalyzed isomerization of the styrene oxide portion of **19** under nonnucleophilic conditions serves as a useful method to form the γ-keto-ester **20** which then undergoes Claisen cyclization to give the 2-aryl-1,3-cyclopentandione **21**. To accomplish the transformation of dione **21** to the corresponding β-chlorenone **23**, we have used a modification of the normal oxalyl chloride procedure[10] in order to avoid problems associated with the acid lability of **23**. A technique suggested by Rapoport[11] to avoid hydrogen chloride production in the conversion of carboxylic acids to their acid chloride derivatives was adapted to our purposes. Accordingly, the dione is converted to its sodium salt **22** prior to reaction with oxaloyl chloride which furnishes the β-chloroenone **23** in excellent yields.

Two closely related pathways are then used to transform the β-enaminone precursor to the target iminium salt. In the first route, the vinylogous primary amide **24**, formed by treatment of **23** with ammonium hydroxide, is sequentially N-allylated with the mesylate derivative of 2-[(trimethylsilyl)methyl]allyl alcohol[8] (**24** → **25**) and N-alkylated with ethyl bromoacetate to form the *N,N*-disubstituted β-aminocyclopentene **27**. A more efficient alternative sequence to **27** involves generation of the amino ester **26** by reaction of chloro enone **23** with ethyl glycinate followed by N-allylation. Finally, the β-enaminone **27** is converted to the *O*-pivaloyl allyliminium perchlorate **10** by a documented[2] silver ion promoted reaction with pivaloyl chloride. This substance, produced as a ca. 1:1 mixture of C–N bond *E,Z* isomers, possesses spectroscopic properties which are in full accord with the expected iminium salt structure **10**.

Exploratory Photochemistry of the [[(Trimethylsilyl)methyl]allyl]iminium Perchlorates 8–10. The next goal established for these model studies was to test the photocyclization processes which serve as methods for installation of the spirocyclic amine portions of the harringtonine alkaloids in sequences based upon strategies outlined above in Scheme II. Accordingly, exploratory studies were initiated to determine the nature and efficiencies of photoreactions of the allyliminium salts **8–10**.

Irradiation of an acetonitrile solution of the *O*-methyl-[[(trimethylsilyl)methyl]allyl]iminium perchlorate **8** (2×10^{-3} mM) is conducted by using light of $\lambda > 280$ nm for time periods between 1 and 23 h. UV spectroscopic analysis of the photoreaction mixture shows that little change has occurred in both the position of intensity of the absorption band maximum during the course of irradiation. Concentration of the crude photolysate followed by aqueous base treatment yields a mixture comprised of mainly the recovered iminium salt **8** and a minor amount of the β-enaminone **15**. It is important to note that the crude photoreaction mixture does not contain detectable quantities of materials which can be assigned the tetracyclic structure **28** or products that could have derived



from **28**. The excited-state behavior of the *O*-pivaloyl tricyclic iminium perchlorate **9** is also characterized by the absence of photocyclization processes leading to the spirocyclic enol ester **29** or closely related substances. Thus, UV monitoring of the progress of photoreactions occuring upon irradiation of **9** in acetonitrile with light of $\lambda > 280$ nm reveals that absorption bands associated with the iminium cation chromophore (290 and 340 nm) decreases in intensity with time and that a new band at 320 nm, associated with a β-enaminone grouping, develops. Indeed, the β-enaminone **15** is the only product isolated after a basic workup of the photolysate. Therefore, it appears that the photochemistry of **9** is dominated by a deacylation reaction rather than by processes induced by sequential electron transfer and desilylation and leading to the spirocyclic amine **29**.

Contrastingly different results are obtained in investigations exploring the photochemical reactivity of the B-ring-incomplete [[(trimethylsilyl)methyl]allyl]iminium perchlorate **10**. Irradiation of an acetonitrile solution of **10** (5×10^{-3} mM) with light of $\lambda > 280$ nm for a time period which brings about ca. 45% conversion, followed by treatment of the photolysate with aqueous sodium bicarbonate, provides after chromatography on Florisil the β-enaminone **27** and spirocyclic amine **30** in respective yields of 55% annd 33%. It is important to note that optimal yields of the desired product **30** are obtained from this photoreaction when conversions of the iminium perchlorate **10** are lower than ca. 50%, owing to the intervention of a secondary, as yet undetermined, photochemical process leading to the destruction of **30**. This yield-diminishing process cannot be easily avoided by irradiation wavelength selection since both **10** and **30** have nearly superimposable UV/absorption spectra. Furthermore, production of the β-enaminone **27** does not occur via an excited-state pathway but rather by reaction of the unconverted salt **10** with aqueous base during the workup of the crude photolysate. Since the β-enaminone **27** can be reconverted to perchlorate salt **10** in nearly quantiative yield, the actual chemical efficiency for the **10** → **30** transformation is ca. 73%. In addition, the quantum efficiency for formation of **30** measured at ca. 2% conversion is 0.024.[12]

(9) Claeson, G.; Jonsson, H. G. *Ark. Kemi* **1969**, *31*, 83.
(10) Clark, R. D.; Heathcock, C. H. *Synthesis* **1974**, 47.
(11) Rapoport, H.; Wilson, C. D. *J. Am. Chem. Soc.* **1962**, *84*, 630.

(12) Attempts at inducing cyclization of the allyliminium perchlorates **8–10** by use of fluoride ion methodologies were unsuccessful. Uncyclized desilylated material was formed in a manner found for more simple model systems studied earlier.[2]

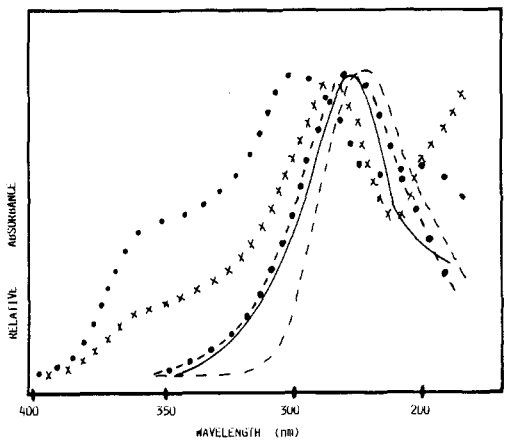
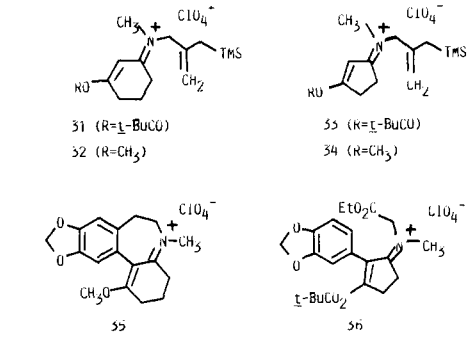


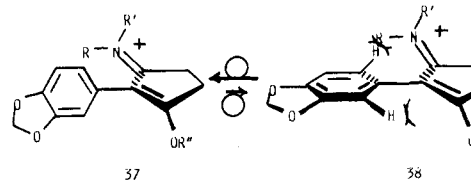
Figure 1. UV spectra of the tricyclic allyliminium perchlorates **8** (···) and **9** (X), the B-ring-incomplete salt **10** (—), the five-membered-ring model salt **33** (- - -), and the six-membered-ring model salt **31** (-·-). Concentrations (in CH_3CN) are adjusted to afford equal absorbances at maxima.

Structure assignment to the spirocyclic amine **30** was made on the basis of characteristic spectroscopic data (see Experimental Section). The presence in **30** of the styryl ester function is consistent with the UV/absorbance maximum at 288 nm. Also, ^{13}C NMR resonances, especially those at 149.9 and 127.0 ppm for the enol ester vinyl carbons, 76.9 ppm for the spirocyclic quaternary center, and 146.2 and 105.3 ppm for the exocyclic methylene carbons, compare favorably with those for analogous carbons in structurally less complex methylenepyrrolidine ring containing spirocyclic systems prepared in previous studies.[2]

Comparative Excited-State Reactivity of the Allyliminium Salts 8–10. The dramatically different photochemical reactivities of the tricyclic [[(trimethylsilyl)methyl]allyl]iminium perchlorates **8** and **9** compared to the B-ring-incomplete analogue **10** are intriguing since at first glance both systems appear to possess the same potential for electron-transfer-initiated photospirocyclization. Possible sources for this difference have been evaluated. It is doubtful that the unreactivity of the tricyclic models can be attributed to the size of the cycloalkene ring comprising a portion of the conjugated iminium cation chromophore. Previous studies[2] have shown that the efficiencies for photospirocyclization of nonaryl-conjugated, β-aminocyclohexenone-derived iminium salts (**1**, $n = 2$) are considerably greater than of their five-membered-ring homologues (**1**, $n = 1$). On the other hand, the contrasting photochemistry of these systems might be due to differences between the rates of photoinitiated, intramolecular electron transfer from allyl to iminium cation groupings. Careful consideration of the excited-state electrochemical properties of the iminium cation chromophores in **8–10** provides information to support this thought.

