Polarography. The reduction potential of 2-phenyl-1-pyrrolinium perchlorate **2**; (0.87 V) was obtained through differential pulsed polarography (Parr Model 174A) at a dropping mercury electrode. The experimental conditions were as follows: concentration of iminium salt, $\sim 2 \times 10^{-4}$ (CH_3CN); concentration of electrolyte (tetraethylammonium perchlorate), 0.1 M; reference electrode, saturated calomel electrode; range, 0 to -1.5 V; sensitivity, 5 μA; scan rate 2 mV/s.

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Photocyclizations of *N*-Allyliminium Salts Leading to the Production of Substituted Pyrrolidines

Jerome L. Stavinoha, Patrick S. Mariano,*[1] Andrea Leone-Bay, Rosemarie Swanson, and Christopher Bracken

Contribution from the Departments of Chemistry, University of Maryland, College Park, Maryland 20742, and Texas A&M University, College Station, Texas 77843.
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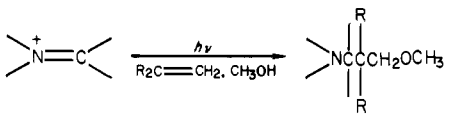
Abstract: The photochemistry of a number of *N*-allyliminium salts has been investigated. Results from the study of 5-vinyl-1-pyrrolinium (**10** and **11**), *N*-allyliminium (**22** and **28**), and 1-allyl-1-pyrrolinium (**40** and **41**) perchlorates demonstrate that photocyclization occurs upon irradiation in methanolic or aqueous acetonitrile solution to generate pyrrolidine containing monocyclic and bridged and fused bicyclic amino ethers and alcohols. The reactions observed are moderate yielding (40–60%) and proceed most probably via the singlet excited state of the conjugated iminium salt chromophores. Electron-transfer mechanisms analogous to those operating in olefin–iminium salt photoadditions appear to be responsible for these photocyclizations.

Introduction

In the preceding article,[2] we described a novel class of photochemical reactions occurring between electron-rich olefins and iminium salts which lead to the generation of interesting photoaddition products. The process, outlined in eq 1, involves, in a



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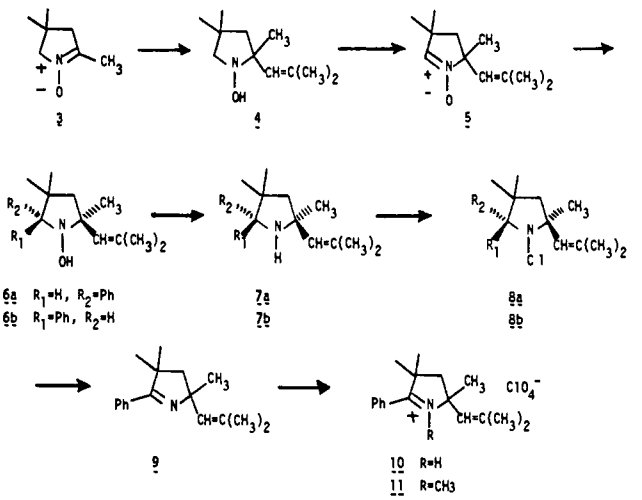
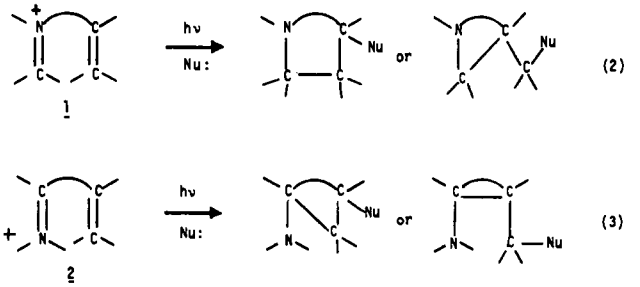
formal sense, the anti-Markovnikov addition of the solvent methanol and the iminium salt to the olefin. Mechanistically, this carbon–carbon bond-forming process appears conveniently rationalized by use of pathways involving initial electron transfer from olefin to excited iminium salt. Importantly, the addition regiochemistry is consistent with predictions based upon the preferred direction of nucleophilic attack by methanol on the intermediate cation radical derived from the olefin. Moreover, the stereochemical course of the photoadditions and the absence of skeletal rearrangements serve as support for a mechanism occurring through short-lived cation–radical pairs. Finally, the addition reactions proceed in reasonably high chemical yeilds despite the fact that in the cases studied carbon–carbon bond formation takes place between two highly crowded centers. Several cases have been presented, for example, where reaction occurs to generate two contiguous quaternary carbons.

The features summarized above are among those considered as key criteria in the evaluation of new and potentially useful synthetic transformations. On this basis, we have initiated a program to explore the synthetic potential of iminium salt photochemistry. Our first challenge was to test the intramolecular version of this process with *N*-alkenyl **1** and *C*-alkenyl **2** iminium salts in order to determine if it would serve as a useful photocyclization method in the preparation of heterocyclic and carbocyclic systems (eq 2 and 3). We now report the results of our initial studies in this area in which the photochemistry of a series of *N*-allyliminium salts have been investigated.[3] The observations

Scheme I





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(1) To whom correspondence should be addressed at Department of Chemistry, University of Maryland, College Park, MD 20742.
(2) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.*, previous paper in this issue.
(3) Mariano, P. S.; Stavinoha, J. L.; Swanson, R. *J. Am. Chem. Soc.* **1977**, *99*, 6781.

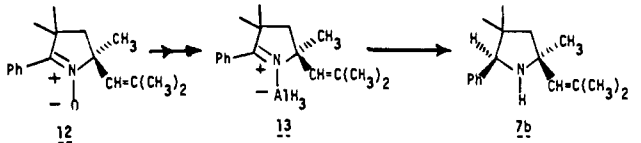
0002-7863/81/1503-3148$01.25/0

made demonstrate that the reaction might serve as a useful method for construction of the pyrrolidine ring in monocyclic and bridged and fused bicyclic systems. In addition, the study has provided additional information in support of electron-transfer mechanisms for olefin–iminium salt photoaddition and photocyclization reactions.

Results

Photochemistry of 2-Phenyl-5-vinyl-1-pyrrolinium Perchlorates. The 2-phenyl-5-isobutenyl-1-pyrrolinium salts **10** and **11** were selected for study as part of our initial investigations in this area of photochemistry. This choice was governed by a number of factors including the ease of synthesis by starting with the known 2,4,4-trimethyl-1-pyrrolin-1-oxide (**3**).[4] The sequence used to transform **3** to the 1-pyrroline **9**, a direct precursor for the corresponding iminium salts, is reasonably straightforward (Scheme I). Addition of isobutenylmagnesium bromide,[5] prepared from "super magnesium",[6] to the nitrone **3** produces the hydroxylamine **4** (70%; mp 42–44 °C). The isobutenylpyrroline oxide **5**, derived from **4** by mercuric oxide oxidation ($CHCl_3$, 98%), is then converted to a 63:37 mixture of the substituted hydroxylamines **6** of undefined stereochemistry. The major isomer selectivity crystallizes from a pentane solution (39%; mp 115–116 °C). The overall yield of this phenyl Grignard addition is nearly quantitative based upon the amount of the epimers of **6** remaining in the mother liquor. The crystalline hydroxylamine is reduced by use of AlH_3 (generated from $LiAlH_4$ and $AlCl_3$, Et_2O, 96%) furnishing the pyrrolidines **7**.

It is interesting to note that **7** is produced as a 9:1 mixture of epimers by starting with a single diastereomer of the hydroxylamine **6**. Moreover, this ratio of the epimeric pyrrolidines **7** is identical with that produced (68%) by AlH_3 reduction of the nitrone **12**, prepared by oxidation of **6a** or **6b** (HgO, CH_2Cl_2,



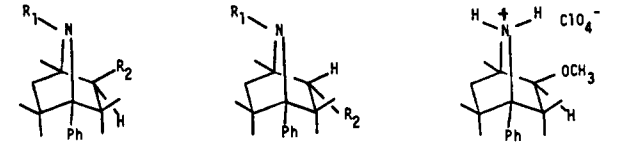
12 **13** **7b**

100%). These reductions most probably proceed via a common imine–aluminate intermediate, **13**, arising by elimination from the hydroxylamine *O*-aluminate. Hydride delivery to **13** should take place from the less-hindered face, trans to the C-5 methyl, yielding the *cis*-phenylmethyl epimer **8a**.[7] Thus, these data suggest that the mechanism for reduction of nitrones and hydroxylamines by use of AlH_3 does not involve simple nucleophilic substitution by hydride on the initially formed hydroxylamine–aluminate complex.

Conversion of the pyrrolidines **7** to pyrroline **9** is accomplished by chlorination (NCS, Et_2O, 100%) to generate the epimeric *N*-chloro amines **8**, followed by dehydrochlorination (KOH, CH_3OH, 72%). Spectroscopic data for **9** serve as supportive evidence for its structural assignment. This substance contains the phenyl-conjugated imine group as evidenced by the resonance at 175.9 ppm in the ^{13}C NMR spectrum, an isobutenyl side chain shown by doublets at δ 1.68 and 1.79 for the allylic methyls, and a multiplet at δ 5.44 for the vinyl hydrogen.

The crystalline *N*-methylpyrrolinium perchlorate **11** (mp 126–127 °C) is derived from **9** by reaction with methyl iodide in ethanol followed by perchlorate anion exchange on Dowex I-X8. The UV spectrum of this salt contained a maximum at 257 nm (log ϵ 3.68). This and the ^{13}C resonance at 192.9 ppm are characteristic of conjugated iminium salt chromophores. Generation of the N-protonated pyrroline **10** can be performed prior to irradiation by the addition of 1.82 equiv of perchloric acid to a methanolic solution of **9**. This results in a simultaneous decrease in the UV absorption band at 234 nm and an appearance of a new maximum at 266 nm (log ϵ 4.05) with an isosbestic point at 247 nm. Complete reversal of this change can be effected by the addition of base.

Irradiation of a methanolic solution of **10** (4.3 mM) with Corex-filtered light leads to the consumption of the pyrrolinium salt and simultaneous formation of a major photoproduct **14ex**



14ex R_1=H, R_2=OCH_3
15ex R_1=H, R_2=OH
16ex R_1=CH_3, R_2=OCH_3

14en R_1=H, R_2=OCH_3
15en R_1=H, R_2=OH
16en R_1=CH_3, R_2=OCH_3

17

which is isolated in pure form (44%) by neutralization and concentration of the crude photolysate followed by TLC on silica gel. GLC analysis of this material indicated that it is contaminated with a trace (ca. 1%) quantity of a substance corresponding most probably to the *endo*-methoxy isomer **14en**. Irradiation of this pyrrolinium salt in 25% (v/v) aqueous acetonitrile brings about similar results. Workup of the photolysate in the manner described above followed by preparative GLC (OV-101, 170 °C) furnishes the *exo*-azabicycloheptanol) **15ex** in 58% yield (mp 96–98 °C). It is important to note here that the reactions of **10**, leading to formation of the 7-azabicyclo[2.2.1]heptane ring system, occur with extreme selectivity, giving one of the two configurational isomers possible as a result of the creation of a new chiral center at C-2.

In an analogous fashion, the *N*-methylpyrrolinium perchlorate **11** undergoes photocyclization when irradiated in methanol to produce after workup the epimeric amino ethers **16ex** and **16en** in a 7:2 exo to endo ratio. Importantly, experiments conducted with the pyrrolinium salts **10** and **11** as dark controls (e.g., refluxing aqueous or methanolic solutions) failed to promote reaction. Thus, the cyclization processes are definitely excited state in nature.

Elucidation of the structures and stereochemistry of the substituted 7-azabicycloheptanyl ethers and alcohols obtained by photocyclization of **10** and **11** was accomplished through the utilization of comparative spectroscopic data, chemical interconversions, and single-crystal X-ray diffraction of the ammonium perchlorate salt **17** derived from **14ex**. The proton NMR spectrum of **14ex** (Table I) contains resonances (δ 0.52 and 0.69) which indicate that two methyl groups are located in the shielding region of the aromatic ring. Three other methyl groups, all bonded to quaternary carbons, a methoxy group, a D_2O exchangeable proton, and a phenyl group are also evident from inspection of the ^1H NMR spectrum. The ^{13}C NMR spectrum (Table I) shows the presence of a quaternary carbon at 78.5 ppm (C-4) and a methine carbon at 98.9 ppm (C-2). In addition, the fact that six signals are observed in the ^{13}C NMR spectrum for the aromatic ring carbons suggests that rotation of this residue is hindered. These data are consistent with assignment of the 7-azabicyclo[2.2.1]-heptan-2-yl methyl ether structure to this substance. However, the absence of vicinally disposed protons in **14ex** or of long-range or through-space interactions prevents a delineation of C-2 stereochemistry by spectroscopic methods.

Confirmation of the structural and stereochemical assignments to **14ex** was made by single-crystal X-ray diffraction on the ammonium perchlorate derivative **17** which was prepared by the addition of 1 equiv of perchloric acid to **14ex**. Benzene was added and repetitively removed in vacuo to azeotropically remove water and effect crystallization. Suitable crystals (mp 288–290 °C) for X-ray crystallography were grown from chloroform. The principal features of the crystallographic study are reported elsewhere.[8]

(4) Bonnett, R.; Brown, R. F. C.; Clark, V. M.; Sutherland, I. O.; Todd, A. *J. Chem. Soc.* **1959**, 2094.
(5) Braude, E. A.; Coles, J. A. *J. Chem. Soc.* **1950**, 2012.
(6) Rieke, R. D.; Bates, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.
(7) We are not certain of the stereochemistry of the major epimer obtained from this reaction. On the basis of the *A* values of CH_3 (1.7) and $CH{=}CH_2$ (1.35) it would appear that the less hindered face is that cis to $CH{=}CH_2$.

(8) Swanson, R.; Stavinoha, J. L.; Mariano, P. S. *Cryst. Struct. Commun.*, in press.

Table I. Characteristic ^1H NMR and ^{13}C NMR Chemical Shifts for the 7-Azabicycloheptanyl Ethers and Alcohols

identity	chemical shifts,[a] ppm				
	14ex	15ex	16ex	16en	17
		Protons			
exo-CH_3	0.52	0.62	0.76	0.82	0.92
	0.69	0.69	0.81	0.85	0.96
endo-CH_3	1.18	1.31	1.17	1.14	1.64
	1.31	1.42	1.36	1.23	1.67
C1 CH_3	1.56	1.52	1.39	1.43	1.76
H-6	1.47	1.62	1.36		2.10
			1.83		2.29
H-2	2.99	3.44	3.06	3.35	3.56
		Carbons			
C1	64.0	64.0	66.6		71.8
C2	98.8	87.1	96.8		92.1
C4	78.5	78.8	82.4		86.0
exo-CH_3	18.3	18.0	15.6		15.5
	24.4	23.9	24.8		23.5
endo-CH_3	26.6	25.8	27.8		27.1
	28.9	28.2	31.8		
C1 CH_3	33.3	32.6	32.8		31.7

[a] Relative to Me_4Si.

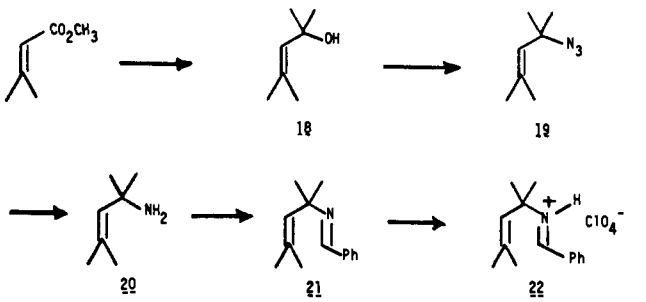
With this information in hand it was then possible to delineate the structures and stereochemistry of the remaining photoproducts arising from irradiation of **10** and **11**. For example, the amine alcohol arising from photocyclization of **10** in aqueous acetonitrile solution was shown to possess the bicyclic structure represented by **15ex** through its conversion to the *exo*-methyl ether **14ex** (NaH, CH_3I, THF, 80%). N-Methylation of **14ex** ($(CH_3O)_2SO_2$, K_2CO_3, THF, 70%) generated a tertiary amine ether identical in all respects with the major photoproduct **16ex** arising from irradiation of **11** in methanol. Finally, comparison of the spectroscopic data for **16ex** and **16en** suggests their C-2 epimeric nature.

