# Exploratory and Mechanistic Aspects of the Electron-Transfer Photochemistry of Olefin–N-Heteroaromatic Cation Systems

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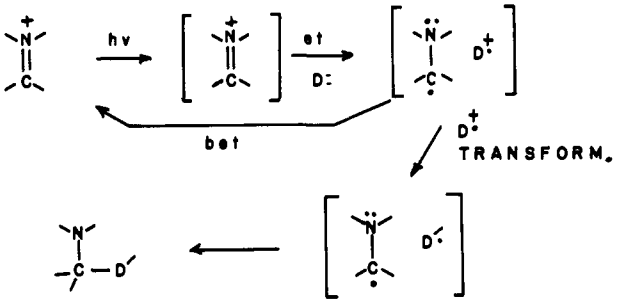
**Abstract:** Exploratory and mechanistic studies have been conducted probing electron-transfer-induced fluorescence quenching and photochemical cyclization processes in olefin–N-heteroaromatic cation systems. The fluorescence of the quinolinium and isoquinolinium perchlorates **1–5** is efficiently quenched by electron-rich olefins at rates near to the diffusion-controlled limit. Plots of calculated free energies for electron transfer vs. the log of the fluorescence quenching rate constants are linear for these perchlorate salts. Also, the fluorescence efficiency of systems containing these N-heteroaromatic cation chromophores decreases dramatically when electron-rich allyl side chains are appended at nitrogen as in the perchlorate salts **6–9**. An interpretation of these results in terms of excited-state electron transfer has been offered. The chemical consequences of excited-state electron transfer in olefin–N-heteroaromatic cation systems has been explored through study of a variety of *N*- and *C*-alkenyl-substituted quinolinium and pyridinium salts. Irradiation of methanolic or aqueous solutions of *N*-prenylquinolinium perchlorate **7** gives after reduction the benzoindolizidines **19** or **20**. Mechanisms for this cyclization reaction as well as a photofragmentation process producing the tetrahydroquinoline **18** involving initial intramolecular electron transfer from the olefin to excited-state quinolinium salt chromophores are presented. The pyridinium salts **26** and **46** undergo analogous photocyclization reactions. In the case of **26**, a secondary photoreduction occurs on the initially formed, 1,2-dihydropyridine ring containing indolizidine **30** to produce the observed product **27**. This process has been investigated, resulting in a proposal for the detailed reduction mechanism. The photochemistry of *N*-allylpyridinium perchlorate **63** demonstrates the competitive nature of excited-state electron transfer and pyridine ring electrocyclization pathways. The cyclopentenylamine **64** is produced in high yield by irradiation of **63** in methanol by a pathway involving electrocyclization, methanol capture, and methanolysis of the intermediate bicyclic aziridinium salt **69**. Lastly, production of the methoxycyclopentanone **76** and cyclopentylamines **81** and **85** by irradiation of the 2-alkenylpyridinium perchlorates **72** and **73** is rationalized by mechanisms involving electron-transfer-induced photospirocyclization followed by dihydropyridine ring opening.

In recent years, exploratory and mechanistic photochemical studies have placed increasing emphasis on a new class of excited-state processes that are initiated by one-electron transfer from or to excited states of organic and inorganic systems.[1] The mounting interest in excited-state quenching and reaction processes activated in this fashion appears to be due to several factors. First, the efficiencies or rates of electron-transfer-sensitized or -initiated reactions are governed in part by the excited- and ground-state electrochemical potentials. Indeed, many cases exist in which electron transfer from sensitizer to acceptor is possible even though classical energy transfer by the exchange mechanism is prohibitively endoergic. Second, the key reactive intermediates in electron-transfer-induced photochemical pathways are ion radicals and not necessarily the initially populated excited states. Thus, the nature of chemical reactions followed in these systems can be predicted on the basis of principles applied in radical ion chemistry.