A key difference between the α-styryliminium cation groups in the tricyclic **8** and **9** and B-ring-incomplete **10** perchlorate salt surfaces upon inspection of the UV spectra of these substances (Figure 1). Specifically, the absorption spectrum of **10**, contaiing a wavelength maximum at 294 nm, is nearly identical with those of the closely related, nonaryl-substituted cycloalkenyliminium perchlorates **31** and **32** (λ_{max} 287 and 275 nm, respectively). In contrast, the tricyclic salts **8** and **9** display multiple UV absorption maxima extending beyond 310 nm, signaling the existence of significant interactions between the dioxy-substituted aromatic and vinyliminium cation π chromophores. Importantly, these data point to the reasonable conclusion that the aryl and vinyliminium cation groups in **10** are unconjugated. Indeed, **10** should exist in a low-energy perpendicular conformation, **37**, owing to the strongly





destabilizing interactions which occur between the *o*-aryl hydrogen and bulky *O*-pivaloyl and N substituents in the planar conformer **38**. Of course, the ethylene tether in the tricyclic salts enforces planar conformations related to **38**.

Conjugation, or the lack thereof, between the electron-rich methylenedioxy-substituted aryl rings and iminium cation chromophores in the allyliminium salts should have two important consequences related to efficiencies of electron transfer steps which are required to initiate cyclization. First, delocalization should cause a reduction in the iminium cation singlet energies ($\Delta E_{0,0}^{S_1}$),[13] a conclusion suggested on the basis of the comparative UV characteristics. The measured and estimated singlet energies of the allyliminium salts **8–10** and a variety of model systems **31–36**, included in Table I, are in full accord with this hypothesis. Secondly, conjugation of these groupings should lead to a decrease (more negative) in the ground state reduction potentials ($E_{1/2}^{S_0}(-)$). Approximate[14] $E_{1/2}^{S_0}(-)$ values for a series of iminium perchlorates including **8–10**, given in Table I, reflect trends predicted on the basis of conjugation effects.

The free energies and, thus, rates[15] of intramolecular electron transfer in the allyliminium salts should be directly dependent upon the excited-state reduction potential ($E_{1/2}^{S_1}(-)$) of the iminium cation moieties which are themselves proportional to $E_{1/2}^{S_0}(-)$ and $\Delta E_{0,0}^{S_1}$ according to the relationships $E_{1/2}^{S_1}(-) = E_{1/2}^{S_0}(-) + \Delta E_{0,0}^{S_1}$ and $\Delta G_{SET} = E_{1/2}^{S_0}(+)(\text{donor}) - E_{1/2}^{S_1}(-)(\text{acceptor})$. Thus, values for ΔG_{SET} shown in Table I can be calculated by making the fair assumption that the oxidn. potential ($E_{1/2}^{S_0}(+)$) for the $CH_2{=}C(CH_2SiMe_3)CH_2$ donor grouping will be ca. 1.9 V.[16] It is significant that the results of these very approximate calculations indicate that intramolecular electron transfer from the allyl π donor to the excited iminium cation groups in the tricyclic salts **8** and **9** should be endoergic. Therefore, electron transfer might ineffec-

(13) On the bais of information uncovered in earlier studies,[1] we expect that reactions should occur from the singlet excited states of the iminium cations.

(14) Electrochemical reduction potentials are estimated from measured half-wave potentials. In the cases of **8** and **9**, reduction is not detected polarographically down to −2 V.

(15) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(16) Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1970**, *102*, 4429 and references cited therein.

Table I. Ground- and Excited-State Electrochemical and Photophysical Properties and Excited-State Electron-Transfer Potentials for Allyliminium Perchlorate and Related Salts

iminium salts	$\Delta E_{0,0}{}^{S_1}$, kcal/mol	ϕ(fluorescence)[d] (excit λ, nm)	$E_{1/2}{}^{S_0}(-)$,[f] V	calcd $E_{1/2}{}^{S_1}(-)$, V	calcd intramolec ΔG_{SET}, kcal/mol
8	80[b]	0.05 (300)	<−2[g]	1.5	12
9	86[b]	0.04 (270)	<−2[g]	1.7	5
35[a]	79[b]	0.01 (310)	<−2[g]	1.4	
10	92[c]	e	−1.1	2.9	−22
31	92[c]	e	−1.1	2.9	−23
32	94[c]	e	−1.5	2.6	−15
33	99[c]	e	−1.3	−3.0	−25
34	101[c]	e	−1.7	−2.7	−17

[a] See Experimental Section for method of preparation. [b] Obtained by intersection of excitation and emission fluorescence bands. [c] Estimated by using the longest wavelength absorption spectral band edge. [d] In EtOH (nondegassed) at 25 °C. [e] Nonfluorescent. [f] In 5% H_2O-CH_3CN with $(n\text{-Bu})_4NClO_4$ (reference Ag^+/Ag). [g] Upper limit estimated since no wave seen. [h] Assuming allylsilane donor grouping with $E_{1/2}(+) = 1.9$ V.

tively compete with alternate modes of excited-state decay via radiationless, emissive, and reactive modes. Indeed, the combined observations that the *N*-allyl (**8** and **9**) and model *N*-methyl (**35**)[17] tricyclic salts fluoresce with about the same efficiencies and that the fluorescence of **35** is not quenched by 3-(trimethylsilyl)propene in the concentration range of 1 mM–0.1 M (EtOH, 25 °C) offer firm support for this conclusion. Unfortunately, the lack of fluorescence from noncyclic iminium salts such as **10** and **36**[18] makes it difficult to demonstrate in a definitive way that the nonaryl-conjugated iminium salts do participate in excited-state electron transfer with allylsilanes.

The electrochemical and excited-state properties of the iminium cation groupings in the allyliminium perchlorates **8–10** appear to offer a critical control of photospirocyclization reaction efficiencies. When structural features enforce conjugation between the electron-rich aryl and vinyliminium cation moieties, intramolecular electron transfer, which is the obligatory first step in photocyclization, is inefficient. Fortunately, steric factors prevent conjugation in the B-ring-incomplete salt **10**. As a result, electron-transfer-promoted photocyclization occurs in this case to produce the spirocyclic amine **30**. Therefore, our investigations have uncovered important information which will serve to guide our future synthetic efforts in this area.

Experimental Section

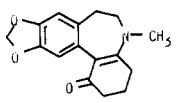
General Methods. ^1H NMR spectra were recorded by using Varian EM-360 and XL-100 FT spectrometers. ^{13}C NMR spectra were recorded by using a Varian XL-100 or Bruker WP-200 spectrometer at an operating frequency of 25.0345 MHz. All ^{13}C NMR spectra were obtained in deuteriochloroform as the solvent, and the chemical shifts are recorded in parts per million relative to tetramethylsilane as an internal standard. Numberings for proton and carbon chemical shift assignments are found in the structures in the text. 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 a G. C. A. McPherson EU-700-56 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer. Elemental analyses were performed by Dr. F. Kassler at the University of Maryland. Melting points were taken on a Griffen Mel-Temp capillary melting point apparatus and are reported uncorrected. Preparative chromatographic separations were accomplished by using the following absorbents: 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. The progress of the photoreactions was followed by UV monitoring of aliquots.