Reaction Multiplicity. The multiplicities of the excited states of **10** and **11** undergoing the photocyclization process described above were investigated by use of sensitization and quenching studies. Benzophenone sensitized irradiation of **10** with uranium-glass-filtered light in methanol results in inefficient production of **14ex** (6%) under conditions which lead to complete disappearance of **10**. Also, photoreduction of benzophenone to benzopinacol is 23% less efficient when irradiation is conducted on methanolic solutions containing **10**. Approximately 40% more benzophenone is recovered after irradiation when **10** is present. These observations could indicate that triplet energy transfer occurs from benzophenone ($E_T \approx 68$ kcal/mol) to the pyrrolinium salt **10** under the sensitized reaction conditions and that the major excited-state photocyclization reaction pathway to **14ex** is through the singlet excited state of **10**. However, in the absence of further data this conclusion remains tentative.

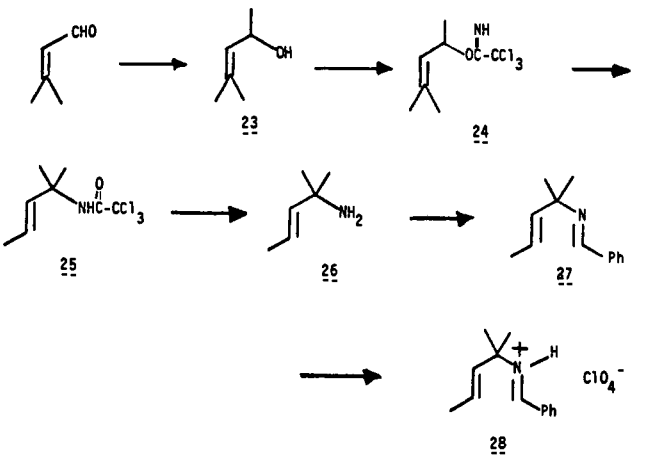
Results from similar studies with the *N*-methylpyrrolinium salt **11** are less demonstrative. This salt is recovered quantitatively after benzophenone-sensitized irradiations in methanol. Likewise, **11** does not quench benzpinacol formation from the triplet of benzophenone. Thus, the triplet energy of benzophenone must be sufficiently lower than that of **11** to make triplet energy transfer prohibitive. Studies employing higher energy triplet sensitizers were not undertaken.

Experiments were also conducted to explore the effect of compounds, known to interact with the singlet excited states of 2-phenyl-1-pyrrolinium salts,[2] on the photoreactivity of the *N*-methyl salt **11**. Irradiation of methanolic solutions of **11** containing low concentrations of the conjugated diene, *cis*-piperylene, results in an enhanced efficiency for production of the cyclization products **15** (See Experimental Section). This unusual result appears to be due to piperylene quenching of the formation of impurities which absorb light competitively with **11**. Indeed, a yellow color develops in the photolysate derived from irradiations in the absence of *cis*-piperylene, whereas the samples containing the diene remained colorless throughout the entire irradiation period. The formation of a new photoproduct of higher boiling point than **15** (GLC) occurred to a significant extent when **11** was irradiated in methanol solution containing high concentrations of *cis*-piperylene. Although this photoproduct was not identified, it most probably results from photoaddition of piperylene to **11** in a fashion analogous to the butadiene 1-phenyl-1-pyrrolinium perchlorate reaction described earlier.[2] Concurrent with the buildup of this new photoproduct is the decrease in production of the N-methylamino ethers **15**.

Scheme II



Scheme III



Photochemistry of Acyclic *N*-Allyliminium Salts. The above results suggest that our hypothesis concerning the use of *N*-allyliminium salt photocyclization reactions as a method for pyrrolidine ring formation might be valid. The generality of this process has been probed by study of two simple, acyclic model systems, the iminium salts **22** and **28**. Synthetic sequences used to prepare the benzaldimines **21** and **27**, precursors of these salts, differ in the method selected for generation of the allylamines **20** and **26**. The tetramethylallylamine **20** is prepared (Scheme II) by starting with methyl β,β-dimethylacrylate. 2,4-Dimethylpent-3-en-2-ol (**18**), derived from this ester by addition of methyllithium, is converted to the azide **19** by treatment with hydrazoic acid (NaN_3, H_2SO_4, $CHCl_3$). Lithium aluminum hydride reduction of **19** proceeds smoothly to afford **20** which condenses with benzaldehyde to furnish the desired aldimine **21**. Overman's procedure[9] for allylamine synthesis was used to prepare **26** (Scheme III). Accordingly, the allylic alcohol **23** is converted to the trichloroacetamide **25** via the nonisolated imidate ester **24**. This is saponified to produce the desired amine **26** which is transformed into the imine **27** by reaction with benzaldehyde. The olefinic π-bond stereochemistry in the iminium salt **28** is established during aza-Claisen rearrangement of the trichloracetimidate. Infrared spectroscopic data for the amide **25**, amine **26**, and imine **27** demonstrate the trans geometry of this bond as is expected for concerted rearrangement of **24** via a six-center transition state having the developing allylic methyl group in a pseudoequatorial orientation.

Generation of the iminium perchlorates **22** and **28** is accomplished in situ prior to irradiation by the addition of 4.4 equiv of

(9) Overman, L. E. *J. Am. Chem. Soc.* **1974**, *96*, 597; **1976**, *98*, 2901.

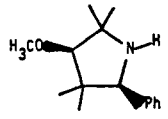
Table II. ^{1}H NMR Spectroscopic Data for the Pyrrolidines **29t**, **29c**, and **30** in the Presence and Absence of Eu(fod)$_3$

protons	chemical shifts[a]		
	29t	**29c**	**30**
CH_3 at C-4[b]	0.55 (1.56)	0.58 (1.42)	0.59
CH_3 at C-4[c]	0.96 (3.14)	0.98 (2.00)	
CH_3 at C-2	1.12 (4.50)	1.11 (4.92)	1.15
CH_3 at C-2	1.26 (7.04)	1.28 (4.20)	1.32
H at C-3	3.08 (3.58)	2.90 (3.33)	3.05
OCH_3	3.38 (1.60)	3.38 (1.26)	3.40
H at C-5	3.83 (3.58)	4.01 (3.72)	4.48
Ph	7.1–7.4 (2 H, 2.58, and 3 H, 0)	7.1–7.4 (2 H, 1.86, and 3 H, 0)	7.1–7.3

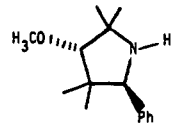
[a] Spectra were recorded in CCl_4 solvent (values in parts per million relative to Me_4Si). The values in parentheses are the shift differences (in parts per million) per mole of Eu(fod)$_3$ per mole of pyrrolidine. [b] Cis to Ph. [c] Trans to Ph.

perchloric acid to the respective imines, **21** and **27**. The UV spectra of these salts contained maxima at 273 nm with molar absorptivities in the range of 16 000. The perchlorate salts remained unreactive after being stirred in methanol solutions for extended time periods in the dark.

Irradiation of methanol solutions containing the tetramethylallyliminium salt **22** (4.98 mM) with Corex-filtered light led to the formation of two photoproducts, **29c** and **29t**, in a ratio of 1:4



29c

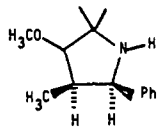


29t

and an overall isolated yield of 51%. The structures and stereochemistry of these materials were elucidated by use of spectroscopic methods. The ^{13}C NMR spectrum of the major product **29t** contained resonances for four methyl, two quaternary, and two methine carbons. The methine carbon signals at 97.6 and 66.7 ppm indicated the presence of O–CH and N–CH–Ph moieties in this photoproduct. This data when combined with that accumulated from the ^{1}H NMR spectra (Table II) of the photoproducts strongly support assignments of the structures of **29c** and **29t** as the epimeric 2,2,4,4-tetramethyl-3-methoxy-5-phenylpyrrolidines. The difference between the chemical shifts for the H-3 methine protons (0.18 ppm) in the proton spectra of **29c** and **29t** might be rationalized by a deshielding effect of the phenyl group on H-3 in the cis isomer. This would require a fixed or predominant conformation having phenyl groups aligned in a bisected (with respect to the ring) geometry, thus avoiding steric interactions with the methyl group at C-4. Indeed, one of the two methyl groups at C-4 in both photoproducts experiences a large upfield shift as would be expected on the basis of its location in the shielding region of the aromatic residue. The orientation necessary for the shielding effect on the methyl protons and deshielding of H-3 is seen by inspection of molecular models to be the expected low-energy conformation of this substance.

The results from lanthanide shift NMR studies aid in a tentative stereochemical assignment. Although much of the data obtained are inconclusive due to the bulky nature of the molecule and, thus, low complexation affinity of the reagent, one result obtained is especially helpful. In both epimers of **29**, the shift reagent can complex both at the amine and ether functional groups. Indeed, if complexation takes place at both centers, the methyl protons at C-2 cis to OCH_3 at C-3 should experience a larger downfield shift than when this dichelation is absent. Chelation effects have been noted in other molecules in which the two or more functional groups involved have about the same complexing ability with the shift reagent.[10,11] Although amines are generally much better complexing agents than ethers, their effectiveness is very dependent upon steric factors.[10] The reduced complexing ability of sterically hindered amines like **29t** and **29c** would make complexation by an ether oxygen more competitive, and, thus, chelation would be a likely possibility. However, the cis relationship between phenyl and methoxy substituents in **29c** would block chelation due to large steric interactions between the phenyl group aligned over the ring and the lanthanide complex. In fact, the results indicate that only in the case of **29t** does a large lanthanide-induced shift (Δ = 7.04 ppm) of one of the methyl proton resonances occur. This effect was noted for the isomer which contains the low-field H-3 proton resonance. Thus, the major photocylization product arising from irradiation of the allyliminium salt **22** is most probably the *trans*-methoxyphenylpyrrolidine.

Gas chromatographic analysis of the photolysate obtained by irradiation of the trimethylallyliminium perchlorate **28** in methanol indicated that two major products, **30** (25%) and **31** (35%) are



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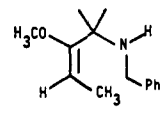

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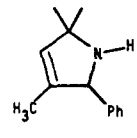

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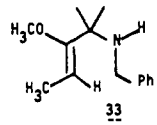

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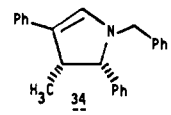

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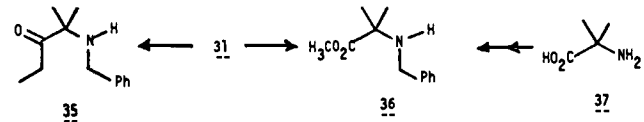
produced. Although separation of these materials on a preparative scale was difficult, it is possible to isolate sufficient quantities of each by liquid chromatography to allow their identification. A third substance, tentatively identified as the 3-pyrroline **32**, is detected in a 7% yield by this method. However, since GLC analysis indicates that this material is not present in the crude photolysate, it is possible that it arises from the pyrrolidinyl ether **30** by loss of methanol during chromatography on silica gel.

The minor photoproduct was identified as the pyrrolidinyl ether **30** on the basis of spectroscopic data which were found to be characteristically similar to those accumulated for the related tetramethyl analogues **29** and other five-membered nitrogen heterocycles (Table II). The relative configurations at the three contiguous chiral centers in **30** were difficult to delineate by use of ^{1}H NMR spectroscopic parameters. However, two pieces of information aided in the assignment of a cis relationship between the phenyl and methyl groups at the C-4 and C-5 positions of **30**. The coupling constant for the H-4 and H-5 protons was found to be 8.0 Hz, a value nearly identical with that between the H-4 and H-5 protons in the spectrum of the known[10] *cis*-diphenylmethyl-2-pyrroline **34**. Another indicator of the cis alignment of methyl and phenyl groups in **30** is the abnormally high field values observed for the resonances of the C-4 methyl protons (δ 0.59) and carbon (15.6 ppm). This suggests that the methyl group at C-4 is located in the shielding region of the adjacent phenyl group. It should be noted that this same effect is operative in the tetramethylpyrrolidines **29** and results in the large upfield carbon and proton chemical shifts for the cis *C4*-methyl group at δ 0.55 and 15.4 ppm.

The major photoproduct **31**, resulting from irradiation of **28**, contains an unusual enol ether linkage as judged by inspection of spectroscopic data and through the observation that it undergoes ready acid-catalyzed hydrolysis to the amino ketone **35**. Since

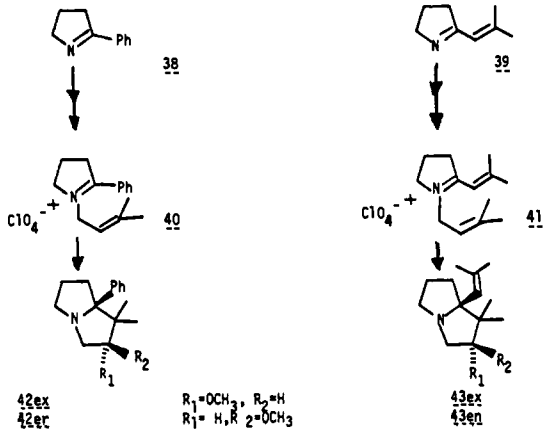


35 **31** **36** **37**

(10) Borel, D.; Gelas-Miahle, Y.; Vessiere, R. *Can. J. Chem.* **1976**, *54*, 1590.

(11) Pascual, C. I.; Meler, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164. This topic is also discussed in: Jackman, L. M.; Sternhell, S. "Applcations of NMR in Organic Chemistry"; Academic Press: New York, 1969; pp 184–188.

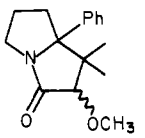
Scheme IV



the origin of this photoproduct could provide additional information about the mechanism involved in the *N*-allyliminium salt photocyclizations, it was essential that an unambiguous proof of the structure of **31** be obtained. This was accomplished through a sequence which correlated this material with *N*-benzyl-α-methylalanate **36**, independently prepared by a straightforward procedure starting with the commercially available α-methylalanine (**37**). Ozonolytic cleavage of **31** produced an amino ester identical in all respects with the synthetic material **36**. These chemical correlations do not provide information about the π-bond stereochemistry of the enol ether **31**. Importantly, a substance tentatively identified as the isomeric ether **33** can be obtained in small quantities by repetitive chromatography of large quantities of the crude photolysate arising from irradiation of **28**. Although it is not certain whether this material is truly a photoproduct of **28** or if it arises from isomerization of **31** during the purification procedure, its spectroscopic parameters have aided in a preliminary stereochemical determination. The substituent shielding coefficients developed by Pascual, Meier, and Simon[11] for predicting chemical shifts of vinyl protons are useful in this regard. Accordingly, protons located cis to a vicinal alkoxy substituent should resonate at lower field than their trans counterparts. The same effects should apply to the allylic methyl substituents. The comparative vinyl (δ 4.92 for **30** and δ 4.54 for **33**) and allylic methyl (δ 1.67 for **30** and δ 1.84 for **33**) proton chemical shifts for the enol esters suggest that major photoproduct **31** possesses the *E* π-bond stereochemistry.

Photochemistry of 1-Allyl-1-pyrrolinium Salts. As discussed above, the major purpose of our exploratory investigations in this area is to gain information about the scope and structural versatility of photocyclizations of *N*-allyliminium salts. The examples presented thus far suggest that the process can be used to construct pyrrolidine-containing monocyclic and bridged bicyclic structures in reasonably high yields from appropriately substituted iminium salts. The generality of this process was further probed by examining its application to the preparation of nitrogen-containing, fused-bicyclic materials. The 1-(dimethylallyl)-1-pyrrolinium perchlorates **40** and **41**, selected for study in this phase, are easily prepared by prenylation of the corresponding 1-pyrrolines **38**[12] and **39** with 3-methylbut-2-en-1-yl bromide followed by perchlorate ion exchange (Scheme IV). The pyrroline **39** is generated by use of the general method of Bielawski[13] through the addition of isobutenyllithium to *N*-vinylpyrrolidone followed by aqueous acid hydrolysis of the intermediate enaminol.

Irradiation of a methanolic solution of the phenylpyrrolinium salt **40** followed by basic workup and molecular distillation leads to isolation of a 1:1 mixture (58%) of the epimeric hydropyrrolizidines **42**. The individual isomers can be obtained by preparative GLC. Consistent with these structure assignments are the ^{1}H NMR spectra of the photoproducts which contain resonances characteristic of methyl groups in highly shielded environments. The presence of two quaternary carbons, one of which is bonded to nitrogen, a methoxy-substituted methine carbon, and the characteristic methylenes of a pyrrolidine ring are all evident from inspection of the ^{13}C NMR data. Stereochemistry and structure were both delineated unambiguously by independent synthesis of **42ex** and **42en** from the stereoisomeric lactams **44**.[2] Lithium aluminum hydride reduction (93%) of a 7:3 mixture of *endo*- and *exo*-methoxy epimers of **44** led to formation of a 7:3 mixture of **42en** and **42ex**, respectively.