Our studies in this area have concentrated on the photochemistry of systems containing the iminium cation grouping ($R_2N^+{=}CR_2$). The excited- and ground-state reduction potentials of systems containing this chromophore allow them to serve as ideal acceptors in electron-transfer-induced, excited-state quenching and reaction processes. In general, reversible electron-transfer and secondary reactions of the donor-derived radical cations are responsible for quenching and photoaddition processes (Scheme I) that have been observed to occur between iminium salts and electron-rich olefins,[2] allylsilanes,[3] alcohols, ethers,[4] and arenes.[5] In addition, our efforts have uncovered examples of intramolecular electron transfer from olefinic to excited iminium salt groupings as part of *N*-allyliminium perchlorate photocyclization processes (Scheme II) serving as useful methods for nitrogen heterocycle synthesis.[6,7]

A consideration of excited-state electrochemical potentials suggests that salts of nitrogen heteroaromatic systems, which contain the iminium salt group within cyclic-conjugated chromophores, should serve as efficient acceptors in excited-state electron-transfer processes. Data from a variety of spectroscopic studies with N-protonated and alkylated monoazaaromatic com-

Scheme I




Scheme II

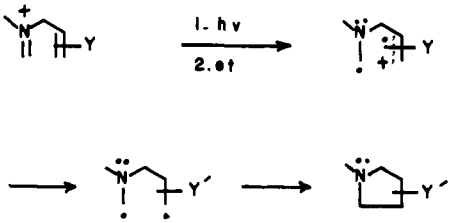



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Table I. Excited-State and Electrochemical Properties of N-Heteroaromatic Salts

| perchlorate salts | UV max,[a] nm ($\epsilon$) | fluorescence max,[a] nm | $\phi_f$[a] ($\lambda$ excit, nm) | $\Delta E_{0,0}$,[b] kcal/mol | $\tau$,[c] ns | $E_{1/2}(-)$,[d] V | $E_{1/2}{}^{S_1}(-)$[g] |
|---|---|---|---|---|---|---|---|
| 1 | 312 (6530) | 414 | 0.88 (312) | 80.3 | 12 | −0.95 | +2.5 |
| 2 | 315 (7230) | 402 | 0.85 (315) | 81.5 | 13 | −0.85 | +2.7 |
| 3 | 336 (3240) | 376 | 0.94 (336) | 81.5 | 23 | −0.98 | +2.6 |
| 4 | 334 (4600) | 380 | 0.94 (334) | 81.3 | 25 | −1.00 | +2.5 |
| 5 | 312 (8280) | 390 | 0.49 (312) | 82.2 | 3 | −1.06 | +2.5 |
| 6 | 317 (7450) | 418 | 0.26 (317) | | | | |
| 7 | 313 (7860) | 415 | 0.02 (313) | | | | |
| 8 | 336 (4280) | 373 | 0.33 (336) | | | | |
| 9 | 336 (4150) | 380 | 0.014 (336) | | | | |
| 10 | | | | 100[e] | | −1.1[f] | +3.2 |
| 11 | | | | 100[e] | | −1.3[f] | +3.0 |
| 12 | | | | 97[e] | | −0.9[f] | +3.3 |

[a] Solvent $CH_3CN$, 25 °C, nondegassed solutions. [b] Determined from intersection of absorption and fluorescence spectral curves. [c] Calculated from absorption spectroscopic parameters.[15b] [d] Measured in $H_2O$–$CH_3CN$ with $(n\text{-Bu})_4NClO_4$ as supporting electrolyte vs. SCE. [e] Estimated from UV absorption spectroscopic data. [f] Approximate values obtained from analogous compounds.[16] [g] Estimated by $E_{1/2}{}^{S_1}(-) = \Delta E_{0,0} + E_{1/2}(-)$.

Table II. Olefin Quenching of Quinolinium and Isoquinolinium Salt Fluorescence

| olefin quencher | olefin $E_{1/2}(+)$,[a] V | $k_q$, $M^{-1}$ $s^{-1}$, for quenching of N-heteroaromati c salts[b] 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| tetramethylethylene | +1.63 | $4.7 \pm 0.1 \times 10^{10}$ | $2.4 \pm 0.1 \times 10^{10}$ | $7.2 \pm 0.2 \times 10^{9}$ | $7.0 \pm 0.3 \times 10^{9}$ | $3.2 \pm 0.2 \times 10^{10}$ |
| α-pinene | +1.71 | $3.2 \pm 0.1 \times 10^{10}$ | $2.3 \pm 0.1 \times 10^{10}$ | $6.6 \pm 0.2 \times 10^{9}$ | $5.8 \pm 0.1 \times 10^{9}$ | $1.5 \pm 0.1 \times 10^{10}$ |
| cyclohexene | +1.98 | $2.1 \pm 0.1 \times 10^{10}$ | $2.0 \pm 0.1 \times 10^{10}$ | $5.2 \pm 0.2 \times 10^{9}$ | $4.5 \pm 0.1 \times 10^{9}$ | $1.2 \pm 0.1 \times 10^{10}$ |
| methyl β,β-dimethylacrylate | +2.63 | $9.0 \pm 0.8 \times 10^{8}$ | $8.8 \pm 0.6 \times 10^{8}$ | $1.7 \pm 0.1 \times 10^{8}$ | $1.7 \pm 0.1 \times 10^{8}$ | $4.1 \pm 0.5 \times 10^{8}$ |
| methyl acrylate | +3.68 | $4.1 \pm 0.1 \times 10^{8}$ | $1.5 \pm 0.1 \times 10^{8}$ | $2.0 \pm 0.1 \times 10^{7}$ | $8.7 \pm 0.3 \times 10^{6}$ | $1.1 \pm 0.1 \times 10^{8}$ |
| acrylonitrile | +3.83 | $3.5 \pm 0.1 \times 10^{7}$ | $1.9 \pm 0.1 \times 10^{7}$ | $3.0 \pm 0.1 \times 10^{6}$ | $1.3 \pm 0.1 \times 10^{6}$ | $7.6 \pm 0.5 \times 10^{6}$ |