2,3,4,5,6,7-Hexahydro-5-[2-[(trimethylsilyl)methyl]-2-propenyl]-1*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepin-1-one (15). A solution of 0.076 g (1.6 mmol) of NaH, 0.204 g (0.79 mmol) of the tricyclic β-aminocyclohexenone **13**,[7] and 0.18 g (0.79 mmol) of [[(trimethylsilyl)methyl]allyl methanesulfonate[8] in 20 mL of THF was stirred at reflux for 2 h, cooled to 25 °C, and poured into an ice/water mixture. The $CHCl_3$ extracts of this solution were concentrated in vacuo to afford after flash chromatography (10% hexane–$CHCl_3$) 0.258 g (85%) of the *N*-[[(trimethylsilyl)methyl]allyl] β-enaminone **15** as a light brown oil: UV max (CH_3CN) 315 nm (ε 13 700), 245 (7500); ^1H NMR ($CDCl_3$) δ 0.003 (s, 9 H, $Si(CH_3)_3$), 1.4 (s, 2 H, CH_2–Si), 1.9 (m, 2 H, J = 6 Hz, C-5 H's), 2.4 (t, 2 H, J = 6 Hz, C-6 H's), 2.5 (t, 2 H, J = 6 Hz, C-4 H's), 2.8 (t, 2 H, J = 5 Hz, C-8 H's), 3.6 (m, 2 H, C-7 H's), 3.6 (s, 2 H, C-1′ H's), 4.6, 4.7 (2 s, 2 H, C-3′ H's), 5.9 (s, 2 H, OCH_2O), 6.5 (s, 1 H, aromatic H), 6.8 (s, 1 H, aromatic H); ^{13}C NMR −1.2 (q, $Si(CH_3)_3$, 21.1 (t, C-5), 24.1 (t, CH_2–Si), 29.7 (t, C-4), 32.6 (t, C-6), 37.6 (t, C-8), 58.6 (t, C-1′), 60.9 (t, C-7), 100.5 (t, C-15), 106.3 (d, C-11), 107.1 (t, C-3′), 113.2 (s, C-2), 112.3 (d, C-14), 128.8 (s, C-10), 133.8 (s, C-9), 141.0 (s, C-2′), 145.2 (s, C-12), 145.7 (s, C-13), 161.0 (s, C-3), 195.0 (s, C-1); IR ($CHCl_3$) 3000, 2950, 2900, 1610, 1540, 1450, 130, 1050, 860, 840 cm^{-1}; high-resolution mass spectrum, m/e 383.1923 ($C_{22}H_{29}NO_3Si$ requires 383.1940).

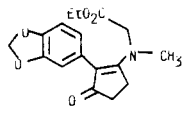
2,3,4,5,6,7-Hexahydro-5-[2-methyl-3-(trimethylsilyl)-2-propenyl]-1*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepin-1-one

(17) The iminium salt **35** is prepared via the corresponding β-enaminone **39** (see Experimental Section).



39

(18) The iminium salt **36** is prepared via the corresponding β-enaminone **40** (see Experimental Section).



40

(16). To a solution of 0.18 g (3.84 mmol) of NaH in anhydrous THF was added 0.33 g (1.28 mmol) of β-enaminone 13[7] in 5 mL of THF. The reaction mixture was stirred at reflux for 1 h at which time 0.284 g (1.28 mmol) of [(trimethylsilyl)methyl]allyl methanesulfonate 8 was added, and the reaction mixture was stirred at reflux for an additional 12 h, cooled to 0 °C, diluted with 5 mL of H_2O, and extracted with $CHCl_3$. The $CHCl_3$ extracts were concentrated in vacuo to afford after HPLC (50% hexane/EtAc Partisil 10) 0.124 g (25%) of 15 and 0.205 g (42%) of 16 as a brown oil: UV max (CH_3CN) 324 nm (ε 10300), 255 (5230); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H, $Si(CH_3)_3$), 1.6 (s, 3 H), 2.0 (m, 2 H, J = 6 Hz, C-5 H's), 2.5 (t, 2 H, J = 6 Hz, C-6 H's), 2.6 (t, 2 H, J = 6 Hz, C-4 H's), 2.8 (t, 2 H, J = 5 Hz, C-8 H's), 3.5 (t, 2 H, J = 5 Hz, C-7 H's), 3.9 (s, 2 H, C-1′ H's), 5.4 (s, 1 H, vinyl H), 5.9 (s, 2 H, OCH_2O), 6.5 (s, 1 H, aromatic H), 6.7 (s, 1 H, aromatic H); ^{13}C NMR 0.3 (q, $Si(CH_3)_3$) 21.2 (t, C-5), 23.6 (q, C-3′), 30.3 (t, C-4), 32.5 (t, C-6), 37.7 (t, C-7), 57.1 (t, C-1′), 61.2 (t, C-8), 100.6 (t, C-15), 106.4 (d, C-11), 112.2 (d, C-14), 115.3 (s, C-2), 12..0 (d, CHSi), 133.9 (s, C-9), 145.7 (s, C-13), 146.3 (s, C-12), 151.2 (s, C-2′), 161.7 (s, C-3), 195.8 (s, C-1); IR ($CHCl_3$) 3000, 2950, 2900, 1615, 1540, 1500, 1475, 1375, 1350, 1300, 1250, 1125, 1040, 940, 870, 840 cm^{-1}; high-resolution mass specltrum, m/e 383.1894 ($C_{22}H_{29}NO_3Si$ requires 383.1835).

3,4,6,7-Tetrahydro-1-methoxy-5-[2-[(trimethylsilyl)methyl]-2-propenyl]-2*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepinium Perchlorate (8). To a solution of 0.158 g (0.412 mmol) of 15 and 0.094 g (0.453 mmol) of $AgClO_4$ in 25 mL of CH_3CN was added 0.26 mL (4.17 mmol) of CH_3I. The resulting mixture was stirred at 25 °C for 12 h and filtered to remove the formed AgI. The filtrate was concentrated in vacuo to provide after flash chromatography (10% MeOH–$CHCl_3$) 0.153 g (97%) of the desired eniminium perchlorate 8: UV max (CH_3CN) 340 nm (ε 5800), 300 (9590), 253 (7850); ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.5 (br s, 2 H, CH_2–Si), 1.8–2.4 (m, 4 H, methylene H's), 2.6–3.2 (m, 4 H, methylene H's), 3.8 (m, 2 H, N–CH_2), 3.9 (s, 3 H, OCH_3), 4.1 (s, 2 H, C-1′ H's), 4.4 (s, 1 H, *gem*-vinyl), 4.7 (s, 1 H, *gem*-vinyl), 5.9 (s, 2 H, OCH_2O), 6.6 (s, 1 H, aromatic H), 6.7 (s, 1 H, aromatic H); ^{13}C NMR –1.5 (q, $Si(CH_3)_3$), 19.3 (t, CH_2–Si), 24.1 (t, C-5), 25.8 (t, C-6), 30.6 (t, C-8), 31.0 (t, C-4), 57.7 (q, OCH_3), 61.2 (t, C-1′), 62.2 (t, C-7), 101.1 (t, C-15), 106.7 (d, C-14), 107.8 (d, C-11), 111.8 (t, C-3′), 112.2 (s, C-2), 124.7 (s, C-9), 132.5 (s, C-10), 138.7 (s, C-2′), 146.1 (s, C-13), 147.7 (s, C-12), 177.4 (s, C-1), 182.8 (s, C-3); IR ($CHCl_3$) 3010, 2950, 1580, 1540, 1500, 1480, 1360, 1250, 1100, 1040, 860, 840, 620 cm^{-1}; high-resolution mass spectrum, m/e 383.1912 ($p^+ - 15$) ($C_{22}H_{29}NO_3Si$ requires 383.1899).

1-(2,2-Dimethyl-1-oxopropoxy)-3,4,6,7-tetrahydro-5-[2-[(trimethylsilyl)methyl]-2-propenyl]-2*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepinium Perchlorate (9). To a solution of 0.094 g (0.245 mmol) of 15 and 0.051 g (0.246 mmol) of $AgClO_4$ in 20 mL of CH_3CN was added a solution of 0.03 mL (0.268 mmol) of pivaloyl chloride in 10 mL of CH_3CN. The resulting mixture was allowed to warm to 25 °C and stir for 12 h, filtered, and concentrated in vacuo giving 0.134 g (97%) of the desired eniminium perchlorate 9: UV max (EtOH) 315 nm (shoulder) (ε 2456), 290 (8070); ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.0 (s, 9 H, $C(CH_3)_3$), 1.55 (br s, 2 H, CH_2–Si), 2.3–3.4 (m, 6 H, methylene H's), 3.42–4.1 (m, 4 H, CH_2CH_2N), 4.38 (br s, 2 H, C-1′ H's), 4.4, 4.7 (s, 2 H, *gem*-vinyl), 5.9 (s, 2 H, OCH_2O), 6.6 (br, 2 H, aromatic H's); ^{13},c NMR –1.5 (q, $Si(CH_3)_3$), 19.4 (t, CH_2–Si), 24.23 (t, C-5), 26.4 (q, $C(CH_3)_3$), 28.6 (t, C-6), 30.4 (t, C-8), 31.9 (t, C-4), 39.0 (s, $C(CH_3)_3$), 61.3 (t, C-1′), 63.5 (d, C-7), 101.4 (t, C-15), 107.2 (t, C-3′), 107.4 (d, C-14), 110.4 (d, C-11), 122.8 (s, C-9), 123.4 (s, C-2), 131.9 (s, C-10), 138.3 (s, C-2′), 146.4 (s, C-13), 148.5 (s, C-12), 170.1 (s, C-1), 174.4 (s, C=O), 179.9 (s, C-3); IR ($CHCl_3$) 3010, 2950, 2900, 1750, 1600, 1500, 1480, 1375, 1360, 1250, 1100, 1075, 940, 850, 620, cm^{-1}; high-resolution mass spectrum, m/e 468.2565 ($C_{27}H_{38}NO_4Si^+$ requires 468.2555).