44

In a similar fashion, photocyclization of the analogous 2-isobutenyl-1-prenylpyrrolinium salt **41** in methanol gives after purification the epimeric pyrrolizidines **43** in a 68% yield. Separation of the endo and exo isomers formed in an ca. 2:1 ratio is accomplished by GLC. The presence of both the pyrrolizidine skeleton and the retained isobutenyl moiety is clearly indicated by proton and carbon spectroscopic data. Unfortunately, information available at this time is insufficient for stereochemical analysis of the major and minor photoproducts.

Photocyclization Quantum Efficiencies. The quantum yields for several of the *N*-allyliminium salt photocyclizations described above were measured at low conversion (ca. 1–4%) by using an optical bench apparatus described in the Experimental Section. The data collected for photocyclization of **10**, **11**, and **22** are accumulated in Table III.

Table III. Quantum Yields for Photocyclizations of the *N*-Allyliminium Salts **10**, **11**, and **22**

N-allyliminium[a,c] perchlorate	product ($\phi_{formation}$)[b]	*N*-allyliminium[a,c] perchlorate	product ($\phi_{formation}$)[b]
10	14ex (0.010)	**22**	**29** (0.007)
11	16 (0.005)		

[a] *N*-Allyliminium salt concentrations were ca. 5×10^{-3} M. [b] Conversions to product were <5%. [c] The solvent was CH_3OH in every case.

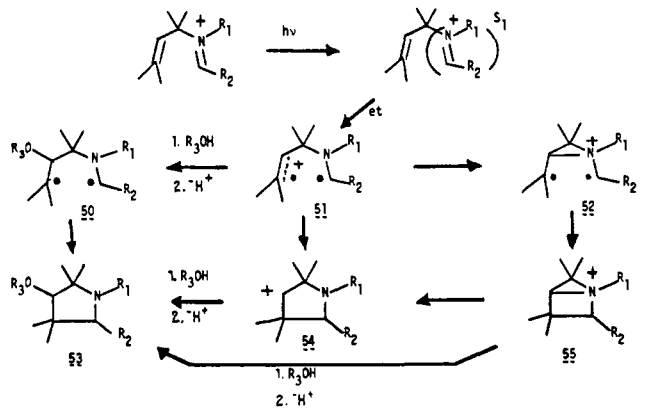
Discussion

The studies described above demonstrate that appropriately substituted *N*-allyliminium salts participate in a reasonably general photocyclization process when irradiated in hydroxylic solvents. This new cyclization method appears to be useful in constructing the 3-hydroxy- or 3-methoxypyrrolidine unit in a variety of monocyclic as well as bridged and fused bicyclic systems. In the cases studied, singlet excited states are responsible for the reactions which proceed in yields which range from 40% to 60%. Moreover, highly substituted pyrrolidines are produced through these pathways by carbon–carbon bond formation between two quaternary centers. The nature of the reactions observed and their stereochemistry require a brief discussion.

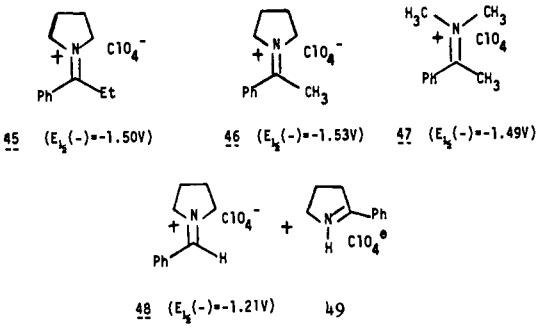
Reaction Mechanism. An accumulation of evidence gained through studies of olefin–iminium salt photoaddition reactions[2] suggests that the structural and stereo- and regiochemical features of the photocyclizations described above can be rationalized in terms of electron-transfer-initiated photochemical reaction mechanisms. Accordingly, intramolecular electron transfer from the olefin π systems, made electron rich by alkyl substitution, to

(12) Starr, D. F.; Bulbrook, H.; Hixon, R. H. *J. Am. Chem. Soc.* **1932**, *54*, 3971. Love, S. J.; Moore, J. A. *J. Org. Chem.* **1968**, *33*, 2361.
(13) Bielawski, J.; Brandange, S.; Lindblom, L. *J. Heterocycl. Chem.* **1978**, *15*, 97.
(14) Grundy, J.; James, B. G.; Patterson, G. *Tetrahedron Lett.* **1972**, 757.
(15) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc., London, Ser. A*, **1958**, *235*, 518.
(16) Saucy, G.; Marbet, R.; Lindlar, H.; Isler, O. *Helv. Chim. Acta* **1959**, *42*, 1945.
(17) Pappas, J. J.; Keaveney, W. P.; Gancher, E.; Berger, M. *Tetrahedron Lett.* **1966**, 4273.
(18) Zervas, L.; Theodoropoulos, D. M. *J. Am. Chem. Soc.* **1956**, *78*, 1359.

Scheme V



singlet excited iminium salt moieties is energetically feasible in the cases we have explored. A qualitative, yet informative, evaluation of electron-transfer efficiencies involves experimentally measurable properties including the donor oxidation potential ($E_{1/2}(+)$), acceptor reduction potential ($E_{1/2}(-)$), and singlet energy ($E_{0,0}$). Rehm and Weller[19] have demonstrated that an excellent correlation exists between the free energy for electron transfer, calculated from these parameters, and the rate constant for electron transfer. Although the electrochemical potentials and singlet energies of olefinic and iminium components of the *N*-allyliminium perchlorates have not been measured directly, reasonable estimates for these can be made by inspection of data for closely related substances. For example, application of trends noted for the reduction potentials of a series of iminium salts (e.g., **45**–**48**)[20] results in predicted $E_{1/2}(-)$ values for the NH salts, **10**,

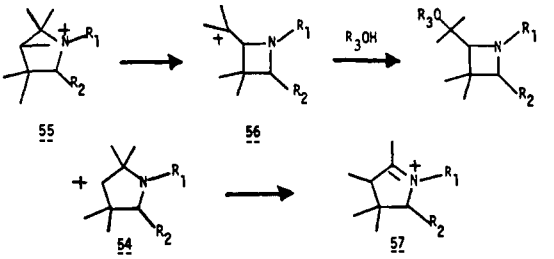


22, and **28**, of ca. −1.2 V and for the *N*-alkyl salts, **11**, **40**, and **41**, of ca. −1.5 V. Oxidation potentials for trisubstituted olefins, estimated from available ionization potentials (IP)[21] and the known relationship between $E_{1/2}(+)$ and IP,[22] should fall in the range of 1.8 V. On this basis, electron transfer to the singlet excited states ($E_{0,0} \approx 80$ kcal/mol) of iminium salts from olefins in the intramolecular systems should be rapid and compete effectively with other modes of excited-state decay of the iminium salt grouping. Indeed, intramolecular quenching of the singlet states of the phenyl-substituted pyrrolinium salt chromophores by the internal olefinic grouping is most probably the process responsible for the lack of fluorescence from these systems as compared with the highly fluorescent ($\phi = 0.6$) model pyrrolinium salt **49**.

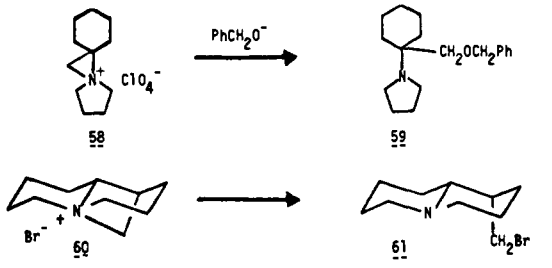
Nucleophilic attack by the solvent, methanol, or water on the charged moiety of the cation diradical **51** (Scheme V) generated by intramolecular electron transfer should be controlled by steric as well as electronic features. In the *N*-allyliminium salt systems studied, the terminal *gem*-dimethyl substitution should direct entry of nucleophiles to produce 1,5-diradicals **50**. Carbon–carbon bonding in **50** would lead to production of the observed 3-pyrrolidinyl ethers or alcohols **53**.

Alternative mechanistic rationale for the photocyclization reactions can be envisaged. For example, intramolecular nucleophilic attack by nitrogen on the radical cation moiety of **51** could occur to produce the aziridinyl dicarbinyl diradical **52** and the bicyclic azetidinium salt **55**. Likewise, **55** might arise through intramolecular [$_\pi$2 + $_\pi$2] cycloaddition pathways from the excited *N*-allyliminium salts. Collapse of the azetidinium salts by heterolytic cleavage of the internal CN bond followed by rapid capture of the resultant carbenium ion **54** by solvent would furnish the pyrrolidine products. Alternatively, the conversion of **55** to **53** could be concerted or the 3-pyrrolidinyl cation **54** might be generated directly from the cation diradical **51**.

The alternative mechanistic pathways considered above would require further refinement in order for them to represent feasible routes for the observed photocyclization reactions. The polycyclic azonium ions, represented by **55** in Scheme V, derived from the *N*-allyliminium perchlorates should hold the potential of reacting via a variety of the other pathways. Thus, cleavage of the external CN bond in **55**, for example, would generate in several of the cases studied a tertiary azetidinylcarbinyl cation **56** and azacyclobutane



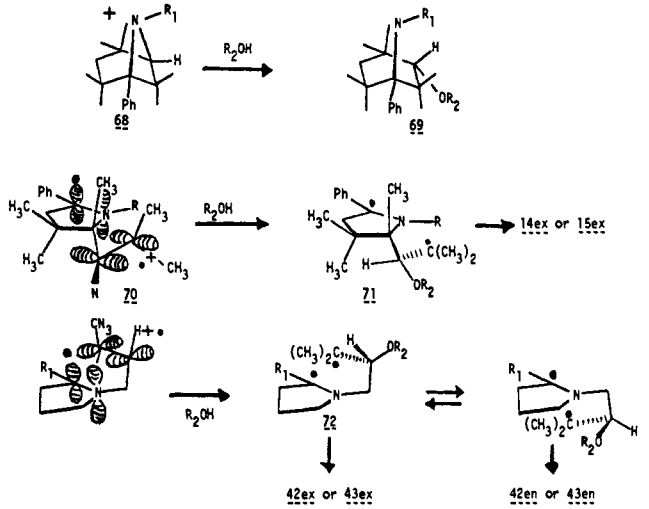
products. Likewise, the 3-pyrrolidinyl cations **54** should undergo rapid rearrangement to the potentially more stable tertiary and nitrogen-stabilized carbenium ions **57**.[23] Thus, if pathways involving the intermediacy of cations related to **54** are operative in photocyclizations of *N*-allyliminium salts, nucleophilic attack is required to be exceedingly rapid. The possible pitfalls associated with bicyclic azonium ion ring-opening selectivity and carbenium ion rearrangements can be eluded if nucleophilic attack occurs in concert with CN bond cleavage (e.g., **55** → **53**). In this event, nucleophiles should enter at the less substituted carbon adjacent to nitrogen, thus producing the five-membered heterocyclic ring systems. Precedent for this control derives from observations of S_N2-type aziridinium and azetidinium ring-opening reactions (e.g., **58** → **59**[24] and **60** → **61**[25]) in which the tendancy for cleavage of the bond to the least substituted α-carbon is demonstrated.



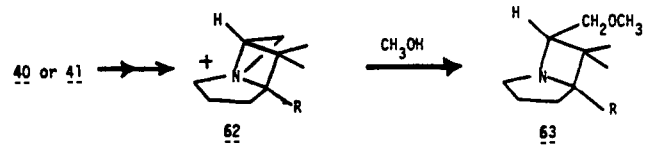
Photocyclization Stereochemistry. Mechanisms invoked to rationalize the structural and regiochemical features of the *N*-allyliminium salt photocyclization reactions must also be consistent with observed structural outcomes of reactions of the *N*-prenylpyrrolinium salts **40** and **41** and the stereochemical features of photocyclizations of the isobutenylpyrrolinium salts **10** and **11**.

(19) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(20) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1970**, *26*, 223.
(21) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937. Watanabe, K. W. *J. Chem. Phys.* **1957**, *26*, 542.
(22) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.
(23) The relative rates of internal vs. external bond cleavage should depend upon the energetic consequences of relief of ring strain vs. carbenium ion stability.
(24) Leonard, N. J.; Kiefer, E. F.; Brady, L. E. *J. Org. Chem.* **1963**, *28*, 2850.
(25) Fodor, G.; Mandava, N.; Welsz, I. *Tetrahedron* **1968**, *24*, 2357. Fodor, G., *J. Am. Chem. Soc.*, **1966**, *88*, 1040. Edwards, O. E.; Fodor, G.; Marion, L. *Can. J. Chem.* **1966**, *44*, 13.

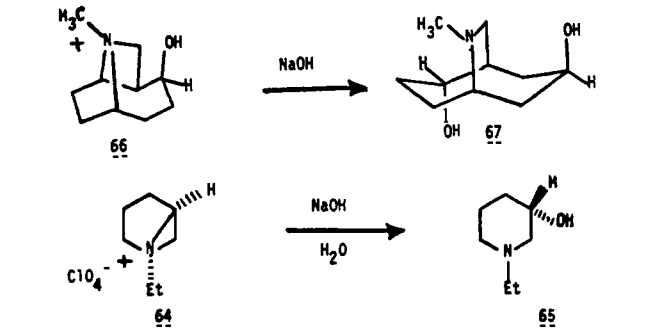
Scheme VI



Importantly, attack by methanol on the secondary center α to nitrogen in a tricyclic intermediate **62** would be less sterically demanding and would lead to production of the unobserved 1-azabicyclo[3.2.0]heptane product **63**.[26] S_N2 displacement at the

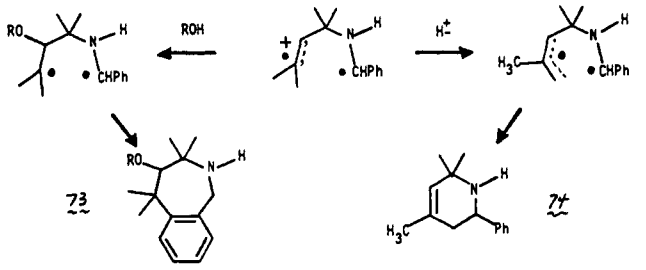


more crowded center in **62**, relieving more strain, would need to occur in order to yield the observed bicyclo[3.3.0]octan-3-yl ethers. Mechanisms for the photocyclizations via direct displacement on bicyclic azonium salts suffer from a more serious problem. The stereochemical courses of reactions proceeding through this pathway would be established during ring opening. Results from studies of several aziridinium and azetidinium salts clearly demonstrate that reactions of this type are stereospecific, with inversion of configuration at the carbon center undergoing reaction (e.g., **64** → **65**[27] and **66** → **67**[28]). Under these guidelines, ring opening

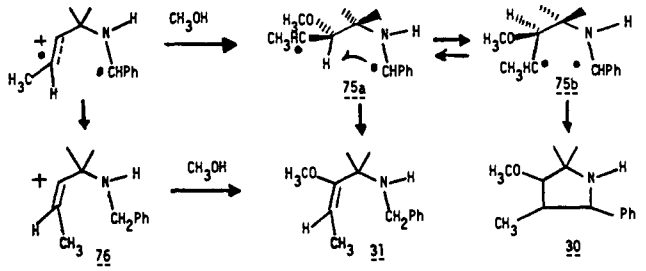


of the tricyclic azonium ions **68** in concert with attack by methanol or water should lead to stereoselective formation of an ether or alcohol product, **69**, having the C-3 functionality endo (Scheme VI). This is opposite from the experimental observation. Likewise, a direct displacement mechanism would predict exclusive formation of endo products from photocyclization of the *N*-prenylpyrrolinium salts **40** and **41**; mixtures of endo and exo diastereomers are generated.

Scheme VII



Scheme VIII



The stereochemical preferences displayed in *N*-allyliminium salt photocyclizations appear to be more easily rationalized by the electron transfer–nucleophilic addition–1,5-diradical cyclization sequences described above. Specifically, the stereoselective formation of the exo ethers and alcohols from **10** is amenable to analysis by this mechanism. The diradical cation **70** generated from $\mathbf{10}^{S_1}$ should be conformationally biased about the pyrrolidine–side chain bond as a result of an alignment of radical cation and amine radical moieties which provides maximum overlap of component orbitals. Additionally, this conformation minimizes repulsive interactions between the ring methyl substituents and the radical cation moiety. Attack by methanol or water at the secondary carbon should proceed more readily from the convex face of **70** in order to avoid steric strain provided by the crowded and reasonably rigid framework. Importantly, the C-3 stereochemistry of the bicyclic product is established at this step and is independent of the lifetime of the 1,5-diradical **71** formed as the ultimate mechanistic intermediate. Interestingly, the stereocontrol should be partially relaxed when a bulky substituent is present on nitrogen since the energetic driving force for conformational preferences would be weakened and entry of a nucleophile from the convex face would be hindered. This formulation then explains why the stereoselectivity for cyclization of the *N*-methyl salt **11** is not as pronounced. Finally, stereochemical control in cyclizations of the acyclic iminium and *N*-prenylpyrrolinium perchlorates is not necessarily expressed during capture of the diradical cation by nucleophiles. If cyclization of the 1,5-diradical intermediates (e.g., **72**) is slow compared to CN bond rotation, the exo/endo diastereomeric ratios will be governed by factors which influence diradical coupling rates.