[a] Estimated from ionization potentials.[13] [b] From Stern-Volmer analysis of fluorescence data on $CH_3CN$ solutions at 25 °C; perchlorate salt concentrations ca. $1 \times 10^{-4}$ m.

pounds implicate pathways of this type in the production of heterocyclic radicals by irradiation in the presence of neutral and anionic electron donors.[8] Likewise, electron transfer has been invoked as the primary step in a variety of addition, reduction, and dimerization reactions occuring between pyridinium and related N-heteroaromatic cations and alcohols, ethers, amines, and carboxylate ions.[9] On the basis of these observations and the results of our earlier studies, we anticipated that electron-rich olefins would serve as efficient donors in carbon–carbon-bond-forming, electron-transfer-induced addition and cyclization reactions with appropriately substituted azaaromatic systems. In order to test this postulate, we have explored the photochemistry of various alkenyl-substituted pyridinium and quinolinium perchlorates. This effort has uncovered the mechanistically and synthetically interesting features of N-heteroaromatic salt photochemistry described below.[10]

## Results and Discussion

**Fluorescence Quenching Studies.** Pertinent data indicative of charge or electron transfer in excited-state systems is found in correlations between rate constants for excited-state quenching and predicted rate constants for electron transfer.[11,12] This feature

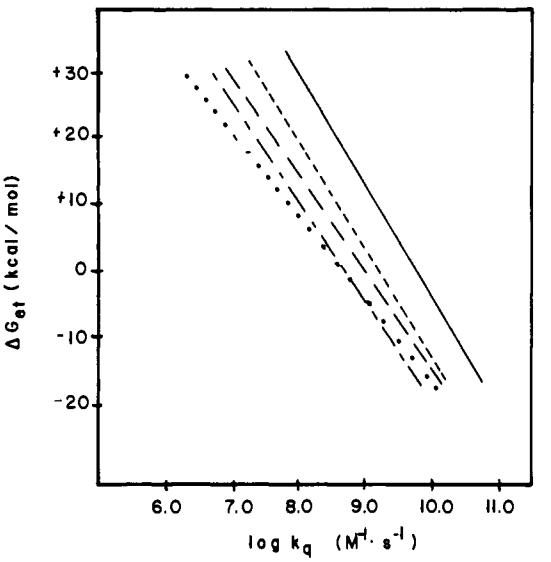


Figure 1. Plot of the calculated free energies for electron transfer from the olefins listed in Table II to the N-heteroaromatic salts 1 (—), 2 (---), 3 (- - -), 4 (--), and 5 (– –) vs. the log of the rate constants for fluorescence quenching from Table II.

was explored initially with the quinolinium and isoquinolinium perchlorates **1–5**, prepared by N-protonation or -methylation of the corresponding heterocycles (see Experimental Section). Pertinent electrochemical and fluorescence spectroscopic data for these salts are included in Table I. The rate constants for fluorescence quenching by olefins with varying oxidation potentials[13] were determined by Stern–Volmer analysis of quenching

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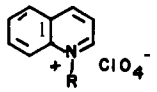
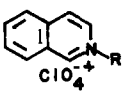
data accumulated for acetonitrile solutions of the perchlorate salt–olefin systems (Table II).