Irradiation of 3,4,6,7-Tetrahydro-1-methoxy-5-[2-[(trimethylsilyl)methyl]-2-propenyl]-2*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepinium Perchlorate (8). A solution of 100 mg (0.20 mmol) of the iminium salt in 130 mL of CH_3CN was irradiated with Corex- or Vycor-filtered light for times ranging from 1 to 23 h. The reactions were followed by UV monitoring which showed no consumption of starting iminium salt. The workup of the crude photolysates involved concentration in vacuo, dissolution in $CHCl_3$, washing with $NaHCO_3$ (saturated) solution, drying, and concentration in vacuo and gave recovered iminium salt 8 and β-enaminone 15, exclusively.

Irradiation of 1-(2,2-Dimethyl-1-oxopropoxy)-3,4,6,7-tetrahydro-5-[2-[(trimethylsilyl)methyl]-2-propenyl]-2*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepinium Perchlorate (9). A solution of 100 mg (0.176 mmol) of the iminium salt 9 in 130 mL of CH_3CN was irradiated with Corex-filtered light for 3 h. Progress of the reaction was followed by UV monitoring which indicated a decrease in absorption maxima at 290 nm with an increasing absorbance at ca. 320 nm characteristic of enaminone 15. The crude photolysate was concentrated in vacuo, and the resulting residue was dissolved in $CHCl_3$ and washed with aqueous saturated $NaHCO_3$. The $CHCl_3$ layer was dried and concentrated in vacuo, giving a residue which was shown to contain the enaminone 15 exclusively, by spectroscopic analysis.

[γ-(Ethoxycarbonyl)propyl]triphenylphosphonium Iodide (17). The procedure of Claeson and Jonsson[9] was used with a slight modification. A mixture of sodium iodide (141.2 g, 0.942 mol) in dry methyl ethyl ketone was stirred at reflux for 30 min after which 94.6 g (0.628 mol) of ethyl 4-chlorobutyrate was added, the solution was stirred for an additional 18 h at reflux and cooled to 25 °C, and the solid was removed by filtration. The filtrate was concentrated in vacuo, giving a residue which was diluted with benzene, washed with water, 25% aqueous sodium thiosulfate, and water, dried, and concentrated to two-thirds of the original volume. Triphenylphosphine (187.7 g, 0.754 mol) was added and the solution stirred at reflux for 14 h. The reaction mixture was concentrated in vacuo, giving crystalline material which was washed with ether to provide 294.0 g (93%) of the desired phosphonium salt 17: mp 188–189 °C;[9] ^1H NMR ($CDCl_3$) δ 1.24 (t, 3 H, OCH_2), 1.7–2.3 (m, 2 H, P^+–CH_2CH_2), 2.84 (t, 2 H, CH_2CO_2), 3.6–4.1 (m, 2 H, P–CH_2), 4.10 (q, 2 H, OCH_3), 7.6–8.1 (br s, 15 H, aromatic).

Ethyl 5-[3,4-(Methylenedioxy)phenyl]-4-pentenoate (18). To a solution of 75.43 g (0.15 mol) of 17, and 22.5 g (0.15 mol) of piperonal in 300 mL of DMF was slowly added 66 mL (0.165 mol) of a NaOEt solution (2.5 M) in ethanol. The reaction progress was monitored by ^1H NMR analysis of removed aliquots for disappearance of aldehydic proton of piperonal. The reaction was normally complete immediately following addition of the NaOEt solution. The reaction mixture was then poured into an ice/water/heptane mixture and extracted with heptane. The organic layer was washed with water, dried, and concentrated in vacuo to give an oily product which can be purified by distillation (100 °C, 0.25 mm) to remove any unreacted piperonal followed by flash chromatography on silica gel (30/70 petroleum ether/CH_2Cl_2) to give 29.1 (78%) of the desired olefin 18 as a pale yellow oil: UV max (CH_3CN) λ_{max} 298 nm (ε 13131), 260 (28030); ^1H NMR ($CDCl_3$) δ 1.15 (t, 3 H, CH_3), 2.40 (m, 4 H, methylene H's), 4.15 (q, 2 H, O–CH_2), 5.96 (s, 2 H, OCH_2O), 5.30–5.89 (m, 1 H, vinylic H), 6.20–6.40 (m, 1 H, vinylic H), 6.70–6.90 (m, 3 H, aromatic); ^{13}C NMR 13.8 (q, CH_3), 23.7, 27.8 (t, C=$CHCH_2$), 33.7, 34.0 (t, $COCH_2$), 59.8 (t, CH_3CH_2), 100.6 (t, O_2–CH_2), 107.7, 108.5, 122.1 (d, aromatics), 126.4, 129.0 (d, vinyl), 129.4, 130.2 (d, vinyl), 131.0, 131.7, 146.1, 146.6, 147.3, 147.7, (s, aromatic), 172.2 (s, C=O); IR (KBr) 2980, 2910, 1735, 1600, 1505, 1495, 1440, 1240, 1045 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.68; H, 6.64.

Ethyl [3,4-(Methylenedioxy)phenyl]-4-epoxypentenoate (19). To a cooled solution (5 °C) of 50.0 g (0.20 mol) of the styryl ester 18 and 60 g (0.26 mol) of K_2HPO_4 in 230 mL of CH_2Cl_2 was slowly added a solution of 52.1 g (0.30 mol) of *m*-chloroperbenzoic acid in 540 mL of CH_2Cl_2. The reaction mixture was stirred for 12 h at 25 °C, filtered to remove solids, washed with 5% aqueous NaOH and H_2O, dried, and concentrated in vacuo to afford 51 g (96.5%) of epoxide 19: ^1H NMR ($CDCl_3$) δ 1.2 (t, 3 H, OCH_2CH_3), 1.7 (t, 2 H, CH_2CO), 2.4 (m, 2 H, CH_2CH_2CO), 3.1 (m, 1 H, C(O)CH–CH_2), 4.0 (d, 1 H, ArCH), 4.1 (q, 2 H, O–CH_2), 5.9 (s, 2 H, OCH_2O), 6.7 (br s, 3 H, aromatic H's); ^{13},c NMR 13.9 (q, CH_2CH_3), 22.3, 27.1, 30.0, 30.5 (t, CH_2CO), 57.0, 58.3 (d, CHO), 58.0, 61.0 (d, CHO), 60.1 (t, CH_2O), 100.8 (t, O_2CH_2), 106.7, 107.8, 119.2, 119.5 (d, aromatics), 131.2, 131.6, 146.9, 147.2, 147.4, 147.8 (s, aromatics), 172.2 (s, C=O); IR (KBr) 2930, 1735, 1490, 1450, 1380, 1250, 1090, 1040, 940, 815 cm^{-1}; high-resolution mass spectrum, m/e 264.0996 ($C_{14}H_{16}O_5$ requires 264.0988).