Competitive Reaction Pathways. The closely related photoaddition reactions of olefin–iminium salt systems are known[2] to generate amino ether products by intermolecular reaction pathways which are analogous to those responsible for photocyclizations. In several of the intermolecular cases, amino olefin adducts were formed due to the operation of sequential electron transfer–proton transfer mechanisms. It is interesting that tetrahydropyridine containing products such as **74** (Scheme VII) which would arise through similar sequences are not observed from irradiation of *N*-allyliminium salts. Likewise, the 1,5-diradical intermediates arising from the acyclic and *N*-prenyliminium salts do not appear to undergo cyclization via attack on the aromatic ring producing

(26) Here again, energy contributions to the transition states for S_N2 displacements in these systems should come from steric factors and relief of ring strain. Literature data are not available so that no conclusions can be made about which of the factors would be of primary importance.

(27) (a) Hammer, C. F.; Heller, S. R. *Chem. Commun.* **1966**, 919. (b) Crist, D. R.; Leonard, N. J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 962.

(28) The reasons why the photocyclization product **30** deriving from **28** contains the cis arrangement of methyl and phenyl groups is not easily understood in terms of the electron-transfer mechanism since it would appear that 1,5-diradical coupling should more readily produce the trans isomer. It should be pointed out that mechanisms via an intermediate azahousane cation could accommodate the observed stereochemistry since it could be argued that both the methyl and phenyl groups in this species would be oriented exo to avoid repulsive interactions with the endo methyl group located at C-5 of the bicyclic framework.

tetrahydrobenzoazepines (e.g., **73**). No effective rationale can be provided to explain the absence of products from these types of reaction modes.

Equally elusive is a useful understanding of why the enol ether **31** is formed as a major product from irradiation of the trimethylallyliminium perchlorate **28**. The corresponding tetramethyl system does not yield even trace quantities of an analogous product. It is likely that **31** arises through disproportionation via a 1,5-hydrogen shift from the diradical **75**. Alternatively, a 1,5-hydrogen atom shift could occur earlier at the cation diradical stage producing **31** by methanol attack on the vinyl cation **76** (Scheme VIII). The surprising feature is that either or both of these disproportionation processes supervenes only when the 1,5-diradical contains two secondary terminal centers and not when one of the terminal carbons is tertiary. This result is contrary to the normal trend in free-radical chemistry where disproportionation routes become competitive with carbon–carbon bond formation when reacting centers are more highly substituted. It is possible that the differences in relative rates of coupling vs. H atom transfer might be related to substituent effects on preferred conformations of the 1,5-diradicals. Accordingly, extended conformations **75a** are required for disproportionation and closed geometries **75b** for pyrrolidine ring production. This conjecture requires further investigation in order to test its validity.

Experimental Section

General Methods. Proton NMR spectra were taken on a Varian T-60 or HA-100 spectrometer using tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained with a JEOL PS-100 spectrometer with a dedicated probe and Nicolet pulsed FT data collection system at an operating frequency of 25.0345 MHz with Me_4Si as an internal standard. Mass spectra were taken on a Du Pont CEC 21-110B high-resolution mass spectrometer. UV data were obtained with a Beckman Model ACTA III spectrometer. Infrared spectra were recorded on a Perkin-Elmer 237B grating infrared spectrophotometer.

Melting points were taken on a Griffin Mel-Temp capillary melting point apparatus and are reported uncorrected. Microanalysis were performed by Galbraith Laboratories, Inc. Preparative chromatographic work was done with either Baker TLC silica gel 7GF or Grace silica gel (Davison grade 923). Gas chromatographic analyses and separations were performed with Varian Model 2700 and 910 chromatographs. Molecular distillations were performed by using a Kugelrohr apparatus.

1-Hydroxy-2-isobutenyl-2,4,4-trimethylpyrrolidine (4). Highly activated magnesium metal was prepared by using the method of Riecke,[6] combining magnesium chloride (20.4 g, 0.214 mol), potassium iodide (17.8 g, 0.207 mol), and potassium metal (15.0 g, 0.107 mol), in anhydrous THF (500 mL) under Ar and heating the mixture at reflux for 2 **h**. After the mixture was cooled to room temperature, isobutenyl bromide (14.4 g, 0.107 mol), prepared by the method of Braude and Coles,[5] was added dropwise. Ten minutes were allowed after addition for complete reaction to occur and 2,4,4-trimethyl-1-pyrroline 1-oxide[4] (11.1 g, 0.087 mol) was added dropwise. The mixture was heated at reflux for 45 min, cooled to 25 °C, and quenched with saturated NH_4Cl. The solution was extracted with ether. The combined ethereal extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo, giving 14.0 g (88%) of **4** as a yellow solid, mp 37–41 °C. The crude hydroxylamine was of sufficient purity to be used directly. Recrystallization from pentane gave 9.80 g (62%) of pure 1-hydroxy-2-isobutenyl-2,4,4-trimethyl pyrrolidine: mp 42–44 °C, IR ($CHCl_3$) 3200, 2940, 2910, 2840, 1620, 1440, 1370, 1070 cm^{-1}; ^1H NMR (CCl_4) δ 1.01 (s, 3 H, *gem*-CH_3), 1.08 (s, 3 H, *gem*-CH_3), 1.24 (s, 3 H, C-2 CH_3), 1.74 (s, 2 H, methylene), 1.64 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.68 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 5.64 (m, 1 H, vinylic H), 7.42 (br s, 1 H, OH); mass spectrum (70 eV), *m/e* (relative intensity) 183 (4, M^+), 169 (12), 168 (100), 136 (13), 128 (38), 127 (46), 123 (16), 110 (14), 96 (11), 95 (11), 81 (18), 69 (10), 55 (19), 53 (10), 41 (27), 39 (12); ^{13}C NMR ($CDCl_3$) δ 130.2 (s, d, olefinic), 68.3 (s, C-2), 67.6 (t, C-5), 51.1 (t, C-3), 33.1 (s, C-4; q, CH_3), 31.1, 30.8, 26.8, 19.3 (q, other methyls); UV (EtOH) λ_{max} 234 nm (log ϵ 2.66); high-resolution mass spectrum, *m/e* 183.162 ($C_{11}H_{21}NO$ requires 183.1623).

5-Isobutenyl-3,3,6-trimethyl-1-pyrroline 1-Oxide (5). 1-Hydroxy-2-isobutenyl-2,4,4-trimethylpyrrolidine (7.68 g, 3.94 mmol) and yellow mercuric oxide (17.13 g, 79.0 mmol) were stirred under N_2 for 1.5 h in anhydrous $CHCl_3$ (240 mL). Additional mercuric oxide (3.14 g, 14.5 mmol) was added, and stirring was continued for 2.25 h. The mixture was filtered through Celite, dried (Na_2SO_4), and concentrated in vacuo, giving 7.0 g (98%) of the nitrone **5** as a yellow oil which was used without further purification: IR ($CHCl_3$) 2940, 2910, 2840, 1580, 1465, 1440, 1370, 1225, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (s, 3 H, *gem*-CH_3), 1.25 (s, 3 H, *gem*-CH_3), 1.64 (s, 3 H, C-5 CH_3), 1.70 (d, 3 H, J = 1.0 Hz, vinyl CH_3), 1.74 (d, 3 H, J = 1.0 Hz, vinyl CH_3), 2.18 (d, J = 13 Hz, 1 H, H of CH_2), 2.39 (d, J = 13 Hz, 1 H, H of CH_2), 5.82 (m, 1 H, vinylic H), 6.75 (s, 1 H, imine H); mass spectrum (70 eV), *m/e* (relative intensity) 181 (42, M^+), 164 (14), 125 (35), 124 (15), 108 (20), 96 (100), 95 (66), 83 (31), 81 (27), 79 (47), 67 (15), 55 (41), 53 (15), 41 (25), 39 (16); UV (MeOH) λ_{max} 235 nm (log ϵ 3.87); ^{13}C NMR ($CDCl_3$) 140.6 (d, C-2), 133.2 (s, isobutenyl quaternary), 128.0 (d, isobutenyl methine), 78.0 (s, C-5), 49.9 (t, C-4), 38.8 (s, C-3), 28.1 (q, CH_3), 27.5 (q, CH_3), 26.5 (q, CH_3), 19.1 (q, CH_3); high-resolution mass spectrum, *m/e* 181.146 079 ($C_{11}H_{21}NO$ requires 181.146 655).

1-Hydroxy-2-isobutenyl-2,4,4-trimethyl-5-phenylpyrrolidine (6). An ether solution (50% v/v) of 5-isobutenyl-3,5,5-trimethyl-1-pyrroline 1-oxide (7.0 g, 36 mmol) was added dropwise to a solution of phenylmagnesium bromide in ether under N_2, prepared from bromobenzene (8.54 g, 54.4 mmol) and magnesium turnings (1.45 g, 59.8 mol). The reaction mixture was heated at reflux for 1 h. After the mixture was cooled to 25 °C, saturated NH_4Cl was added carefully. The ether layer was separated, washed with brine (Na_2SO_4), and concentrated in vacuo to give a mixture of diastereomeric hydroxylamines **6** and some biphenyl. Recrystallization from pentane gave 3.63 g (39%) of one diastereomer as white needles: mp 115–116 °C; IR ($CHCl_3$) 3540, 3030, 2940, 2900, 2840, 1610, 1580, 1470, 1440, 1370, 1320, 1075 cm^{-1}; ^1H NMR (CCl_4) δ 0.54 (s, 3 H, *gem*-CH_3), 1.08 (s, 3 H, *gem*-CH_3), 1.28 (s, 3 H, CH_3 at C-2), 1.70 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.74 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.86 (s, 2 H, methylene), 3.38 (s, 1 H, benzylic H), 4.11 (s, 1 H, OH), 5.54 (m, 1 H, vinylic H), 7.24 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 259 (14, M^+), 245 (17), 244 (100), 186 (40), 123 (61), 117 (9), 91 (15), 41 (11); UV (EtOH) λ_{max} 264 nm (log ϵ 2.57), 258 (2.64), 252 (2.62); ^{13}C NMR ($CDCl_3$) δ 139.6 (s, aromatic C-1), 133.6 (d, isobutenyl methine), 130.2 (s, isobutenyl quaternary), 127.9, 126.8 (d, other aromatics), 76.1 (d, C-5), 64.6 (s, C-2), 52.1 (t, C-3), 35.8 (s, C-4), 29.9, 27.9, 26.9, 19.9, 19.1 (q, methyls); high-resolution mass spectrum, *m/e* 259.193 627 ($C_{17}H_{25}NO$ requires 259.193 605).

2-Isobutenyl-2,4,4-trimethyl-5-phenylpyrrolidine (7). Crystalline 1-hydroxy-2-isobutenyl-2,4,4-trimethyl-5-phenylpyrrolidine (5.0 g, 0.0218 mol) in 5 mL of ether was added dropwise to a mixture of lithium aluminum hydride (4.2 g, 0.11 mol) and aluminum chloride (4.2 g, 0.032 mol) in 50 mL of ether under N_2. The resulting mixture was heated at reflux for 2 h. After the mixture was cooled to 25 °C, 30% (w/w) NaOH was carefully added. The ether layer was washed with brine, dried (Na_2SO_4), concentrated in vacuo, giving 4.5 g (96%) of the diastereomeric pyrrolidines **7a** and **7b** in a 9:1 ratio (GLC) as a clear oil which were used without further purification: IR ($CHCl_3$) 3020, 2935, 2900, 2840, 1620, 1590, 1470, 1445, 1350, 1320, 1075 cm^{-1}; ^1H NMR (major diastereomer; CCl_4) δ 0.62 (s, 3 H, *gem*-CH_3), 1.02 (s, 3 H, *gem*-CH_3), 1.35 (s, 3 H, C-2 CH_3), 1.70 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.77 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.8–1.9 (m, 3 H, methylene and NH), 4.00 (s, 1 H, benzylic), 5.62 (m, 1 H, vinylic), 7.3 (m, 5 H, aromatic); mass spectrum (70 eV), *m/e* (relative intensity) 243 (4, M^+), 228 (20), 187 (30), 173 (12), 172 (100), 91 (11), 83 (8); UV (EtOH) λ_{max} 251 nm (log ϵ 2.48), 257 (2.45), 263 (2.35); high-resolution mass spectrum, *m/e* 243.197 726 ($C_{17}H_{25}N$ requires 243.198 695).

1-Chloro-2-isobutenyl-2,4,4-trimethyl-5-phenylpyrrolidine (8). A mixture of 2-isobutenyl-2,4,4-trimethyl-5-phenylpyrrolidine (6.1 g, 25.1 mmol) and *N*-chlorosuccinimide (3.42 g, 25.6 mmol) in ether (200 mL) was stirred under N_2 in the dark for 30 h. Water was added, and the ether layer was separated, washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give 6.95 g (100%) of a white solid (mp 51–54 °C) consisting of the two diastereomeric (9:1) *N*-chloropyrrolidines **8**: IR ($CHCl_3$) 3025, 2905, 2940, 1720, 1490, 1470, 1450, 1375, 1365, 1075 cm^{-1}; ^1H NMR (CCl_4; major diastereomer) δ 0.55 (s, 3 H, *gem*-CH_3), 1.13 (s, 3 H, *gem*-CH_3), 1.42 (s, 3 H, C-2 CH_3), 1.73 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.77 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.94 (s, 2 H, methylene), 3.92 (s, 1 H, benzylic), 5.49 (m, 1 H, vinylic), 7.22 (br, s, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 277 (4, M^+), 264 (33), 252 (100), 242 (7), 186 (11), 131 (8), 123 (47), 91 (9), 41 (6); UV (EtOH) λ_{max} 264 nm (log ϵ 2.75), 258 (2.78), 252 (2.72); high-resolution mass spectrum, *m/e* 277.158 992 ($C_{12}H_{24}NCl$ requires 277.159 743).

5-Isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrroline (9). 1-Chloro-2-isobutenyl-2,4,4-trimethyl-5-phenylpyrrolidine (30.0 g, 0.108 mol) was heated at reflux in methanolic KOH (155 g in 1300 mL) for 20 h under N_2. The mixture was poured into ice–water and extracted with chloroform. The chloroform extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give ca. 30 g of a yellow oil which was purified by column chromatography on silica gel with hexane as the initial eluent and 5% ether–hexane as the final eluent. This gave 18.9

g (72%) of the pyrroline **9** as a yellow oil: IR ($CHCl_3$), 3020, 2940, 2890, 2840, 1605, 1370, 1355, 1340, 1315, 1300, 996 cm^{-1}; ^1H NMR (CCl_4) δ 1.32 (s, 3 H, *gem*-CH_3), 1.36 (s, 3 H, C-5 CH_3), 1.68 (d, J = 1.0 Hz, 3 H, vinylic CH_3), 1.79 (d, J = 1.0 Hz, 3 H, vinylic CH_3), 1.90 (d, J = 13 Hz, 1 H, H of CH_2), 2.10 (d, J = 13 Hz, 1 H, H of CH_2), 5.44 (m, 1 H, vinyl), 7.26 (m, 3 H, aromatic H), 7.70 (m, 2 H, aromatic H); UV (EtOH) λ_{max} 234 nm (log ϵ 3.88); mass spectrum (70 eV), *m/e* (relative intensity) 241 (63, M^+), 226 (78), 186 (24), 185 (97), 184 (52), 172 (21), 170 (16), 123 (100), 104 (19), 91 (20), 82 (28), 81 (20), 77 (18), 67 (61), 41 (39); ^{13}C NMR ($CDCl_3$) δ 175.9 (s, imine C), 135.2 (s, aromatic C-1), 133.5 (d, isobutenyl methine), 129.5 (s, isobutenyl quaternary), 128.0, 127.5 (d, other aromatics), 72.0 (s, C-5), 55.6 (t, C-4), 51.2 (s, C-3), 30.2, 28.4, 27.8, 26.9, 13.4 (q, methyls); high-resolution mass spectrum, *m/e* 241.183 716 ($C_{17}H_{23}N$ requries 241.183 045).