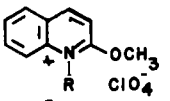
The rate constants for fluorescence quenching by the olefins appear to be well correlated with those predicted[12] for electron transfer to the singlet excited N-heteroaromatic salts. Indeed, plots of log $k_q$ vs. calculated $\Delta G_{et}$ (Figure 1) for the olefin–salt pairs reflect the near-linear dependence of quenching rates on olefin oxidation potentials.[13] Importantly, the electron-rich olefins, tetramethylethylene, $\alpha$-pinene, and cyclohexene, serve as efficient quenchers of the fluorescence of all of the salts. The quenching rate constants approach the diffusion-controlled limit (ca. $1 \times 10^{10}$ $M^{-1}$ $s^{-1}$ in $CH_3CN$) even though exchange-energy transfer in these cases is prohibitively endoergic. It should be noted that the emission and absorption spectroscopic properties of mixtures of the olefins and N-heteroaromatic perchlorates fail to reveal ground- or excited-state complex formation in acetonitrile solution. Unfortunately, the solubility characteristics of the salts prevent inspection of these systems in solvents of lower polarity where exciplex emission should be more efficient. Likewise, a similar fluorescence quenching study with simple N-substituted pyridinium salts is not feasible due to the absence of reliable singlet-state emission from these systems.[14] A further indication of quenching comes from inspection of the fluorescence properties of the *N*-methyl-, *N*-allyl-, and *N*-prenylquinolinium and -isoquinolinium perchlorates. In both the quinoline (**2**, **6**, and **7**) and isoquinoline



1 (R = H)
2 (R = $CH_3$)



3 (R = H)
4 (R = $CH_3$)



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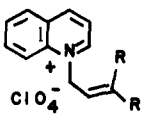
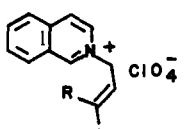
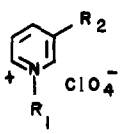


6 (R = H)
7 (R = $CH_3$)

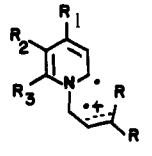


8 (R = H)
9 (R = $CH_3$)



10 ($R_1$ = $R_2$ = H)
11 ($R_1$ = $CH_3$, $R_2$ = H)
12 ($R_1$ = $CH_3$, $R_2$ = $CO_2CH_3$)

(**4**, **8**, **9**) series, replacement of the *N*-methyl group by olefin-containing allyl and prenyl side chains results in dramatic decreases in the fluorescence quantum yields (Table I). The diminution of emission efficiency by nearly 2 orders of magnitude in these cases appears to be due to decreases in singlet excited-state lifetimes[15] brought about by reversible intramolecular electron transfer via the intermediacy of cation diradical intermediates related to **13**.



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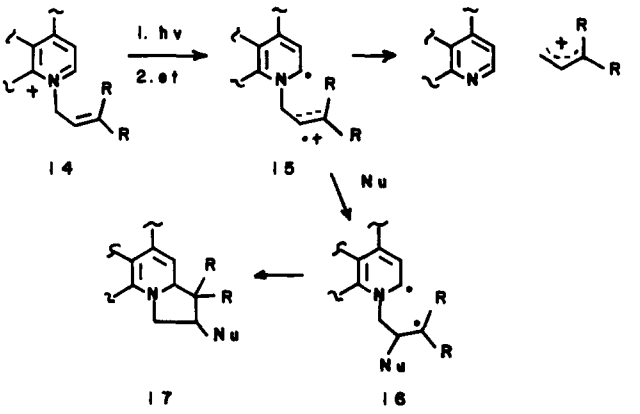
The combined observations and data presented above can be employed in deriving qualitative predictions that either inter- or intramolecular electron transfer from electron-rich olefins to the excited states of the N-heteroaromatic salts should serve as an efficient pathway for production of olefin-derived cation radicals as part of radical-pair or diradical intermediates. The remaining sections of this paper summarize observations we have made in studies of the chemical consequences of this process.