Ethyl 5-[3,4-(Methylenedioxy)phenyl]-4-oxolevulinate (20). To a cooled solution (5 °C) of epoxide **19** (18.6, 0.07 mol) in 100 mL of benzene was slowly added 4.3 mL (0.04 mol) of boron trifluoride etherate. The resulting solution was stirred at 25 °C for 1.0 h and concentrated in vacuo to give a residue which was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed with aqueous saturated NH_4Cl and H_2O, dried, and concentrated in vacuo to give an orange oil which was purified by flash chromatography on silica gel (CH_2Cl_2) to give 16.2 g (87%) of the desired keto ester **20** as a pale yellow viscous oil: UV max (CH_3CN) 286 nm (ϵ 7045), 234 (8030); ^1H NMR ($CDCl_3$) δ 1.2 (t, 3 H, CH_3), 2.6 (m, 4 H, methylene H's), 3.6 (s, 2 H, Ar CH_2), 4.1 (q, 2 H, O–CH_2), 5.9 (s, 2 H, OCH_2O), 6.m (br s, 3 H, aromatic H's); ^{13}C NMR 13.9 (q, CH_2CH_3), 28.0 (t, CH_2CO), 36.2 (t, CH_2C=O), 4..3 (t, CH_2CO), 60.3 (t, CH_2O), 100.8 (t, O_2CH_2), 108.2, 109.6, 122.4 (d, aromatics), 146.6, 147.8 (s, C-3′, aromatics), 172.4 (s, C=O), 206.1 (s, C=O); IR (KBr) 2990, 2905, 1738, 1505, 1490, 1450, 1250, 1990, 1045, 930, 810 cm^{-1}; high-resolution mass spectrum, *m/e* 264.099m ($C_{14}H_{16}O_5$ requires 264.0998).

2-[3,4-(Methylenedioxy)phenyl]-1,3-cyclopentanedione (21). To a refluxing solution of 5.1 g (0.13 mol) of NaH in 75 mL of THF was slowly added a solution of the keto ester **20** (15.9 g, 0.06 mol) in 300 mL of THF over a 10-h period. The reaction mixture was cooled to 0 °C, and its pH was adjusted to 2 by addition of saturated HCl in EtOH. The resulting mixture was concentrated in vacuo and the residue dissolved in 250 mL of Et_iO and 50 mL of a 10% aqueous HCl. The solid product that forms is separated by filtration, washed with Et_2O, and dried in vacuo over P_2O_5 to afford 12.2 g (93%) of the dione **21**. This substance is of sufficient purity for further reactions; however, it is easily recrystallized from ethanol to give a pale yellow solid: mp 240 °C (dec; UV max (H_2O) 266 nm (ϵ 11 591); ^1H NMR (Me_2SO-d_6) δ 2.5 (br s, 4 H, methylene H's), 6.0 (s, 2 H, OCH_2O), 6.95 (d, 1 H, aromatic H), 7.50 d, 2 H, aromatic H's); ^{13},c NMR (Me_2SO-d_6) δ 30.2 (t, C-4, C-5), 100.2 (t, C-12), 107.3 (d, C-10), 107.4 (d, C-7), 113.1 ns, C-2), 120.5 (d, C-11), 125.9 (s, C-6), 144.8 (s, C-9), 146.4 (s, C-8), 193.6 (s, C-1, C-3); IR (KBr) 2920, 2870, 1705, 1575, 1455, 1365, 1300, 1250, 1045, 940, 860, 800 cm^{-1}; high-resolution mass spectrum, *m/e* 218.0581 ($C_{12}H_{10}O_4$ requires 218.0591). Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.00; H, 4.66.

Sodium Salt of 2-[3,4-(Methylenedioxy)phenyl]cyclopentane-1,3-dione (22). A solution of dione **21** (30.0 g, 0.137 mol) and 5.5 g (0.138 mol) of NaOH in 200 mL of H_O was stirred at 25 °C for 30 min, diluted with C_6H_6, and concentrated in vacuo to afford, after drying in vacuo over P_2O_5, 32.9 g (100%) of the sodium salt **22** as a tan solid: UV max (H_2O) 266 nm (ϵ 6272); ^1H NMR (D_2O) δ 2.25 (s, 4 H, methylene H's), 5.7 (s, 2 H, OCH_2O), 6.7 (m, 3 H, aromatic H's); ^{13}C NMR (D_2O) 32.5 (t, C-4, C-5), 100.8 (t, C-12), 108.5 (d, C-10), 109.0 (d, C-7), 114.3 (s, C-2), 121.8 (d, C-11), 128.6 (s, C-6), 144.5 (s, C-9), 146.8 (s, C-8), 204.6 (s, C-1, C-3).

1-Chloro-2-[3,4-(methylenedioxy)phenyl]cyclopentenone (23). To a cooled solution (0 °C) of **2i** (17 g, 0.07 mol) in 250 mL of C_6H_6 was slowly added a solution of 12.4 mL (0.142 mol) of oxalyl chloride in 50 mL of C_6H_6. The resulting mixture was stirred at reflux for 16 h, cooled to 0 °C, filtered, poured into water, washed with 5% aqueous $NaHCO_3$ and brine, dried, and concentrated in vacuo to give the desired chloro enone **23** as a light brown oil which was purified by flash column chromatography (CH_2Cl_2) (R_f 0.5 in CH_2Cl_2), giving 13.4 (80%) of **23**: UV max (CH_3CN) 292 (ϵ 8080), 235 (16 160); ^1H NMR ($CDCl_3$) δ 2.85 (m, 4 H, methylene H's), 6.0 (s, 2 H, OCH_2O), 7.0 (m, 3 H, aromatic H's); ^{13},c NMR 33.1 (t, C-5), 35.4 (t, C-4), 101.1 (t, C-12), 108.2 (d, C-10), 109.3 (d, C-7), 122.8 (s, C-6), 123.1 (d, C-11), 138.8 (s, C-2), 147.5 (s, C-9), 147.8 (s, C-8), 163.0 (s, C-3), 202.6 (s, C-1); IR (KBr) 3030, 2900, 1705, 1605, 1490, 1445, 1350, 1300, 1245, 1045, 935, 805, 740 cm^{-1}; high-resolution mass spectrum, *m/e* 236.0237 ($C_{12}H_9ClO_3$ requires 236.0249).

3-Amino-2-[3,4-(methylenedioxy)phenyl]cyclopentenone (24). Into a solution of 11.5 g (48.6 mmol) of chloro enone **23** and 60 mL of NH_4OH in 200 mL of THF was bubbled ammonia gas with stirring for 6 days. The formed solid was separated by filtration and washed with ether, hot water, and ether again to afford **23** as a white solid. The filtrate from above was dried, concentrated in vacuo, and purified by flash column chromatography (5% $MeOH/CH_2Cl_2$, R_f 0.36), giving additional **24**. The total amount of pure **24** is 8.6 g (81.5%): ^1H NMR (Me_2SO-d_6) δ 2.55 (m, 4 H, methylene H's), 3.32 (s, 2 H, NH_2), 6.0 (s, 2 H, OCH_2O), 6.9 (d, 3 H, aromatic H's); ^{13}C NMR (Me_2SO-d_6) 26.0 (t, C-4), 32.8 (t, C-5), 100.4 (t, C-12), 108.0 (d, C-10), 108.4 (d, C-7), 109.6 (s, C-2), 121.0 (d, C-11), 127.0 (s, C-6), 144.3 (s, C-9), 146.8 (s, C-8), 172.6 (s, C-3), 199.4 (s, C-1); IR (KBr) 3285, 2900, 1655, 1580, 1480, 1450, 1300, 1230, 1100, 1040, 930, 800, 720 cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 65.98; H, 5.11; N, 6.21.

3-[[2-[(Trimethylsilyl)methyl]-2-propenyl]amino]-2-[3,4-(methylenedioxy)phenyl]-2-cyclopenten-1-one (25). To a cooled solution (−78 °C) of **24** (1.2 g, 5.52 mmol) in 30 mL of THF was added 4.21 mL (1.45 M, hexane), of *n*-BuLi over a 20-min period. The resulting orange mixture was stirred at −30 °C for 1.0 h and at 25 °C for 1 h. The reaction mixture was cooled to 0 °C, and a solution of 2-[(trimethylsilyl)methyl]-2-propenyl methanesulfonate[8] (1.3k g, 6.1 mmol) in 10 mL of THF was added. The mixture was stirred at reflux for 3 h, cooled to 25 °C, poured into a cooled (0 °C) 5% aqueous $NaHCO_3$ solution, and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo, giving a residue which was purified by flash column chromatography (silica gel) (2% $MeOH/CH_2Cl_2$, R_f 0.28) to afford 1.2 g (63.4%) of enaminone **25** as a light brown oil: UV max (CH_3CN) 278 nm (ϵ 18 863); ^1H NMR ($CDCl_3$) δ 0.08 (s, 9 H, $Si(CH_3)_3$), 1.56 (s, 2 H, CH_2–Si), 2.59 (m, 4 H, methylene H's), 3.76, 4.79 (d, 2 H, C=CH_2), 5.45 (t, 1 H, N-H), 5.96 (s, 2 H, OCH_2O), 6.85 (m, 3 H, aromatic H's); ^{13}C NMR −1.4 (q, $Si(CH_3)_3$), 24.0 (t, $CH_2Si(CH_3)_3$), 24.3 (t, C-4), 33.1 (t, C-5), 49.5 (d, C-1′), 100.7 (t, C-12), 107.8 (t, C-3′), 108.6 (d, C-10), 109.2 (d, C-7), 113.0 (s, C-2), 121.4 (d, C-11), 125.9 (s, C-6), 143.4 (s, C-2′), 145.9 (s, C-9), 147.8 (s, C-8), 172.6 (s, C-3), 200.2 (s, C-1); IR (neat) 3290, 3080, 2960, 2900, 1650, 1585, 1500, 1460, 1415, 1320, 1240, 1160, 1045, 940, 860, 840 cm^{-1}; high-resolution mass spectrum, *m/e* 343.1600 ($C_{19}H_{25}NO_3Si$ requires 343.1604).