Protonation Study of 5-Isobutenyl-3,3,5-trimethyl-2-phenyl-2-pyrroline. To a methanolic solution of 5-isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrroline (6.722×10^{-5} M) were added small increments of $HClO_4$ (3.33×10^{-8} M) in methanol, causing a simultaneous decrease in the UV maximum at 234 nm and an appearance of a new absorption at 266 nm (ϵ 11 300) with an isosbestic point at 247 nm. Protonation was complete after the addition of 1.82 equiv of $HClO_4$. Complete reversal of the above change was noted upon addition of base.

Irradiation of 5-Isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrrolinium Perchlorate (10). Preparation of 2-*exo*-Methoxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (14ex). An argon-purged solution containing 5-isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrroline (260 mg, 1.08 mmol) and 70% (w/w) perchloric acid (280 mg, 1.95 mmol) in 250 mL of freshly distilled methanol was irradiated for 40 min in a preparative photolysis apparatus consisting of a water-cooled quartz immersion well containing a 450-W, Hanovia, medium-pressure lamp and a Corex filter. The photolysate was concentrated in vacuo, giving a solid which was dissolved in chloroform, washed with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo. TLC (silica gel, 50% ether–hexane) gave the bicyclic amine **14ex** (130 mg, 44%) as a slightly yellow oil: IR ($CHCl_3$) 3050, 3020, 2940, 2905, 2840, 1600, 1490, 1460, 1375, 1350, 1100 cm^{-1}; ^1H NMR (CCl_4) δ 0.52 (s, 3 H, *exo*-methyl), 0.69 (s, 3 H, *exo*-methyl), 1.18 (s, 3 H, *endo*-methyl), 1.31 (s, 3 H, *endo*-CH_3), 1.47 (m, 2 H, methylene), 1.56 (s, 3 H, C-1 CH_3), 2.16 (br s, 1 H, NH, D_2O exchangeable), 2.99 (s, 1 H, C-2 methine H), 3.36 (s, 3 H, OCH_3), 7.2 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 273 (<1, M^+), 244 (4), 217 (9), 188 (13), 187 (78), 186 (33), 173 (10), 172 (100), 157 (6), 91 (6), 41 (5); high-resolution mass spectrum, *m/e* 258.186 434 ($C_{17}H_{24}NO$ requires 258.185 780), 217.145 946 ($C_{14}H_{19}NO$), 187.135 542 ($C_{13}H_{17}N$), 186.127 253 ($C_{13}H_{16}N$), 172.113 562 ($C_{12}H_{14}N$); UV λ_{max} 253 nm (log ϵ 2.68), 259 (2.67), 265 (2.56); ^{13}C NMR (acetone-d_6) δ 142.3 (s, aromatic C-1), 128.7, 128.3, 127.8, 126.5, 125.4 (d, other aromatics), 98.8 (d, C-2), 78.5 (s, C-4), 64.0 (s, C-1), 60.5 (q, OCH_3), 53.4 (t, C-6), 52.9 (s, C-3), 45.3 (s, C-5), 33.3, 28.9, 26.6, 24.4, 18.3 (q, methyls).

Anal. Calcd for $C_{18}H_{27}NO$: C, 79.07; H, 9.95; N, 5.12. Found: C, 79.45; H, 9.82; N, 5.20.

A dark control experiment was run in the following manner. A methanol solution of butenyl-3,3,5-trimethyl-2-phenyl-1-pyrroline **9** (51.6 mg, 0.214 mmol) and perchloric acid (59 mg, 0.41 mmol) was placed in the dark, and Ar was bubbled through the solution for 5.5 h. The solution was concentrated in vacuo, giving a mixture that was dissolved in chloroform, washed with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo, resulting in the recovery of the pyrroline **9** (ca. 50 mg) as confirmed by ^1H NMR, GLC, and TLC analyses. Heating a 2-mL aliquot of the above solution at reflux for 24 h followed by the workup procedure described gave recovered pyrroline.

Irradiation of 5-Isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrroline (9). Degassed solutions of the pyrroline **9** (150–250 mg), in either methanol, acetonitrile, or *tert*-butyl alcohol (200 mL), were irradiated by using Vycor-filtered light for varying periods of time up to 14 h. Disappearance of the pyrroline was detected by UV and GLC analyses. However, only minor quantities of products were detected in the reaction mixture by GLC analysis and no products (besides polymeric material) could be isolated upon concentration of the photolysate in vacuo.

2-*exo*-Methoxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]-hept-1,4-ylideneammonium Perchlorate (17). The perchloric salt **17** was obtained quantitatively in the following manner. An equimolar quantity of aqueous perchloric acid (70% w/w) and 2-*exo*-methoxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (**14ex**) were combined. Benzene was repetitively added and removed at reduced pressure to azeotropically remove water. The crystalline material obtained by this procedure was dissolved in chloroform; crystallization was effected by allowing a stream of N_2 to pass over the solution until crystals appeared. These were filtered, washed with cold $CHCl_3$, and dried, giving pure perchlorate salt: mp 288–290 °C dec; IR (KBr pellet) 3050, 2900, 1605, 1450, 1375, 1345, 1305, 1215, 1100, 765, 715 cm^{-1}; ^1H NMR (acetone-d_6) δ 0.92 (s, 3 H, *exo*-CH_3), 0.96 (s, 3 H, *exo*-CH_3), 1.64 (s, 3 H, *endo*-CH_3), 0.96 (s, 3 H, *exo*-CH_3), 1.64 (s, 3 H, endo CH_3), 1.67 (s, 3 H, endo CH_3), 1.76 (s, 3 H, CH_3 at C-1), 2.10 (d, J = 14 Hz, 1 H, H of CH_2), 2.29 (d, J = 14 Hz, 1 H, H of CH_2), 3.76 (s, 3 H, OMe), 3.56 (s, 1 H, methine H), 7.5 (m, 5 H, aromatic); UV (EtOH) λ_{max} 251 nm (log ϵ 2.27), 257 (2.33), 263 (2.21); ^{13}C NMR (acetone-d_6) δ 129.7 (s, C-1 aromatic), 129.1, 126.9, 124.9 (3 d, other aromatics), 92.1 (d, C-3), 86.0 (s, C-4), 71.8 (2, C-1), 61.3 (q, OCH_3), 51.6 (s, C-3), 49.2 (t, C-6), 44.6 (s, C-5), 32–29.0 (3 methyls, not distinguishable from acetone signals), 23.5 (q, CH_3), 15.5 (q, CH_3).

Anal. Calcd for $C_{18}H_{28}NO_5Cl$: C, 57.82; H, 7.55; N, 3.75; Cl, 9.48. Found: C, 57.51; H, 7.44; N, 3.61; Cl, 9.28.

Irradiation of 5-Isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrrolinium Perchlorate (10). Preparation of 2-*exo*-Hydroxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (15ex). An argon-purged solution of 200 mL of distilled water and 50 mL of acetonitrile containing 5-isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrroline (260 mg, 1.08 mmol) and 70% (w/w) perchloric acid (280 mg, 1.95 mmol) was irradiated (Corex) for 70 min. The photolysate was concentrated in vacuo. The crude reaction mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo, giving 245 mg of a yellow oil. The yield of the alcohol **15ex** was 58% based on GLC analysis of the crude product mixture. Isolation was accomplished by preparative GLC with a 2% OV-101 column at 170 °C, giving **15ex** as a white solid: mp 96–98 °C; IR ($CHCl_3$) 3350, 2940, 2845, 1600, 1490, 1460, 1375, 1075, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.62 (s, 3 H, *exo*-CH_3), 0.69 (s, 3 H, *exo*-CH_3), 1.31 (s, 3 H, *endo*-CH_3), 1.42 (s, 3 H, *endo*-CH_3), 1.52 (s, 3 H, CH_3 at C-1), 1.62 (s, 2 H, methylene), 2.86 (br s, 2 H, NH and OH), 3.44 (s, 1 H, C-2 methine H), 7.3 (m, 5 H, aromatic); mass spectrum (70 eV), *m/e* (relative intensity) 259 (<1, M^+), 203 (19), 188 (17), 187 (54), 186 (26), 173 (14), 172 (100), 160 (9), 157 (9), 91 (8); UV (EtOH) λ_{max} 252 nm (log ϵ 2.54) 257 (2.53), 264 (2.43); ^{13}C NMR ($CDCl_3$) δ]40.5 (s, C-1 aromatic), 127.9, 127.4, 126.2, 124.6 (d, other aromatics), 87.1 (d, C-2), 78.8 (s, C-4), 64.0 (s, C-1), 52.2 (t, C-6), 51.0 (s, C-3), 45.7 (s, C-5), 32.5, 28.2, 25.8, 23.9, 18.0 (q, methyls).

Anal. Calcd for $C_{17}H_{24}NO{\cdot}H_2O$: C, 73.61; H, 9.81; N, 5.05. Found: C, 74.02; H, 9.63; N, 5.03.

A dark control experiment was run in the following manner. A mixture of the pyrroline **9** (260 mg, 1.08 mmol) and perchloric acid (280 mg, 1.95 mmol) in 200 mL of H_2O and 50 mL CH_3CN was degassed with Ar and heated at reflux for 7 h. The solvent was removed in vacuo, giving a material which was dissolved in chloroform, washed with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo to give only recovered pyrroline (ca. 250 mg) as shown by ^1H NMR, GLC, and TLC analyses.

5-Isobutenyl-1,3,3,5-tetramethyl-2-phenyl-1-pyrrolinium Perchlorate (11). 5-Isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrroline (1.0 g, 4.15 mmol) and methyl iodide (7.5 mL, 120.5 mmol) in 70 mL of absolute ethanol were heated at reflux under N_2 for 4.5 h. The ethanol was removed in vacuo, yielding the crude salt as a foam. Trituration with benzene (ca. 200 mL) effected crystallization. Filtration followed by drying gave 0.60 g (38%) of the iminium iodide (mp 168–170 °C). Perchlorate anion-exchange chromatography (Dowex 1-X8) produced 0.58 g (38%) of the pure perchlorate salt **11** as a white solid: mp 126–127 °C; IR (KBr pellet) 3035, 2955, 2900, 2840, 1650, 1470, 1445, 1380, 1325, 1215, 1100, 765, 740, 715 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.43 (s, 6 H, *gem*-methyls), 1.82 (m, 6 H, vinyl methyls), 1.92 (s, 3 H, CH_3 at C-5), 2.57 (d, J = 13 Hz, 1 H, H of CH_2), 2.73 (d, J = 13 Hz, 1 H, H of CH_2), 3.43 (s, 3 H, *N*-methyl), 5.94 (m, 1 H, vinyl H), 7.7 (m, 5 H, aromatic); UV (EtOH) λ_{max} 257 nm (log ϵ 3.68); ^{13}C NMR (acetone-d_6) δ 192.9 (s, imine C), 138.4 (s, C-1 aromatic), 132.7, 129.9, 128.7, 127.8, 127.4, 126.7, 125.9 (d, aromatics and olefinics), 79.0 (s, C-5), 51.2 (s, C-3), 49.8 (t, C-4), 35.9 (q, NCH_3), 26.9 (q, CH_3), 26.7 (q, CH_3), 26.2 (q, *gem*-methyls), 19.6 (q, CH_3).

Anal. Calcd for $C_{18}H_{26}NO_4Cl$: C, 60.75; H, 7.36; N, 3.94; Cl, 9.96. Found: C, 60.49; H, 7.54; N, 3.76; Cl, 9.59.

Irradiation of 5-Isobutenyl-1,3,3,5-tetramethyl-2-phenyl-1-pyrrolinium Perchlorate (11). Preparation of *exo*- and *endo*-2-Methoxy-1,3,3,5,5,7-hexamethyl-4-phenyl-7-azabicyclo[2.2.1]heptanes (16ex and 16en). An argon-purged solution of 5-isobutenyl-1,3,3,5-tetramethyl-2-phenyl-1-pyrrolinium perchlorate (252 mg, 0.705 mmol) in freshly distilled methanol (250 mL) was irradiated (Corex) for 3.75 h. The photolysate was concentrated in vacuo. The crude mixture was then dissolved in chloroform, washed with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo, giving a yellow oil. The amine **16** was purified by preparative TLC (silica gel, ether) to yield 44 mg (22%) of the *endo*- and *exo*-methoxy isomers (24:76 ratio by GLC, respectively). Separation was accomplished by preparative GLC (2% OV-101, 165 °C).

For **16ex**: IR ($CHCl_3$) 3050, 3015, 2940, 2900, 1600, 1490, 1445, 1375, 1120, 980 cm^{-1}; ^1H NMR (CCl_4) δ 0.76 (s, 3 H, *exo*-CH_3), 0.81 (s, 3 H, *exo*-CH_3), 1.17 (s, 3 H, *endo*-CH_3), 1.36 (s, 3 H, *endo*-CH_3), 1.39 (s, 3 H, CH_3 at C-1), 1.36 (d, J = 12 Hz, 1 H, H of CH_2), 1.83 (d, J = 12 Hz, 1 H, H of CH_2), 2.47 (s, 3 H, NCH_3), 3.06 (s, 1 H, methine), 3.36 (s, 3 H, OCH_3), 7.2 (m, 5 H, aromatic); mass spectrum (70 eV), *m/e* (relative intensity) 287 (1, M^+), 256 (6), 231 (8), 216 (4), 202 (10), 201 (68), 200 (67), 187 (13), 186 (100), 171 (5), 170 (4), 91 (6), 56 (8), 41 (5); UV (EtOH) λ_{max} 253 nm (log ϵ 2.60), 258 (2.52), 263 (2.34); ^{13}C NMR ($CDCl_3$) 138.7 (s, C-1 aromatic), 131.7, 127.0, 126.7, 125.6 (d, other aromatics), 96.8 (d, C-2), 82.4 (s, C-4), 66.6 (s, C-1), 60.4 (q, OCH_3), 53.1 (t, C-6), 50.9 (s, C-3), 45.3 (s, C-5), 33.2 (q, CH_3), 32.8 (q, CH_3), 31.8 (q, CH_3), 27.8 (q, CH_3), 24.8 (q, CH_3), 15.6 (q, CH_3); high-resolution mass spectrum, *m/e* 287.225 820 ($C_{19}H_{29}NO$ requires 287.224 905).

For **16en**: ^1H NMR (CCl_4) δ 0.82 (s, 3 H, *exo*-CH_3), 0.85 (s, 3 H, *exo*-CH_3), 1.14 (s, 3 H, *endo*-CH_3), 1.23 (s, 3 H, *endo*-CH_3), 1.43 (s, 3 H, CH_3 at C-1), 2.47 (s, 3 H, NCH_3), 3.35 (s, 1 H, H at C-2), 3.40 (s, 3 H, OCH_3), 7.1–7.4 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 287 (4, M^+), 272 (14), 256 (6), 231 (18), 216 (5), 202 (26), 201 (57), 200 (54), 187 (17), 186 (100), 91 (10), 56 (14), 41 (11); high-resolution mass spectrum, *m/e* 287.225 548 ($C_{19}H_{29}NO$ requires 287.224 905).

A dark control was run in the following manner. The *N*-methyl salt **11** (50 mg, 0.14 mmol) was heated at reflux for 4.3 h in 50 mL of methanol. The solution was concentrated in vacuo. ^1H NMR analysis showed that no reaction had occurred.

Preparation of 2-*exo*-Methoxy-1,3,3,5,5,7-hexamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (16ex) from 2-*exo*-Methoxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (14ex). A solution of 2-*exo*-methoxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (70 mg, 0.26 mmol) in anhydrous THF (1 mL) containing 39 mg (0.28 mmol) of suspended K_2CO_3 was stirred under Ar while dimethyl sulfate (30 μL, 0.31 mmol) was added. The mixture was then heated at reflux for 5 h. Additional dimethyl sulfate (30 μL) was added, and the mixture was heated at reflux for 4 h longer. The reaction mixture was poured into H_2O and extracted with chloroform. The chloroform extracts were washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo, giving 68 mg (69%) of **16ex**, 16% of the starting bicyclic ether, and 15% of small amounts of uncharacterized products (GLC). The *N*-methyl amine was purified by GLC (2% OV-101, 175 °C) and was found to be identical in all respects, with the material obtained from irradiation of the *N*-methylpyrrolinium perchlorate **11** (^1H NMR, GLC, and TLC).