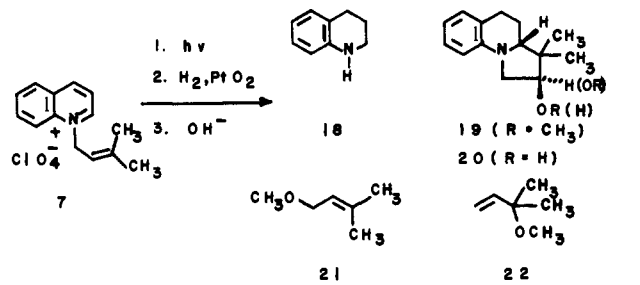
Scheme III




14 15 17 16

**Photocyclization of *N*-Prenylquinolinium Perchlorate.** In previous investigations of *N*-allyliminium salt photochemistry, we had observed that intramolecular electron-transfer pathways were responsible for photocyclization reactions leading to production of substituted pyrrolidines in synthetically useful yields.[6,7] Similar routes should be available to *N*-allyl salts of nitrogen heteroaromatic systems **14**. In these cases, the diradical cations **15**, generated by excited-state electron transfer, could be trapped by nucleophiles to produce the delocalized 1,5-diradicals **16**, serving as precursors of products **17** containing 1,2-dihydropyridine and related unsaturated heterocyclic ring systems (Scheme III). The structural outcome of cyclization reactions of this type as well as the potential for generating interesting dihydropyridine ring systems stimulated an exploration of chemical and mechanistic aspects of substituted *N*-allylpyridinium and -quinolinium salt photochemistry.

Our initial investigations were focused on the *N*-prenylquinolinium perchlorate **7**, a substance prepared earlier for fluorescence measurements (vide supra). Irradiation of a nitrogen-purged, methanolic solution of **7** with flint glass ($\lambda > 310$ nm) filtered light, followed by immediate hydrogenation ($PtO_2$) of the




7 18 19 (R = $CH_3$) 20 (R = H) 21 22

crude photolysate, neutralization, and chromatographic separation (silica gel), afforded 1,2,3,4-tetrahydroquinoline (**18**) (23%) and the stereoisomeric (1:1.6) benzoindolizidines **19** (27%, $\phi$ = 0.004). The quinolinium salt was transformed to a mixture of **18** (37%) and the epimeric indolizidinyl alcohols **20** (21%) upon irradiation in 25% aqueous acetonitrile followed by reduction, neutralization, and chromatography.

Several features of these reactions require comment. Firstly, on the basis of the fluorescence quenching results reported earlier, it is reasonable to postulate that the benzoindolizidine-forming process most probably occurs from the singlet excited state of 7[17]

(14) To our knowledge, fluorescence from unsubstituted pyridinium salts has yet to be detected. In our laboratory we have been unable to observe singlet emission from a variety of these salts.

(15) The effect of replacement of methyl by allyl and prenyl groups in the quinolinium and isoquinolinium salt systems on $\phi_f$ as expected is not due to an effect on $k_f$ since calculated $k_f$ values from UV absorption spectroscopic data are unchanged in the series.

(16) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970.

(17) (a) Intramolecular electron transfer in the singlet excited states of these systems having only $\pi$–$\pi^*$ singlet and triplet configurations available should be much more efficient than intersystem crossing. Indeed, it is well-known that the phosphorescence quantum yield for N-heterocycles such as quinoline are dramatically reduced in hydroxylic solvents in which the lowest energy triplet and singlet states have $\pi$–$\pi^*$ configurations.[17b] (b) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905. Li, R.; Lin, E. C.; *Ibid.* **1972**, *57*, 605. Janic, I.; Kawski, A. *Adv. Mol. Relaxation Processes* **1973**, *5*, 185.

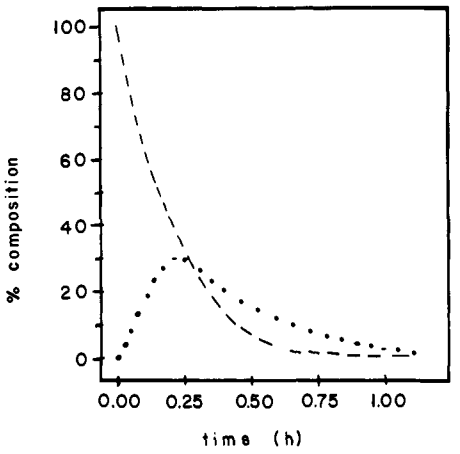
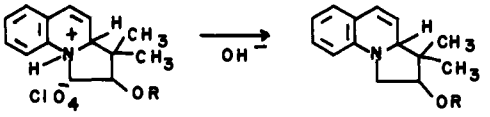



**Figure 2.** Progress of the photoconversion of the *N*-prenylpyridinium perchlorate **26** to indolizidine **27**. Plotted are the time courses for disappearance of **26** (--) and formation of **27** (—).