3-[[(Ethoxycarbonyl)methyl]amino]-2-[3,4-(methylenedioxy)phenyl]-2-cyclopenten-1-one (26). A mixture of chloro enone **23** (11 g, 46.5 mmol), ethyl glycinate hydrochloride (8.3 g, 59.5 mmol), triethylamine (17.2 mL, 123.4 mmol), and K_2CO_3 (12 g, 86.8 mmol) in 230 mL of benzene andd 460 mL of THF was stirred at reflux for 2 days, cooled to 25 °C, and filtered. The filtrate was concentrated in vacuo, giving a residue which was dissolved in 200 mL of $CHCl_3$, washed with 200 mL of saturated aqueous NH_4Cl and H_2O, dried, and concentrated in vacuo to give a brown oil which after flash column chromatography (silica gel) (2% $MeOH/CH_2Cl_2$, R_f 0.44) afforded 12.0 g (85.2%) of **26** as a pale brown solid: mp 12..6–130.5 °C; UV max (CH_3CN) 278 nm (ϵ 19 091); ^1H NMR ($CDCl_3$) δ 1.28 (t, 3 H, CH_3), 4.10 (d, 2 H, N–CH_2e, 4.22 (q, 2 H, O–CH_2), 4.62 (m, 4 H, methylene H's), 4.10 (d, 2 H, NCH_2), 4.22 (q, 2 H, O–CH_2), 5.91 (s, 2 H, OCH_2O), 6.12 (t, 1 H, NH), 6.83 (m, 3 H, aromatic H's); ^{13}C NMR 14.0 (q, CH_3), 24.7 (t, C-4), 33.1 (t, C-5), 45.0 (t, CH_2O), 61.8 (CH_2N), 100.8 (t, C-12), 108.6 (d, C-10), 109.4 (d, C-7), 114.7 (s, C-2), 121.7 (d, C-11), 125.8 (s, C-6), 146.3 (s, C-9), 148.0 (s, C-8), 169.3 (s, O—C=O), 171.5 (s, C-3), 200.7 (s, C-1); IR (neat) 3335, 3060, 2980, 2900, 1740, 1640, 1580, 1500, 1480, 1440, 1400, 1235, 1200, 1120, 990, 1040, 935, 855, 810 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.34; H, 5.80; N, 4.92.

3-[[(Ethoxycarbonyl)methyl][2-[(trimethylsilyl)-methyl]-2-propenyl]amino]-2-[3,4-(methylenedioxy)-phenyl]-2-cyclopenten-1-one (27). To a cooled solution (−78 °C) of 0.324 g (1.07 mmol) of the enamino ester **25** in ca. 5 mL of THF was added 2.6 mL (2.46 mmol) of a 0.95 mM LDA/THF solution. The mixture was warmed to 0 °C, and a solution of 0.272 g (1.07 mmol) of [(trimethylsilyl)methylallyl]allyl iodide in 1.0 mL of THF was added. The reaction mixture was stirred at 25 °C for ca. 6 h, poured in ice/$NaHCO_3$ (5% solution), and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried and concentrated in vacuo to give a residue which was purified by flash column chromatogrpahy on silica gel (1% EtOH/ether) to give 0.418 g (91%) as a light brown oil: UV max (CH_3CN) 278 nm (ϵ 24 454); ^1H NMR ($CDCl_3$) δ −0.06 (s, 9 H, $Si(CH_3)_3$), 1.09 (t, 3 H, CH_3), 1.90 (s, 2 H, Si–CH_2), 2.46 (m, 4 H, methylene H's), 3.61 (s, 2 H, NCH_2C=C), 3.75 (s, 2 H, $C(O)CH_2N$), 3.94 (q, 2 H, OCH_2), 4.59 (d, 2 H, J = 7.5 Hz, C=CH_2), 5.80 (s, 2 H, OCH_2O), 6.57 (d, 3 H, aromatic H's); ^{13}C NMR −1.5 (q, $Si(CH_3)_3$), 13.9 (q, CH_3), 23.8 (t, CH_2Si), 27.1 (t, C-4), 32.9 (t, C-5), 51.3 (t, C-1′), 57.3 (t, CH_2O),

61.2 (t, CH_2N), 100.6 (t, C-12), 107.9 (t, C-3'), 108.1 (d, C-10), 110.8 (d, C-7), 114.9 (s, C-2), 123.8 (d, C-11), 127.8 (s, C-6), 140.9 (s, C-2'), 146.4 (s, C-9), 147.1 (s, C-8), 168.8 (s, O—C=O), 171.2 (s, C-3), 202.5 (s, C-1); IR (neat) 3080, 2950, 1745, 1670, 1575, 1490, 1450, 1300, 1233, 1200, 1100, 1040, 930, 852, 835 cm^{-1}; high-resolution mass spectrum, m/e 429..1971 ($C_{23}H_{31}NO_5Si$ requires 429.1984).

3-[[(Ethoxycarbonyl)methyl][2-[(trimethylsilyl)methyl]-2-propenyl]amino]-2-[3,4-(methylenedioxy)phenyl]-2-cyclopenten-1-one (27). A solution of the enaminone **26** (200 mg, 0.66 mmol) and 55 mg (1.14 mmol) of NaH in 20 mL of benzene was stirred at reflux for 2.0 h and cooled to 25 °C, and a solution of 0.25 g (1.12 mmol) 2-[(trimethylsilyl)methyl]-2-propenyl methanesulfonate[8] in 10 mL of benzene was added. The reaction mixture was stirred at reflux for 12 h, cooled to 25 °C, poured into 5% aqueous $NaHCO_3$, and extracted with $CHCl_3$. The organic layer was dried and concentrated in vacuo, giving a residue which following flash column chromatography on silica gel (2% $MeOH/CH_2Cl_2$) gave 0.224 g (79.2%) of the desired enaminone **27**.

***N*-[(Ethoxycarbonyl)methyl]-*N*-[3-(pivaloyloxy)-2-[3,4-(methylenedioxy)phenyl]cyclopent-2-enylidene]-*N*-[2-[(trimethylsilyl)methyl]-2-propenyl]ammonium Perchlorate (10).** To a cooled (0 °C) solution of **27** (500 mg, 1.16 mmol) and 250 mg (1.20 mmol) of $AgClO_4$ in 10 mL of CH_3CN was slowly added a dilute solution of 0.148 mL (1.20 mmol) pivaloyl chloride in 40 mL of CH_3CN. The resulting solution was stirred at 0 °C for 1.0 h and 25 °C for an additional 1 h and filtered. The filtrate was concentrated in vacuo, giving a pale yellow solid which was carefully washed with petroleum ether/ether (3:1), giving the desired eniminum salt **10** was a mixture of *E*/*Z* isomers: UV max (CH_3CN) 294 nm (ϵ 23 800); ^1H NMR ($CDCl_3$) δ −0.2, 0.1 (ns, 9 H, $Si(CH_3)_3$), 1.05 (s, 9 H, $C(CH_3)_3$), 1.15 (m, 3 H, CH_3e, 1.4, 1.5 (s, 2 H, CH_2–Si), 3.45 (br s, 4 H, methylene H's), 4.0 (q, 2 H, O–CH_2), 4.3, 4.5 (br s, 4 H, C*H*–N–CH_2), 4.9 (m, 2 H, exocyclic methylene), 5.85 (s, 2 H, OCH_2O), 6.80 (s, 3 H, aromatic H's); ^{13}C NMR −1.57, −1.86 (q, $Si(CH_3)_3$, 13.7, 13.8 (q, CH_3), 24.2, 24.5 (t, Si–CH_2e, 26.3 (q, $(CH_3)_3$), 30.5 (t, C-5), 32.0, 32.2 (t, C-4), 39.8 (s, $C(CH_3)_3$), 52.7, 53.7 (t, C-1'), 62.2, 62.5 (t, CH_2N), 63.0, 63.1 t, CH_2O), 101.5 (t, C-12), 108.6 108.7 (d, C-10), 109.9, 110.2 (d, C-7), 112.4, 113.2 (t, C-3'), 121.9, 122.2 (s, C-6), 123.5 (s, C-2), 123.7, 124.1 (d, C-11), 137.6, 138.0 (s, C-2'), 145.3 (s, C-1), 148.0 (s, C-9), 148.6 (s, C-8), 165.9, 166.7 (s, O—C=O), 172.5 (s, O—C=O), 188.0, 188.6 (s, C-3); IR ($CHCl_3$) 2950, 2900, 1749, 1645, 1500, 1490, 1380, 1240, 1200, 1090, 1040, 930, 900, 845 cm^{-1}; high-resolution mass spectrum, m/e 513.2719 ($C_{28}H_{40}NO_6Si$ requires 513.2749).