Preparation of 2-*exo*-Methoxy-1,3,3,5,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (16ex) from 2-*exo*-Hydroxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (15ex). 2-*exo*-Methoxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (22.5 mg, 0.087 mmol) was added to NaH (19 mg of a 55% oil dispersion washed with hexane, 0.436 mmol) in anhydrous THF under Ar, and the mixture was stirred for 5 min. Methyl iodide (50 μL, 0.155 mmol) was then added, and the mixture was refluxed for 9 h. After the mixture was cooled to 25 °C, water was carefully added. The solution was extracted with ether. The combined ethereal extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo, giving 24 mg of a yellow oil which was found to consist of 80% of the bicyclic ether **14ex**, 9% of the starting alcohol, and 10% of the *N*-methyl bicyclic ether **16ex** based on GLC analysis. The bicyclic ether and the *N*-methyl ether were identical with materials obtained from the photochemical processes (^1H NMR, GLC, and TLC).

Benzophenone-Sensitized Irradiation of 5-Isobutenyl-3,5,5-trimethyl-2-phenyl-1-pyrrolinium Perchlorate (10). An argon-purged solution containing 5-isobutenyl-3,5,5-trimethyl-2-phenyl-1-pyrroline (0.60 g, 2.49 mmol) and benzophenone (6.00 g, 33.0 mmol) in 250 mL of methanol was irradiated for 1.5 h through a uranium-glass filter. Solid $NaHCO_3$ was then added, and the mixture was stirred for 3 min before being filtered. The filtrate was concentrated in vacuo, giving a material which was dissolved in chloroform. The chloroform layer was washed with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography (silica gel, 5% ether–hexane to methanol) was used to separate the various components: benzophenone (5% ether–hexane, 3.03 g), benzpinacol (5% ether–hexane, 1.08 g), benzhydrol (10% ether–hexane, 0.1 g), 2-*exo*-methoxy-1,3,3,5,5-pentamethyl-4-phenyl-7-azabicyclo[2.2.1]heptane (20% ether–hexane, 41 mg after preparative TLC on silica gel, 30% ether–hexane), 1,1-diphenyl-1,2-ethanediol (50% ether–hexane, 1.12 g).

A control irradiation was run in the absence of the pyrrolinium salt **10** under the same conditions as above. The results from column chromatography were as follows: benzophenone (1.73 g), benzpinacol (1.41 g), benzhydrol (0.1 g), 1,1-diphenyl-1,2-ethanediol (1.22 g). Irradiation of the iminium salt (unsensitized) through a uranium-glass filter for 1.5 h showed (GLC) no decrease in the amount of starting imine and no buildup of the usual photoproducts.

Table IV. Relative Amounts of 16 and New Photoproduct from Irradiation of 11 in Methanol Containing Various *cis*-Piperylene Concentrations

[*cis*-piperylene], M	rel amt of products[a]		total,[b] mmol
	16	new photoproduct	
0	0.316	0	0.316
0.01	0.686	0.004	0.690
0.05	1.170	0.054	1.224
0.20	1.183	0.180	1.376
0.50	0.924	0.460	1.384

[a] Determined by GLC analysis with triphenylmethane as the internal standard (mol of product/mol of standard). [b] Amount of new photoproduct plus amount of **10**.

Benzophenone-Sensitized Irradiation of 5-Isobutenyl-1,3,3,5-tetramethyl-2-phenyl-1-pyrrolinium Perchlorate (11). An argon-purged solution containing 5-isobutenyl-1,3,3,5-tetramethyl-2-phenyl-1-pyrrolinium perchlorate (514 mg, 1.45 mmol) and benzophenone (5.50 g, 33.0 mmol) in 200 mL of methanol was irradiated for 45 min through a uranium-glass filter. The photolysate was concentrated in vacuo. The crude mixture dissolved in chloroform was washed with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography was used to separate the various components (silica gel, 5% ether–hexane to methanol): benzophenone (3.45 g), benzpinacol (1.48 g), benzhydrol (0.1 g), 1,1-diphenyl-1,2-ethanediol (0.86 g), 5-isobutenyl-1,3,3,5-tetramethyl-2-phenyl-1-pyrrolinium perchlorate (ca. 0.5 g).

A control irradiation was run in the absence of iminium salt under the same conditions as above. The results from column chromatography are as follows: benzophenone (3.08 g), benzpinacol (1.42 g), benzhydrol (0.1 g), 1,1-diphenyl-1,2-ethanediol (1.05 g).

Triplet Quenching Experiment. Aliquots (50 mL) of a 2.81×10^{-3} M solution of the *N*-methylpyrrolinium salt **11** in methanol containing varying concentrations of *cis*-piperylene (0.05 M) were irradiated in a merry-go-round apparatus for a fixed time period after being degassed with N_2 for 15 min. The sample were concentrated in vacuo, and 50 mL of chloroform was added to each. The chloroform solutions were washed with saturated $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated in vacuo. Then, 200 mL of a solution containing 270 mg of triphenylmethane in 75 mL of chloroform was added to each sample, and the product distributions were analyzed by GLC (OV-101, 150 °C). At high piperylene concentrations, a new peak appeared which was not identified. The data obtained from these experiments are found in Table IV.

5-Isobutenyl-3,5,5-trimethyl-2-phenyl-1-pyrroline 1-Oxide (12). 1-Hydroxy-5-isobutenyl-3,5,5-trimethyl-2-phenylpyrroline (1.0 g, 3.86 mmol) and yellow mercuric oxide (1.61 g, 7.43 mmol) were stirred under N_2 for 2.5 h in CH_2Cl_2 (25 mL) which had been dried over $CaCl_2$. Additional mercuric oxide (0.3 g, 1.4 mmol) was added, and stirring was continued for 2.75 h. The mixture was filtered through Celite, dried (Na_2SO_4), and concentrated in vacuo to give the crude nitrone **12** (1.0 g, 100%; mp 55–57 °C) which was used without further purification: IR ($CHCl_3$) 3015, 2950, 2905, 2840, 1570, 1525, 1435, 1370, 1345, 1230, 1160, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3 H, *gem*-CH_3), 1.39 (s, 3 H, *gem*-CH_3), 1.69 (s, 3 H, C-5 CH_3), 1.73, 1.74 (s, 6 H, vinyl methyls), 2.18 (d, 1 H, J = 13 Hz, H at C-4), 2.45 (d, 1 H, J = 13 Hz, H at C-4), 5.87 (m, 1 H, vinyl H), 7.3–7.5 (m, 3 H, aromatic H), 7.8–8.0 (m, 2 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 257 (59, M^+), 240 (100), 184 (65), 129 (85), 95 (31), 91 (63), 77 (41), 41 (39); UV (EtOH) λ_{max} 242 nm (log ϵ 3.71); ^{13}C NMR ($CDCl_3$) 146.0 (s, C-2), 132.5 (s, C-1 aromatic), 129.5 (s, isobutenyl quaternary), 129.1 (d, isobutenyl methine), 128.7 (d, para aromatic), 128.2 (d, ortho aromatic), 128.1 (d, meta aromatic), 76.2 (s, C-5), 50.1 (t, C-4), 42.2 (s, C-3), 28.8, 28.6 (q, vinyl methyls), 27.3, 26.5, 19.1 (q, other methyls); high-resolution mass spectrum, *m/e* 257.178 986 ($C_{17}H_{23}NO$ requires 257.177 95).

2,4-Dimethyl-3-penten-2-ol (18). Methyl β,β-dimethylacrylate[13] (5.00 g, 43.9 mmol) was added dropwise at 0 °C under Ar to an ether solution (ca. 125 mL) of methyllithium prepared from lithium wire (3.47 g, 0.50 mol) and methyl iodide (41.0 g, 0.284 mol). The mixture was stirred for an additional hour at 0 °C before water was carefully added. The ethereal layer was separated, washed with brine, dried (Na_2SO_4), and concentrated in vacuo, giving 4.4 g (88%) of **18** as a clear oil which was used without further purification. An analytical sample was obtained by preparative GLC (14% XE-60, 100 °C): IR ($CHCl_3$) 3350, 2945, 2900, 2850, 1660, 1450, 1350, 1225, 1155, 1125, 1075, 965, 940, 925, 920, 800

cm^{-1}; ^{1}H NMR (CCl_4) δ 1.25 (s, 6 H *gem*-methyls), 1.63 (d, J = 1.5 Hz, vinyl CH_3), 1.79 (d, J = 1.5 Hz, 3 H, vinyl CH_3), 2.64 (br s, 1 H, OH), 5.25 (m, 1 H, vinyl H); mass spectrum (70 eV), m/e (relative intensity) 114 (3, M^+), 99 (21), 96 (100), 81 (82), 79 (21), 68 (17), 57 (17)8 56 (18), 55 (11), 54 (32), 43 (17), 41 (41), 39 (35), 29 (20), 18 (29); UV (EtOH) λ_{max} 229 nm (ϵ 4406); high-resolution mass spectrum, m/e 96.093 428 (C_7H_{12} = M − H_2O requires 96.093 900).

2-Azido-2,4-dimethyl-3-pentane (19). Sodium azide (11.1 g, 170.8 mmol) was added to 100 mL of chloroform, and the mixture was cooled at 0 °C. As a stream of Ar was passed over the mixture, 2.64 mL of concentrated H_2SO_4 (4.86 g, 49.6 mmol) was added dropwise, and the mixture was stirred at 0 °C for 10 min. The alcohol **18** (5.54 g, 48.6 mmol) in ca. 3 mL of chloroform was added dropwise, and stirring was continued for 10 min before the reaction was quenched with ice-cooled water. The chloroform layer was separated, washed with brine, dried (Na_2SO_4 and K_2CO_3), and concentrated in vacuo, giving 5.0 g (74%) of **19** as an oil which was used without further purification. An analytical sample was obtained by preparative GLC (XE-60, 100 °C): IR ($CHCl_3$) 2940, 2900, 2840, 2095, 1700, 1445, 1370, u1240, 1165, 1135, 900 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.31 (s, 6 H, *gem*-methyls), 1.74 (d, J = 1.5 Hz, 3 H, vinyl CH_3), 1.85 (d, J = 1.5 Hz, 3 H, vinyl CH_3), 5.18 (m, 1 H, vinyl H); mass spectrum (70 eV), m/e (relative intensity) 139 (<1, M^+), 111 (43), 97 (52), 96 (93), 81 (33), 69 (11), 56 (18), 55 (100), 53 (23), 43 (18), 42 (63), 41 (48), 39 (51), 29 (25), 28 (86), 27 (28); UV (EtOH) λ_{max} 221 nm (ϵ 1054); high-resolution mass spectrum, m/e 111.105 295 ($C_7H_{13}N$ = M − N_2 requires 111.104 795).

2-Amino-2,4-dimethyl-3-pentene (20). Lithium aluminum hydride (0.43 g, 11.4 mmol) was added to 20 mL of anhydrous ether, and the mixture was cooled to 0 °C under Ar. The azide **19** (1.29 g, 9.28 mmol) in 2 mL of ether was added dropwise to the mixture, and stirring was continued for 1 h at 0 °C. Water was then carefully added. The etheral layer was separated and washed with 10% HCl and brine, dried (Na_2SO_4), and concentrated in vacuo, yielding 0.52 g of unreacted azide. The HCl portion was neutralized with cold 10% NaOH and extracted with ether. The ethereal layer was washed with brine, dried (Na_2SO_4), and concentrated by fractional distillation, giving the amine **20** (ca. 0.5 g, 50%). An analytical sample was obtained by preparative GLC (14% SE-60, 105 °C): ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6 H, *gem*-methyls), 1.67 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.79 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 5.28 (m, 1 H, vinyl H); mass spectrum (70 eV), m/e (relative intensity) 113 (<1, M^+), 112 (3), 99 (10), 98 (100), 96 (20), 81 (20), 50 (41), 55 (12), 53 (12), 42 (41), 41 (21), 34 (17), 27 (11); ^{13}C NMR ($CDCl_3$) δ 135.2 (d, methine olefinic C), 131.5 (s, quaternary olefinic C), 50.3 (s, C-2), 32.5 (q, 2 methyls), 27.6 (q, CH_3), 18.8 (q, CH_3); high-resolution mass spectrum, m/e 97.102 094 (C_7H_{13} = M − NH_2 requires 97.101 725).

2-Aza-3,3,5-trimethyl-1-phenyl-1,4-hexadiene (21). To the amine **20** (0.465 g, 4.1 mmol) was added benzaldehyde (0.436 g, 4.1 mmol), and the mixture was heated at 100 °C for 10 h under Ar. Molecular distillation (40–50 °C, 0.02 torr) produced **21** as an oily solid (0.448 g, 54%) shown to be pure by GLC analysis: IR ($CHCl_3$) 3055, 2920, 2920, 2880, 1680, 1625, 1490, 1365, 1160, 1070, 970 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.34 (s, 6 H, *gem*-methyls), 1.57 (d, J = 1.0 Hz, vinyl CH_3), 1.71 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 5.32 (m, 1 H, vinyl H), 7.28 (m, 3 H, aromatic H), 7.65 (m, 2 H, aromatic H), 8.17 (s, 1 H, imine H); mass spectrum (70 eV), m/e (relative intensity) 201 (9, M^+), 186 (27), 145 (29), 106 (15), 104 (14), 97 (100), 96 (22), 91 (11), 81 (17), 77 (12), 55 (45), 31 (23), 29 (13); UV (MeOH) λ_{max} 246 nm (ϵ 16 100); ^{13}C NMR ($CDCl_3$) δ 157.1 (d, imine C), 137.3 (s, C-1 aromatic), 134.3 (s, quaternary olefinic C), 131.9 (d, methine olefinic C), 130.1 (d, para aromatic), 128.4 (d, meta aromatic), 127.9 (d, ortho aromatic), 60.8 (s, C-3), 30.6, 29.9, 27.6, 27.1 (q, methyls); high-resolution mass spectrum m/e 201.151 237 ($C_{14}H_9N$ requires 201.151 745).

Protonation of 2-Aza-3,3,5-trimethyl-1-phenyl-1,4-hexadine (21). To 2-aza-3,3,5-trimethyl-1-phenyl-1,4-hexadiene (**21**; 3.00 mL, 4.318×10^{-5} M) in methanol were added small increments of $HClO_4$ (3.33×10^{-3} M in methanol). This caused a simultaneous decrease in the UV maximum at 246 nm and an appearance of a new absorption at 273 nm (ϵ 16 700) with an isosbestic point at 258 nm. Protonation was complete after the addition of 4.38 equiv of $HClO_4$. Complete reversal of the above change was noted upon addition of base.

4-Methyl-3-penten-2-ol (23). To a solution of methyllithium (0.10 mol) in 100 mL of anhydrous ether at 0 °C was added 5.0 g (60 mmol) of 3-methyl-2-butenal[16] in 30 mL of anhydrous ether over 30 min under a N_2 atmosphere. The reaction mixture was warmed to 25 °C, stirred for 1 h, cooled to 0 °C, and quenched by slow addition of water. The ethereal layer was separated, washed with water, dried, and concentrated in vacuo to yield 4.6 g (77%) of the desired alcohol **23** as a light yellow oil (95% purity by GLC, 5 ft × $^1/_8$ in, 4% SE-30 on Variport 30, temperature program 75–110 °C at 1 °C/min, differential pressure 14 psig, retention time 4 min); ^{1}H NMR δ 5.12 (d of heptet 1 H, J = 8 and 1 Hz, olefinic H), 4.40 (d, of quart, 1 H, J = 8 and 7 Hz, H-2), 3.57 (s, 1 H, OH), 1.67 (d, 6 H, J = 1 Hz, CH_3's), 1.12 (d, 3 H, J = 7 Hz, CH_3); IR 3640, 3370, 2927, 1443, 1377, 1065, 858 cm^{-1}; ^{13}C NMR 133.7 (s, C-4), 129.5 (d, C-3), 64.7 (d, C-2), 25.6 (q, *cis*-methyl), 23.6 (q, *trans*-methyl), 18.0 ppm (q, C-1).

4-Methyl-3-pentenyl-2-trichloroacetimidate (24). This material was produced from the alcohol **23** by a modification of the Overman procedure.[9] A stoichiometric quantity of sodium hydride was used instead of the recommended catalytic quantity. A workup using the literature procedure yielded a crude brown oil representing 60% of the desired imidate **24**: ^{1}H NMR δ 8.15 (br, s, 1 H, NH), 5.72 (d of quartz, 1 H, J = 9 and 7 Hz, H-2), 5.25 (d, of heptet, 1 H, J = 9 and 1 Hz, H-3), 1.78 (d, 6 H, J = 1 Hz, geminal CH_3), 12.9 (d, 3 H, J = 7 Hz, CH_3); IR 3359, 2977, 2944, 1625, 1444, 1375, 1334, 1282, 1074, 1028, 964, 862, 647 cm^{-1}. This material was added directly without further purification.