Formation of the Spirocyclic Amine 30 by Irradiation of the Iminium Perchlorate 10. A nitrogen purged solution of eniminium salt **10** (200 mg, 0.326 mmol) in 100 mL CH_3CN was irradiated with Corex-filtered light for 80 min, while the UV absorbance was monitored at 294 nm to 55% its original value. To the photolysate was then added 45 mg (0.54 mmol) of $NaHCO_3$. The mixture was concentrated in vacuo, giving a residue which was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried and concentrated in vacuo to afford a pale brown viscous oil which is shown by ^1H NMR analysis to be a mixture of cyclized spirocyclic product **30** and starting enamione **27**. Seperation was accomplished by flash column chromatography with Florisil (50% petroleum ether/ether), giving 77 mg (55%) of **27** and 47 mg (33%) of the desired spirocyclic amine **30** as a light yellow oil: UV max (CH_3CN) 288 nm (ϵ 4100); ^1H NMR ($CDCl_3$) δ 1.18 (s, 9 H, $C(CH_3)_3$), 1.32 (m, 3 H, CH_3), 2.0–2.8 (m, 4 H, methylene H's), 3.08 (m, 2 H, CH_2—C=C), 3.82 (d, d, 2 H, N–CH_2), 4.18 (m, 4 H, O–CH_2e, 4.86 (br s, 2 H, C=CH_2e, 5.91 (s, 2 H, OCH_2O), 6.73 (d, 1 H, aromatic H-10), 7.11 (dd, 1 H, aromatic H-11), 7.34 (d, 1 H, aromatic H-7); ^{13}C NMR[3] 14.2 (q, CH_3), 26.7 (t, C-4), 27.1 (q, $C(CH_3)_3$), 29.7 (t, C-5), 39.0 (s, $C(CH_3)_3$), 44.7 (t, C-3'), 50.4 (t, C-1'), 55.6 (t, CH_2N), 60.5 (t, O–CH_2), 76.9 (s, C-3), 100.8 (t, C-12), 105.3 (t, C=CH_2), 107.8 (d, C-10), 109.7 (d, C-7), 123.2 (d, C-11), 126.4 (s, C-6), 12.0 (s, C-2), 146.2 (s, C-2'), 147.3 (s, C-9), 147.8 (s, C-8), 149.9 (s, C-1), 171.3 (s, O—C=O), 175.8 (s, O—C=O); IR (neat) 3080, 2950, 1738, 1656, 1540, 1500, 1480, 1440, 1370, 1235, 1200, 1040, 930, 910, 809, 730 cm^{-1}; high-resolution mass specltrum, m/e 441.2121 ($C_{25}H_{31}NO_6$ requires 441.2189).

3-[Methyl[(ethoxycarbonyl)methyl]amino]-2-[3,4-(methylenedioxy)phenyl]-2-cyclopenten-1-one (40). A solution of **26** (200 mg, 0.66 mmol) and 48 mg (1.0 mmol) of NaH in 20 mL of C_6H_6 was stirred at reflux for 2.0 h and cooled to 25 °C, and 0.164 mL (2.63 mmol) of CH_3I was added. The resulting mixture was stirred at reflux for 2 days, cooled to 25 °C, poured into 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo, giving a crude oil which following purification by flash column chromatography on silica gel (2% $MeOH/CH_2Cl_2$, R_f 0.38) gave 178 mg (85%) desired enaminone **40** as pale yellow crystals: mp 141.0–141.5 °C; ^1H NMR ($CDCl_3$) δ 1.25 (t, 3 H, CH_3e, 2.5 (m, 4 H, methylene H's), 2.95 (s, 3 H, NCH_3), 3.88 (s, 2 H, N–CH_2e, 4.1/ (q, 2 H, O–CH_2), 5.90 (s, 2 H, OCH_2O), 6.65 (d, 3 H, aromatic H's); ^{13}C NMR 13.9 (q, CH_3), 27.4 (t, C-4), 33.0 (t, C-5), 40.4 (q, NCH_3), 54.3 (t, CH_2), 61.2 (t, CH_2O), 100.7 (t, C-12), 107.8 (d, C-10), 111.0 (d, C-7), 115.3 (s, C-2), 123.9 (d, C-11), 128.1 (s, C-6), 146.4 (s, C-9), 147.2 (s, C-8), 168.6 (s, O—C=O), 171.5 (s, C-3), 202.3 (s, C-1); IR (neat) 2980, 2960, 1743, 1665, 1580, 1500, 1400, 1300, 1230, 1200, 1110, 1040, 930, 810 cm^{-1}; high-resolution mass spectrum, m/e 317.1276 ($C_{17}H_{19}NO_5$ requires 317.1317).

***N*-[(Ethoxycarbonyl)methyl]-*N*-methyl-*N*-[3-(pivaloyloxy)-2-[3,4-(methylenedioxy)phenyl]cyclopent-2-enylidene]ammonium Perchlorate (36).** To a cooled solution (0 °C) of enaminone **40** (50 mg, 0.158 mmol) and 33.4 mg (0.160 mmol) of $AgClO_4$ in 10 mL of CH_3CN was added a solution of 20 μL (0.16 mmol) of pivaloyl chloride in 15 mL of CH_3CN. The resulting solution was stirred at 0 °C for 30 min and then at 25 °C for an additional 30 min, filtered, and concentrated in vacuo, giving a crude residue which was washed with Et_2O to give 79.3 mg (100%) of the desired eniminium salt **36** as a mixture of *E*,*Z* isomers: UV (CH_3CN) max 285 nm (ϵ 28 996); ^1H NMR ($CDCl_3$) δ 1.13 (s, 9 H, $C(CH_3)_3$), 1.31 (m, 3 H, CH_3), 3.18–3.58 (m, 7 H, methylene H's, NCH_3), 4.13 (q, 2 H, O–CH_2), 4.33, 4.63 (s, 2 H, $NCH_2C(O)$), 5.98 (br s, 2 H, OCH_2O), 6.78 (m, 3 H, aromatic H's); high-rsolution mass spectrum, m/e 317.1252 (M − 85) ($C_{17}H_{19}NO_5$ requires 317.1216).

2,3,4,5,6,7-Hexahydro-5-methyl-1*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepin-1-one (39). A solution of 0.188 g (3.9 mmol) of NaH and 0.50 g (1.95 mmol) of β-enaminone **13**[7] in 40 mL of anhydrous THF was stirred at reflux for 1.5 h and cooled to 0 °C. To this solution was added 1.2 mL (19.5 mmol) of CH_3I. The resulting mixture was stirred at 25 °C for 4 h, poured into ice–water, and extracted wit $CHCl_3$. The chloroform extracts were dried and concentrated in vacuo to afford an oil which was purified by flash chromatography on silica gel (10% hexane–$CHCl_3$), yielding 0.49 g (93%) of the desired *N*-methyl enaminone **39** as a light brown oil: UV max (CH_3CN) 320 nm (ϵ 19 750), 250 (9600); ^1H NMR ($CDCl_3$) δ 1.8–2.8 (m, 8 H, methylene H's), 2.85 (s, 3 H, NCH_3), 3.65 (m, 2 H, (–CH_2), 5.82 (s, 2 H, OCH_2O), 6.52 (s, 1 H, aromatic H), 6.75 (s, 1 H, aromatic H); ^{13}C NMR 20.7 (t, C-5), 29.9 (t, C-4), 32.4 (t, C-6), 37.3 (t, C-8), 40.3 (q, N-CH_3), 63.7 (t, C-7), 100.5 (t, C-15), 106.3 (d, C-11), 112.0 (d, C-14), 113.4 (s, C-2), 129.4 (s, C-10), 133.3 (s, C-9), 145.4 (s, C-12), 145.9 (s, C-13), 161.4 (s, C-3), 195.1 (s, C-1); IR ($CHCl_3$) 3000, 2950, 2900, 1625, 1550, 1500, 1480, 1375, 1350, 1325, 1250, 1050, 950 cm^{-1}; high-resolution mass spectrum, m/e 271.1198 ($C_{16}H_{17}NO_3$ requires 271.1159).

3,4,6,7-Tetrahydro-1-methoxy-5-methyl-2*H*-(1,3)benzodioxolo[5,6-*d*](1)benzazepinium Perchlorate (35). To a solution of 244 mg (0.89 mmol) **39** and 203 mg (0.98 mmol) of $AgClO_4$ in 25 mL of CH_3CN was added 0.55 mL (8.9 mmol) of CH_3I. The resulting mixture was stirred at 2k °C for 36 h and filtered to remove the formed AgI. The filtrate was concentrated in vacuo to provide after flash chromatography (1% MeOH–$CHCl_3$) 355 mg (94%) of the desired eniminium perchlorate **35**: UV max (CH_3CN) 330 nm (ϵ 5800), 300 (9200), 253 (8200); ^1H NMR ($CDCl_3$) δ 1.95–2.3 (m, 4 H, methylene H's), 2.6–3.2 (m, 4 H, methylene H's), 3.35 (s, 3 H, NCH_3), 3.84 (m, 2 H, N–CH_2), 3.9 (s, 3 H, OCH_3), 5.95 (s, 2 H, OCH_2O), 6.7 (s, 2 H, aromatic H's); ^{13}C NMR 19.5 (t, C-5), 26.4 (t, C-6), 31.7 (t, C-8), 32.5 (t, C-4), 45.5 (q, NCH_3), 58.4 (q, OCH_3), 63.5 (t, C-7), 102.6 (t, C-15), 107.9 (d, C-14), 112.3 (s, C-2), 112.7 (d, C-11), 127.0 (s, C-9), 134.0 (s, C-10), 147.2 (s, C-13), 148.8 (s, C-12), 177.4 (s, C-1), 182.7 (s, C-3); IR ($CHCl_3$) 3025, 2950, 1600, 1550, 1480, 1370, 1260, 1100, 950, 625 cm^{-1}; high-resolution mass spectrum, m/e 271.1204 (p^+ − 15) ($C_{16}H_{17}NO_3$ requires 271.1189).

Quantum Yield Measurement for Photospirocyclization of [[(Trimethylsilyl)methyl]allyl]iminium Perchlorate 10.

Quantum yields were measured by using a "linear optical bench" system described earlier[2] and employing a filter solution combination with three 1-cm compartments containing separately 2.0 M (252.72 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. Product analyses for the spirocyclicamine **30** was performed by HPLC (Partisil M-9 10/50). Conversions were in the range of 1.7–1.9%.

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Registry No. **8**, 87862-67-7; **9**, 87862-69-9; (*E*)-**10**, 87862-81-5; (*Z*)-**10**, 87862-90-6; **13**, 80348-06-7; **15**, 87862-64-4; **16**, 87862-65-5; **17**, 7743-26-2; **18**, 87862-70-2; **19**, 87862-71-3; **20**, 87862-72-4; **21**, 87862-73-5; **22**, 87862-74-6; **23**, 87862-75-7; **24**, 87862-76-8; **25**, 87862-77-9; **26**, 87862-78-0; **27**, 87862-79-1; **30**, 87862-82-6; **35**, 87862-88-2; (*E*)-**36**, 87862-85-9; (*Z*)-**36**, 87862-92-8; **39**, 87862-86-0; **40**, 87862-83-7; $CH_2{=}C(CH_2SiMe_3)CH_2OSO_2Me$, 74532-54-0; $ClCH_2(CH_2)_2CO_2Et$, 3153-36-4; Ph_3P, 603-35-0; $EtO_2CCH_2NH_3Cl$, 623-33-6; piperonal, 120-57-0.

Structure of Majusculamide C, a Cyclic Depsipeptide from *Lyngbya majuscula*

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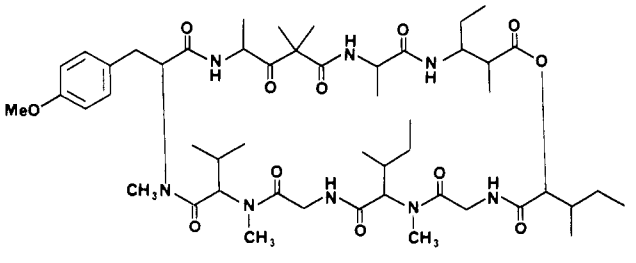
Majusculamide C, a novel cyclic depsipeptide that inhibits the growth of a number of fungal plant pathogens, has been shown to consist of seven α-amino acid units, one β-amino acid unit, and one hydroxy acid unit. The structures of the units have been determined by acid hydrolysis of the fungicide to glycine, L-alanine, L-*N*-methylvaline, L-*N*,*O*-dimethyltyrosine, L-*N*-methylisoleucine, racemic 2-amino-4-methylpentanone, 3-amino-2-methylpentanoic acid of undefined stereochemistry, and *N*-[2(*S*)-hydroxy-3(*S*)-methylpentanoyl]glycine. Sequencing of the units implied from the structures of the hydrolysis products has been achieved by mass spcetral and proton NOE studies.

Lyngbya majuscula is a toxic blue-green alga which grows abundantly on the pinnacles in the lagoon of Enewetak Atoll in the Marshall Islands.[3] At least two distinct varieties of *L. majuscula* grow in the lagoon, one that is found in shallow water (<6 m) and another which inhabits deep water (7.5–30 m). Two major lipophilic constituents of the shallow water variety are majusculamide A, a lipodipeptide identified as *N*-[(2*R*)-2-methyl-3-oxodecanoyl]-D-*N*,*O*-dimethyltyrosyl-*L*-*N*-methylvalinamide, and majusculamide B, the *N*-[(2*S*)-2-methyl-3-oxodecanoyl] epimer of majusculamide A.[4] A major lipophilic constituent in the deep water variety is majusculamide C (**1**), a novel cyclic depsipeptide that controls



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the growth of a number of fungal plant pathogens such as *Phytophthora infestans*, the causative organism of tomato late blight, and *Plasmopora viticola*, the causative organism of grape downy mildew.[5]

Majusculamide C is not present in the shallow water variety, nor are majusculamides A and B found in the deep water variety.[6] None of the majusculamides are responsible for the toxicity of *L. majuscula*, even though majusculamide C is fairly cytotoxic. The toxicity is attributed to aplysiatoxin, debromoaplysiatoxin, and lyngbyatoxin A, three highly inflammatory agents that have been shown to be powerful tumor promoters.[7,8] In this report we describe the structure determination of majusculamide C.

Isolation. The majusculamide C producing variety of *L. majuscula* grows abundantly on most of the pinnacles in the lagoon of Enewetak. Similar deep water varieties of *L. majuscula* have not been found to date in Hawaii or other areas of the Pacific such as Kwajalein, Johnston, and Fanning Islands. The alga used in this work was collected from Reefer 8 and South Medren Pinnacles at Enewetak. The lipophilic extract of the alga was subjected to absorption chromatography, gel filtration, and reverse-phase chromatography to obtain the depsipeptide as a colorless amorphous solid in 0.05–0.1% yield based on the dry weight of the alga. Attempts to crystallize majusculamide C have so far failed in our hands.

Structure Determination. Majusculamide C was found to have an elemental composition $C_{50}H_{80}N_8O_{12}$ based on a molecular weight of 984 daltons from field-desorption and fast-atom bombardment mass spectrometry and de-

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(2) Work performed while on sabbatical leave from the Department of Chemistry, Whitman College, Walla Walla, WA.
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(5) Moore, R. E.; Mynderse, J. S. U.S. Patent 4 342 751, 1982.
(6) In our earlier papers we erroneously referred to the deep water variety of *L. majuscula* from Enewetak as *L. gracilis*. Moore, R. E. *Bioscience* **1977**, *27*, 797.
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