2-Methyl-*trans*-3-pentenyl-3-trichloroacetamide (25). A solution of 20 g (82 mmol) of imidate **24** in 50 mL of anhydrous benzene was refluxed for 12 h. Concentration in vacuo yielded a dark red oil which was filtered through silica gel (Sargent-Welch, 60–200 mesh, 6 × 4 cm) with toluene as eluant. Concentration of the solution in vacuo yielded 16.8 g (84%) of the rearranged amide **25**: ^{1}H NMR δ 6.33 (br, s, 1 H, NH), 5.62 (d, 2 H, olefinic), 1.73 (m, 3 H, CH_3), 1.48 (s, 6 H, geminal CH_3); IR 3436, 2954, 1730, 1498, 1452, 1384, 1365, 1298, 865, 695 cm^{-1}; mass spectrum (70 ev), m/e (relative intensity) 247 (1.4), 243 (3.2)8 232 (14.6), 230 (43.1), 228 (46.2), 212 (3.1), 210 (19.2), 208 (28.5), 121 (2.5), 119 (6.2), 117 (6.3), 85 (13.1), 84 (6.2), 83 (100), 82 (15.4), 67 (22.3), 55 (32.3). This material was used without further purification.

2-Amino-2-methyl-*trans*-3-pentene (26). A solution of 20 g (82 mmol) of amide **25** in 50 mL of 6 N sodium hydroxide was refluxed for 6 h, cooled, and extracted with ether. The ethereal layer was washed with pH 8.5 water, dried over anhydrous potassium carbonate, and fractionally distilled to yield approximately 15 mL of a 50% solution of methanol and desired amine **26**. Since it was very difficult to derive usable quantities of pure amine **26** by distillation, the methanol solution was used in the following condensation reaction. Preparative gas chromatography (10% SE-30 on Chromosorb P, 80 °C) yielded a sample of **26** for identification: ^{1}H NMR δ 5.5 (m, 2 H, olefinic), 1.63 (m, 3 H, allylic), 1.12 (s, 6 H, geminal CH_3); IR 3671, 3035, 2955, 1450, 1380, 1370, 1250, 975, 875, 700 cm^{-1}.

2-Aza-3,3-dimethyl-1-phenyl-*trans,trans*-1,4-hexadiene (27). The solution of 2-amino-2-methyl-3-pentene (**26**, ca. 8 g) in methanol (8 mL) obtained as a distillation residue in the previous step was added to 8.5 mL (83 mmol) benzaldehyde in 40 mL of anhydrous benzene. The resulting solution was refluxed with the azeotropic removal of water for 36 h. Concentration in vacuo and molecular distillation (85 °C, 0.05 mm) yielded 5.6 g (36% from acetamide **26**) of 1-aza-3,3-dimethyl-1-phenyl-1,4-hexadiene (**27**). Further purification could be achieved by repeated molecular distillation or preparative gas chromatography (10% SE-30 on Variport 30, 165 °C): ^{1}H NMR δ 8.12 (s, 1 H, benzylic), 7.43–7.54 (m, 2 H, ortho), 7.24–7.34 (m, 3 H, meta and para), 5.51 (m, 2 H, olefinic), 1.74 (m, 3 H, allylic CH_3), 1.30 (s, 6 H, geminal CH_3); ^{13}C NMR 157 (s, C-1), 138.4 (d, C-4), 137 (s, aromatic C-1), 130.2, 128.5, 128.0 (d, aromatic), 123.5 (d, C-5), 61.0 (s, C-3), 28.4 (q, geminal CH_3), 18.0 ppm (q, C-6); IR 3077, 3035, 2976, 2933, 2870, 1965, 1890, 1818, 1773, 1702, 1639, 1451, 1376, 1161, 969, 901, 862, 691 cm^{-1}; UV λ_{max} (ϵ) 246 nm (14,740); mass spectrum (70 eV), m/e (relative intensity) 287 (14.6), 172 (8.7), 131 (15.6), 122 (14.8), 106 (5.3), 105 (16.8), 104 (10.7), 91 (7.4), 90 (6.1), 89 (5.0), 84 (26.2), 83 (100), 77 (14.3), 67 (7.6), 55 (32.8), 55 (9.0), 43 (8.6), 42 (6.6), 41 (31.1), 39 (11.9); high-resolution mass spectrum, m/e 187.136 844 ($C_{13}H_{17}N$ requires 187.136 095).

Photolysis of the Perchlorate Salt 22 of 2-Aza-3,3,5-trimethyl-1-phenyl-1,4-hexadiene. Preparation of *cis*- and *trans*-3-Methoxy-2,2,4,4-tetramethyl-5-phenylpyrrolidines (29). An Ar-purged solution of 250 mL of methanol containing 2-aza-3,5,5-trimethyl-1-phenyl-1,4-hexadiene (250 mg, 1.24 mmol) and 70% (w/w) perchloric acid (782 mg, 545 mmol) was irradiated (Corex) for 1 h. To the photolysate was added sodium bicarbonate (0.6 g). After filtration the photolysate was concentrated in vacuo. The crude product was dissolved in chloroform, washed with saturated sodium bicarbonate, and purified by molecular distillation (35–60 °C, 0.025 torr) to give 147 mg (51%) of a mixture of the two diastereomeric pyrrolidinyl ethers **29c** and **29t** in a ratio of 18:82 (GLC). The two diastereomers were separated by preparative GLC (10% OV-101, on Variport 30 at 176 °C). The pyrrolidines could also be obtained from the crude photolysate by preparative TLC (silica gel, 40% ether–hexane, R_f 0.46–0.33).

Major isomer **29t**: IR ($CHCl_3$) 3020, 2970, 2930, 2880, 1770, 1450, 1360, 1110 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.55 (s, 3 H, CH_3 at C-4 cis to Ph),

0.96 (s, 3 H, CH_3 at C-4 trans to Ph), 1.12 (s, 3 H, *gem*-CH_3 at C-2), 1.26 (s, 3 H, CH_3 at C-2), 3.08 (s, 1 H, CH α to CH_3), 3.39 (s, 3 H, OCH_3), 3.83 (s, 1 H, benzylic H), 7.1–7.4 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 233 (4, M^+), 148 (11), 147 (100), 146 (21), 91 (11), 42 (4), 41 (5); UV (EtOH) λ_{max} 258 nm (ϵ 647), 264 (455), 268 (353); ^{13}C NMR ($CDCl_3$ δ 139.5 (s, C-1 aromatic), 127.8 (d, meta aromatic), 127.6 (d, ortho aromatic), 127.0 (d, para aromatic), 97.6 (d, C-3), 66.7 (d, C-5), 60.1 (q, OCH_3), 57.3 (s, C-2), 46.1 (s, C-4), 32.5, 26.1, 25.8, 15.4, (q, methyls); high-resolution mass spectrum, *m/e* 233.178 577 ($C_{15}H_{23}NO$ requires 233.177 955).

Minor isomer (**29c**): ^1H NMR (CCl_4) δ 0.58 (s, 3 H, C-4 CH_3, cis to Ph), 0.98 (s, 3 H, C-4 CH_3 trans to Ph), 1.11 (s, 3 H, *gem*-CH_3 at C-2), 1.28 (s, 3 H, *gem*-CH_3 at C-2), 2.90 (s, 1 H, H α to OCH_3), 3.38 (s, 3 H, OCH_3), 4.01 (s, 1 H, benzylic H at C-5), 7.1–7.4 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 233 (1, M^+), 186 (5), 148 (12), 147 (100), 146 (24), 132 (20), 106 (5), 97 (5), 91 (13), 55 (5), 42 (6), 41 (7), 18 (6); high-resolution mass spectrum, *m/e* 233.178 934 ($C_{15}H_{23}NO$ requires 233.177 955).

A dark control was run in the following manner. A solution of 50 mL of methanol containing 2-aza-3,3,5-trimethyl-1-phenyl-1,4-hexadiene (50 mg, 0.31 mmol) and 70% (w/w) perchloric acid (200 mg, 1.39 mmol) was stirred at 25 °C for 3 h. The solution was worked up in the photochemical reaction. ^1H NMR analysis showed that no reaction had occurred.

Photolysis of 2-Aza-3,3-dimethyl-1-phenyl-1,4-hexadiene Perchlorate (28). Preparation of the Photoproducts 30, 31, and 33. A solution of 400 mg (2.4 mmol) of imine **27** and 1.38 g (9.61 mmol) of 70% perchloric acid in 400 mL of dry, spectrograde methanol was purged with dry nitrogen for 20 min and irradiated in the preparative apparatus through a Corex filter for 1 h. The photolysate was neutralized with 1.33 g of potassium carbonate and concentrated in vacuo, producing a crude photolysate which was dissolved in chloroform, washed with aqueous sodium bicarbonate and water, dried, and concentrated in vacuo to yield 0.41 g (103%) of crude material. Silica gel column chromatography (ether–hexane) gave 0.32 g (80%) of a reddish oil which was subjected to low-pressure liquid chromatography on a silica gel EM-60, size C column. Injection was made in a minimal volume (ca. 180 μL) of 50% ethylacetate–hexane. Elution with 15% ethyl acetate–hexane at a flow rate of 5 mL/min produced several fractions of semipure photoproduct which by repetitive GLC gave three main photoproducts, identified as (*E*)-5-4,4-dimethyl-3-methoxy-6-phenyl-2-hexene (**31**), *cis*-3-methoxy-5-phenyl-2,2,4-trimethylpyrrolidine (**30**), and (*Z*)-5-aza-4,4-dimethyl-3-methoxy-6-phenyl-2-hexene (**33**). The isolated yields for these three photoproduces average 30%, 20%, and 3%, respectively. Spectral data for these photoproducts follow. For **31**: ^1H NMR δ 7.3–7.1 (m, 5 H, aromatic), 4.92 (q, 1 H, J = 7 Hz, vinyl H), 3.70 (s, 3 H, CH_3O), 3.52 (s, 2 H, benzylic), 2.40 (br, 1 H, NH), 1.67 (d, 3 H, J = 7 Hz, allylic CH_3), 1.20 (s, 6 H, geminal CH_3); ^{13}C NMR 160.2 (s, OC=), 140.0 (s, aromatic C-1), 128.5, 128.3, 126.9 (d, aromatics), 105.6 (d, CC=), 61.0 (q, OCH_3), 58.3 (s, $(CH_3)_2C$), 47.8 (t, benzylic), 26.7 (q, geminal CH_3), 11.3 (q, CH_3C=); IR 3003, 1669, 1456, 1383, 1314, 1192, 1134, 1076, 704 cm^{-1}; UV λ_{max} (ϵ) 220 nm (1925); mass spectrum (70 eV), *m/e* (relative intensity) 219 (0.7), 204 (28.8), 114 (8.0), 112 (20.0), 108 (6.4), 106 (6.4), 91 (100), 81 (7.4), 77 (4.8), 65 (12.4); high-resolution mass spectrum, *m/e* 219.161 445 ($C_{14}H_{21}NO$ requires 219.162 305). For **30**: ^1H NMR δ 7.3–7.1 (m, 5 H, aromatic), 4.48 (d, 1 H, J = 8 Hz, H-5), 3.40 (s, 3 H, CH_3O), 3.05 (d, 1 H, J = 6 Hz, H-3), 231 (m, 1 H, H-4), 1.58 (br, 1 H, NH), 1.32 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 0.59 (d, 3 H, J = 7 Hz, H-4'); ^{13}C NMR 140.5 (s, aromatic C-1), 127.8, 127.7, 126.8 (d, aromatics), 95.3 (s, C-3), 61.0 (d, C-5), 60.1 (q, OCH_3), 59.1 (s, C-2), 42.1 (d, C-4), 29.7 (q, CH_3), 22.2 (q, CH_3), 15.6 (q, CH_3); IR 2983, 2939, 1690, 1452, 1367, 1175, 1112, 701 cm^{-1}; UV λ_{max} (ϵ) 225 nm (2280), shoulder at 285 (451); mass spectrum (70 eV), *m/e* (relative intensity) 219 (3.2), 204 (3.3), 185 (4.1), 148 (11.1), 147 (100), 146 (18.4), 145 (7.1), 132 (4.9), 106 (4.8), 104 (6.6), 91 (15.6), 83 (6.5), 77 (5.3), 58 (5.5), 55 (4.6), 43 (16.2), 42 (7.3), 41 (7.9), 39 (4.9); high-resolution mass spectrum, *m/e* 219.161 007 ($C_{14}H_{21}NO$ requires 219.162 305). For **33**: ^1H NMR δ 7.4–7.15 (m, 5 H, aromatic), 4.54 (q, 1 H, J = 7 Hz, vinyl H), 3.58 (s, 2 H, benzylic), 3.50 (s, 3 H, OCH_3), 1.84 (d, 3 H, J = 7 Hz, allylic CH_3), 1.32 (s, 6 H, *gem*-CH_3).

Hydrolysis of 5-Aza-4,4-dimethyl-3-methoxy-6-phenyl-2-hexene (31). A solution containing 50 mg (0.23 mmol) of 5-aza-4,4-dimethyl-3-methoxy-6-phenyl-2-hexene (**31**) and 0.5 mL of 10% sulfuric acid in 5 mL of ether was stirred overnight at 25 °C, washed with aqueous sodium bicarbonate, dried, and concentrated in vacuo to yield 41 mg (88%) of 2-aza-3,3-dimethyl-1-phenylhexan-4-one (**35**): ^1H NMR δ 7.1–7.4 (m, 5 H, aromatic), 3.49 (s, 2 H, benzylic CH_2), 2.54 (q, 2 H, J = 8 Hz, CH_2), 2.09 (br, 1 H, NH), 1.22 (s, 6 H, gem-CH_3), 1.01 (t, 3 H, J = 8 Hz, CH_3); ^{13}C NMR 215.8 (s, C-4), 140.5 (s, aromatic C-1), 128.4, 128.2, 127.0 (d, aromatic), 63.2 (s, quaternary, $C(CH_3)_2$), 48.5 (t, benzylic CH_2), 29.8 (t, CH_2), 24.7 (q, CH_3), 8.0 (q, CH_3); IR 3085, 3047, 2992, 2936, 2880, 1715, 1455, 1383, 1370, 1099, 699 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 204 (6.5), 149 (13.5), 148 (96), 147 (5.8), 146 (5.0), 92 (12.2), 91 (100), 86 (7.8), 84 (11.8), 65 (10.6), 42 (7.3), 41 (6.4), 39 (6.4), 39 (6.4), 29 (6.9).

Ozonolysis of 5-Aza-4,4-dimethyl-3-methoxy-6-phenyl-2-hexane (31). A solution of 65 mg (0.30 mmol) of 5-aza-4,4-dimethyl-3-methoxy-6-phenyl-2-hexene (**31**) in 50 mL of methanol in a glass bubbling tower was immersed in a dry ice/acetone bath at −77 °C. A stream of ozone in oxygen was passed through the solution for approximately 1 min. The initially yellow solution cleared and then rapidly turned blue. At this point the ozone flow was terminated, and 75 mg of dimethyl sulfide was added. The reaction was then worked up according to the procedure of Pappas[17] to yield 56 mg (92%) of methyl *N*-benzyl-α-aminoisobutyrate (**195**) which contained some traces of the free acid. This material was found to be identical (^1H NMR, ^{13}C NMR, IR, GLC, mass spectrum) with the independently synthesized material.

Synthesis of Methyl *N*-Benzyl-α-aminoisobutyrate (36). To a solution of 3.65 mL (5.95 g, 50 mmol) of thionyl chloride in 40 mL of anhydrous methanol at −10 °C was added 5.16 g (50 mmol) of solid α-aminoisobutyric acid (Alrich). The solid slowly dissolved and the reaction was stirred for 6 h, the last 30 min at reflux. The material was concentrated in vacuo to yield the acid chloride as a thick oil which solidified on standing. This acid chloride was used directly in the procedure of Zervas and Theodoropoulos,[18] producing 3.2 g (31%) of the crude methyl ester as a red oil. Addition of carbon tetrachloride, removal of the precipitate, and concentration in vacuo yielded 2.6 g (25%) of semipure (ca. 80%) methyl ester. Purification by GLC (10% SE-30 on Variport 30, 170 °C) yielded the *N*-benzyl methyl ester **36** as a clear oil: ^1H NMR δ 7.3 (m, 5 H, aromatic), 3.71 (s, 3 H, OCH_3), 3.58 (s, 2 H, benzylic CH_2), 1.70 (s, 1 H, NH), 1.32 (s, 6 H, CH_3); ^{13}C NMR 177.4 (s, C=O), 140.3 (s, aromatic C-1), 128.4, 127.0 (d, aromatic), 59.3 (s, $C(CH_3)_2$), 51.8 (q, CH_3O), 49.1 (t, $PhCH_2$), 25.4 ppm (q, CH_3); IR 2988, 2961, 1726, 1453, 1435, 1384, 1367, 1262, 1191, 1139, 696 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 192 (1), 149 (10), 148 (80), 92 (10), 91 (100), 65 (13), 41 (10); high-resolution mass spectrum, *m/e* 192.102 057 (M − 15) ($C_{11}H_{14}NO_2$ requires 192.102 440).

Preparation of 2-Isobutenyl-1-pyrroline (39). 2-Isobutenyl-1-pyrroline was prepared according to the method of Bielawski[13] from *N*-vinyl-2-pyrrolidone and isobutenyllithium in 40% yield. The reaction was carried out at 0 °C, and the product was purified by molecular distillation, giving 2-isobutenyl-1-pyrroline (**39**) as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.05 (d, 1 H, vinyl), 3.90 (t, 2 H, α to N), 2.60 (t, 2 H, allylic), 2.05 (m, 2 H, methylene), 2.00 (s, 3 H, methyl), 1.90 (s, 3 H, methyl); UV (CH_3OH) λ_{max} 236 nm (13 400); IR (film) 3000, 2450, 1670, 1600, 1575, 1450, 1380, 1110 cm^{-1}; high-resolution mass spectrum, *m/e* 123.0984 ($C_8H_{13}N$ requires 123.0894).

1-(3-Methyl-2-butenyl)-2-phenyl-1-pyrrolinium Perchlorate (40). An ether solution (2 mL) of 2-phenyl-1-pyrroline[12] (0.40 g, 2.7 mmol) and 1-bromo-3-methyl-2-butene (0.45 g, 3.00 mmol) was stirred at 25 °C under Ar for 19 h. The resulting oily solid was tritrated with ether; the residual ether was removed by concentration in vacuo, and the reaction mixture was subjected to molecular distillation (to 50 °C, 0.05 torr) to remove starting pyrroline. Anion-exchange chromatography (Dowex 1-X8, methanol) was used to obtain the perchlorate salt **40** (0.83 g, 96%) as an oil which was used without further purification. An analytical sample of the bromide salt was prepare by recrystallization from methyl ether ketone (mp 98.5–101 °C). The spectra data for the perchlorate salt are as follows: ^1H NMR (acetone-d_6) δ 1.64 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 2.2–2.8 (m, 2 H, CH_2 at C-4), 3.5–3.9 (m, 2 H, CH_2 at C-3), 4.0–4.8 (m, 4 H, methylenes α to N), 5.48 (m, 1 H, vinyl H), 7.4–8.0 (m, 5 H, aromatic H); UV (CH_3OH) λ_{max} 255 (ϵ 12 070); ^{13}C NMR (acetone-d_6) δ 186.9 (s, C=N), 142.2 (s, C-1 aromatic) 137.2 (d, para aromatic), 129.8 (d, ortho aromatic), 129.2 (d, meta aromatic), 128.0 (s, disubstituted olefin), 115.2 (d, monosubstituted olefin), 60.8 (t, CH_2 α to N and allylic), 50.2 (t, C-5), 41.4 (t, C-3), 25.6 (q, CH_3), 18.7 (t, C-4), 18.2 (q, CH_3); mass spectrum (70 eV), *m/e* (relative intensity) (Br^- salts) 213 (56), 145 (68), 144 (100), 117 (30), 115 (16), 104 (14), 91 (14), 69 (29), 41 (32); high-resolution mass spectrum (bromide), *m/e* 213.151 225 ($C_{15}H_{19}N$ = M − 1 requires 213.151 748).

Anal. Calcd for $C_{15}H_{20}NBr$: C, 61.23; H, 6.85; N, 4.76; Br, 27.16. Found: C, 57.78; H, 7.31; N, 4.68; Br, 26.27.

Preparation of 1-Prenyl-2-isobutenyl-1-pyrrolinium Perchlorate (41). A solution of 2-isobutenyl-1-pyrroline (0.895 g) and freshly distilled prenyl bromide (1.00 g) was stirred under argon at 25 °C for 12 h. A methanol solution of the brown oily reaction mixture was subjected to anion-exchange chromatography on Dowex X1-8 resin to give 1-prenyl-2-isobutenyl-1-pyrrolinium perchlorate as a yellow oil: 1.90 g (92%); ^1H NMR ($CDCl_3$) δ 6.2 (br s, 1 H, vinyl), 5.1 (t, 1 H, vinyl), 4.2 (m, 4 H, α to N), 3.4 (t, 2 H, allylic), 2.2 (t, 2 H, methylene), 2.05 (s, 6 H,

methyl), 1.65 (s, 6 H, methyl), UV (absolute CH_3OH) 265 nm (7980); IR (film) 3000, 2950, 1660, 1600, 1580, 1460, 1395, 1115 cm^{-1}; high resolution mass spectrum, *m/e* 172.282 517 ($C_{13}H_{22}N$ requires 172.282 629).

Photolysis of 1-(3-Methyl-2-butenyl)-2-phenyl-1-pyrrolinium Perchlorate (40). Preparation of *endo*- and *exo*-3-Methoxy-4,4-dimethyl-5-phenyl-1-azabicyclo[3.3.0]octanes (40). An argon-purged solution containing 1-(3-methyl-2-butenyl)-2-phenyl-1-pyrrolinium perchlorate (250 mg, 0.80 mmol) in 200 mL of methanol was irradiated for 1 h through a Corex filter. Solid K_2CO_3 was added, and the mixture was stirred for 3 min before the mixture was filtered and concentrated in vacuo. The photolysate was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4e, and concentrated in vacuo. The pyrrolizidines **42** were further purified by molecular distillation (0.025 torr, 45–55 °C) to give an oil (114 mg, 58%) as ca. a 1:1 mixture of epimers **42ex** and **42en**. Separation was accomplished by GLC (5% SE-60, 2 m × $^5/_{16}$ in., 155 °C), with the exo isomer **42ex** having the longer retention time.

endo-3-Methoxy-4,4-dimethyl-5-phenyl-1-azabicyclo[3.3.0]octane (**42en**): IR ($CHCl_3$) 3035, 3950, 3925, 2855, 1675, 1480, 1465, 1445, 1365, 1110, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50 (s, 3 H, *exo*-methyl), 1.18 (s, 3 H, *endo*-CH_3), 1.5–4.0 (m, 9 H, all ring protons), 3.22 (s, 3 H, OCH_3), 7.1–7.5 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 245 (0.7, M^+), 159 (39), 158 (100), 146 (20), 117 (14), 115 (15), 104 (13), 103 (30), 91 (29), 77 (24), 71 (15), 51 (11), 42 (16), 41 (36), 39 (16); UV (EtOH λ_{max} 252 nm (ϵ 471), 258 (491), 264 (489), 268 (443); ^{13}C NMR ($CDCl_3$) δ 146.1 (s, C-1, aromatic), 127.3 (d, meta aromatic), 126.9 (d, ortho aromatic), 125.8 (d, para aromatic), 91.6 (d, C-3), 81.8 (s, C-5), 58.6 (t, C-2), 57.8 (q, OCH_3), 55.2 (t, C-3), 47.4 (s, C-4), 34.7 (t, C-6), 27.5 (q, CH_3), 24.9 (t, C-7), 19.6 (q, CH_3); high-resolution mass spectrum, *m/e* 245.176 844 ($C_{16}H_{23}NO$ requires 245.177 955).

exo-3-Methoxy-4,4-dimethyl-5-phenyl-1-azabicyclo[3.3.0]octane (**42ex**): IR ($CHCl_3$) 3040, 2950, 2915, 2850, 1450, 1370, 1160, 1120, 1030, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.45 (s, 3 H, *exo*-CH_3), 1.20 (s, 3 H, endo CH_3), 1.2–2.2 (m, 4 H, methylenes at C-5 and C-6), 2.5–3.3 (m, 4 H, methylenes α to N), 3.35 (s, 3 H, OCH_3), 1.10–7.55 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 245 (10), 216 (13), 214 (21), 168 (7), 160 (7), 159 (10), 158 (76), 146 (100), 103 (24), 91 (8), 77 (9), 41 (6); UV (EtOH) λ_{max} 252 nm (ϵ 538), 258 (480), 264 (376), 267 (301); ^{13}C NMR ($CDCl_3$) δ 145.6 (s, C-1 aromatic), 127.4 (d, meta aromatic), 126.8 (d, ortho aromatic), 125.9 (d, para aromatic), 85.5 (d, C-3), 81.5 (s, C-5), 58.3 (t, q, C-2, OCH_3), 56.3 (t, C-8), 46.1 (s, C-4), 36.0 (t, C-6), 24.9 (q, CH_3), 22.7 (t, C-7), 19.7 (q, CH_3) high-resolution mass spectrum, *m/e* 245.177 573 ($C_{16}H_{23}NO$ requires *m/e* 245.177 955).

A dark control was run in the following manner. The phenyl pyrrolinium salt **40** (315 mg, 1.00 mmol) was heated at reflux for 1.0 h in 200 mL of methanol. The solution was concentrated in vacuo. ^1H NMR analysis showed none of the corresponding pyrrolizidines **42** are obtained.

Photolysis of 1-Prenyl-2-isobutenyl-1-pyrrolinium Perchlorate (41). Preparaton of the Hydropyrrolizidines 43. A solution of 1-prenyl-2-isobutenyl-1-pyrrolinium perchlorate (0.200 g) in 250 mL of dry, degassed methanol was irradiated in a preparative apparatus with Corex-filtered light for 1.0 h. The crude photolysate was neutralized by being stirred over potassium carbonate, filtered through Celite, and concentrated in vacuo. The resulting mixture of solid potassium carbonate and golden oil was dissolved in dichloromethane and water. The organic layer was separated, dried (Na_2SO_4), and concentrated in vacuo, giving a mixture of the diastereomeric 2-methoxy-3,3-dimethyl-2a-isobutenylpyrrolizidines **43ex** and **43en** as a brown oil (0.173 g, 87%). The diastereomers were separated by GLC (20% SE-30 on ABS Anakrom, 15 ft × $^5/_{16}$ in., 175 °C, flow rate 16 mL/min). The spectral data for these compounds follow.

Major isomer (R_f 12 min): ^1H NMR ($CDCl_3$) δ 5.05 (br s, 1 H, vinyl), 3.45 (t, 1 H, α to methoxy), 3.26 (s, 3 H, methoxy), 2.80 (m, 2 H, α to N), 2.63 (br s, 4 H, methylenes), 2.50 (dd, 2 H, α ω N), 1.84 (s, 3 H, methyl), 1.70 (s, 3 H, methyl), 1.04 (s, 3 H, methyl) and 0.98 (s, 3 H, methyl); ^{13}C NMR ($CDCl_3$) δ 130.8 (d, vinyl), 139.8 (s, vinyl), 91.4 (d, α to methoxy), 87.6 (s, α to N), 58.5 (q, methoxy), 58.1 (t, α to N), 55.2 (t, α to N), 49.0 (s, *gem*-dimethyl), 33.6 (t, methylene), 28.1 (q, methyl), 26.7 (t, methylene), 24.8 (q, methyl), 19.9 (q, methyl), 18.9 (q, methyl); IR (film) 2980, 2850, 1600, 1450, 1380, 1090 cm^{-1}; high-resolution mass spectrum, *m/e* 223.268 577 ($C_{14}H_{25}NO$ requires 223.267 408).

Minor isomer (R_f 10 min): ^1H NMR ($CDCl_3$) δ 5.01 (br s, 1 H, vinyl), 3.55 (t, 1 H, α to methoxy), 3.34 (s, 3 H, methoxy), 3.00 (dd, 2 H, α to N), 2.60 (m, 2 H, α to N), 1.88 (s, 3 H, methyl), 1.70 (s, 3 H, methyl), 1.64 (br s, 4 H, methylene), 1.07 (s, 3 H, methyl), 0.92 (s, 3 H, methyl); ^{13}C NMR ($CDCl_3$) δ 132.5 (s, vinyl), 129.2 (d, vinyl), 85.4 (d, α to methoxye, 80.3 (s, α to N), 58.3 (q, methoxy), 57.8 (t, α to N), 56.0 (t, α to N), 47.0 (s, *gem*-dimethyl), 35.0 (t, methylene), 28.0 (q, methyle, 24.9 (t, methylene), 23.0 (q, methyl), 19.4 (q, methyl), 18.1 (q, methyl); IR (film) 2990, 2880, 1670, 1450, 1380, 1105 cm^{-1}; high-resolution mass spectrum, *m/e* 223.770 511 ($C_{14}H_{25}NO$ requires 223.267 408).

Quantum Yield Measurements. Quantum yields were measured by using a "linear optical bench" system equipped with a high-pressure, 200-W, mercury lamp (Illumination Industries Model CA-200-8003), the output of which was focused with a quartz collimator and passed through a quartz-faced, water-cooled, filer solution cell with three 1-cm compartments containing separately, 1.0 M (262.86 g/L) nickel sulfate hexahydrate in 5% sulfuric acid, 0.8 M (224.88 g/L) cobalt sulfate heptahydrate in 5% sulfuric acid, and 0.0001 M (0.0325 g/L) bismuth chloride in 10% hydrochloric acid. The UV transmission of this filter was 250–310 nm, with a maximum at 280 nm. The filtered light passed through a beam splitter which diverted light 90°. The light not diverted passed through two quartz-faced, water-cooled cells aligned in series. During actinometer calibration runs, both the front and back cells were filled with 0.006 M potassium ferrioxalate. During photolysis runs, the front cell contained iminium salt solutions. The back cell contained potassium ferrioxalate in order to monitor light not absorbed by the substrate. The diverted light was received by a silicon solar cell in order to monitor the light output. The signal received by the solar cell was amplified and fed through a Raytheon RC-4151 voltage/frequency converter. Integration this this signal was performed by counting the frequency transmitted by the converter.

The amount of light not diverted was determined by calibration of the solar cell with ferrioxalate actinometry.[15] The light absorbed by the front cell containing the potassium ferrioxalate was determined at several different percent conversions ranging from 0.3 to 1.2% (0.1–0.4 millieinstein). A plot of the number of millieinsteins vs. the number of counts obtained from the electronic counter for each run gave the following equation determined by a least-squares analysis: no. of millieinstein = 2.91 × 10^8 × no. of counts + 0.01. The confidence factor (r^2) was 0.998. The light output for each photolysis was obtained by using this equation.

Product analyses were performed by GLC (5 ft × $^1/_8$ in, 1.5% OV-101 on Chromosorb G, flow rate 9 mL/min) after the reaction mixtures were worked up as in the preparative runs by using either triphenylmethane or pyrene (as indicated below) as an internal standard. Conversions in quantum yield runs were maintained in the region of 0.4–5%.

Summary of Quantum Yield Results for Irradiation of *N*-Allyliminium Salts in Methanol. The data are listed as follows: iminium salt (mmol); run number; product (mmol); quantum yield of formation; percent conversion; GLC internal standard; column temperature.

5-Isobutenyl-3,3,5-trimethyl-2-phenyl-1-pyrrolinium perchlorate (**10**) (0.37 mmol); run 1; 0.86 millieinstein; pyrrolidine **14ex** (7.07 × 10^{-3} mmol); Φ = 0.008; 1.91% conversion; triphenylmethane; 160 °C. Run 2; 0.58 millieinsteinf pyrrolidine **14ex** (6.34 × 10^{-3} mmol); Φ = 0.011; 1.71% conversion; triphenylmethane; 160 °C.

5-Isobutenyl-1,3,3,5-trimethyl-2-phenyl-1-pyrrolinium perchlorate (**11**) (0.21 mmol); run 1; 1.79 millienstein; pyrrolidine product **15** (9.82 × 10^{-3} mmol); Φ = 0.005; 4.67% conversion; pyrene; 164 °C. Run 2; 160 millienstein; pyrrolidine product **15** (7.6 × 10^{-3} mmol); Φ = 0.005; 3.63% conversion; pyrene; 164 °C.

Perchlorate salt of 2-aza-1-phenyl-3,3,5-trimethyl-1,4-hexadiene (**22**) (0.19 mmol); run 1; 0.38 millieinstein; pyrrolidines **29** (2.68 × 10^{-3} mmol); Φ = 0.007; 1.38% conversion; triphenylmethane; 140 °C. Run 2, 0.42 millieinsteinf pyrrolidines **29** (2.84 × 10^{-3} mmol); Φ = 0.007; 1.49% conversion; triphenylmethane; 140 °C.

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