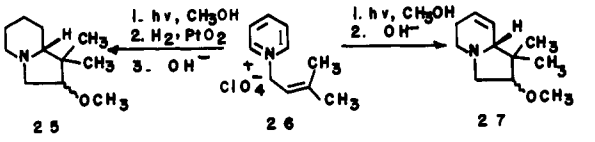
via the mechanistic pathway outlined in Scheme III. Importantly, the hydrogenation step must be performed prior to neutralization of the crude photolysate in order to detect observable quantities of indolizidine products. This can be attributed to the extreme lability of 1,2-dihydroquinoline ring containing indolizidine **24**,




**23** **24**

which would be produced upon deprotonation of indolizidinium salt **23** present in the photolysate rendered acidic by the simultaneous generation of 1 equiv of $HClO_4$. The second feature concerns the mechanism for conversion of **7** to quinolinium perchlorate, the precursor of the tetrahydro product **18**. Results of dark control reactions and analysis of the five-carbon compounds corresponding to the prenyl side chain suggest that excited-state fragmentation of **7** occurs to produce quinoline and the prenyl cation. Significantly, the methyl ethers **21** and **22** are produced in ca. 1.4:1 ratio from irradiation of methanolic solutions of **7**. Methanolysis of prenyl bromide also produces ethers **21** and **22** in a similar ratio. On the basis of these observations, it appears that quinoline formation occurs by either a direct excited-state heterolytic cleavage of **7** or an electron-transfer-induced pathway involving homolytic cleavage of the intermediate diradical cation (e.g., **15**) as depicted in Scheme III.[18]

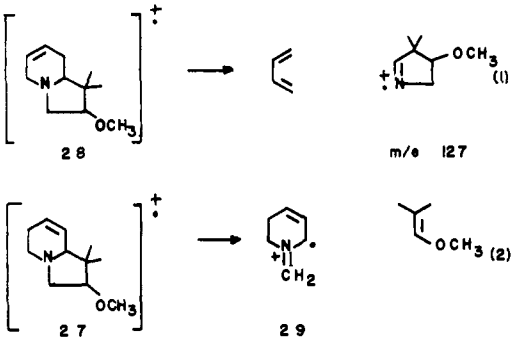
**Photocyclization of *N*-Prenylpyridinium Perchlorate.** Investigation of *N*-allylpyridinium salt photochemistry has provided additional information about the nature of intramolecular electron transfer in olefin–N-heteroaromatic salt systems and about the potential for secondary photochemical reactions of initially formed indolizidine photoproducts containing the 1,2-dihydropyridine ring system. *N*-Prenylpyridinium perchlorate (**26**), prepared by reaction of pyridine with prenyl bromide followed by perchlorate-ion exchange, undergoes efficient cyclization to give the stereoisomeric



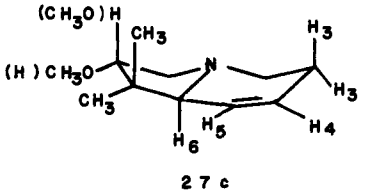

**25** **26** **27**

perhydroindolizidines **25** upon irradiation in methanol with Corex-filtered light followed by hydrogenation of the crude photolysate, neutralization, and molecular distillation. Surprisingly, the epimeric hexahydroindolizidines **27** are produced exclusively when the catalytic hydrogenation step is not performed following irradiation of **26** under the same conditions. The product yields from the indolizidine **25** and **27** forming reactions were identical over a wide range of conversions of **26**. In addition, the yields in each case reached a maximum value of 60% at ca. 50% conversion (Figure 2) and decreased upon further irradiations.

Several important questions arising from these observations and concerning product structures and the mechanism for formation of **27** need to be addressed. Support for structure assignments to indolizidines **25** and **27** and for the $\pi$-bond location in **27** derive from analysis of the spectroscopic data and the observed, near-quantitative conversion of **27** to **25** by catalytic hydrogenation. For example, the high-resolution mass spectrum of **27** contains a parent peak corresponding to the molecular formula $C_{11}H_{19}NO$ and a base peak at *m/e* 95 ($C_6H_9N$) and is lacking a peak at *m/e* 127. The latter observations suggest an indolizidine structure having the $\Delta^4$- rather than $\Delta^3$-$\pi$-bond location as found in the regioisomer **28**. Accordingly, retro (4 + 2) fragmentation of the parent ion of **28** is expected to occur efficiently and produce the unobserved pyrroline cation radical at *m/e* 127 (eq 1).[20] On the




other hand, the stabilized radical ion **29** results from an expected fragmentation of **27**$^+$· (eq 2). Additional evidence supporting the proposed structure assignment is found in the $^1H$ NMR spectrum of one of the pure epimers of **27**. The upfield ($\delta$ 5.59) portion of the complex AB pattern for the olefinic proton resonances possesses additional, strong splitting due to coupling of the H-4 proton with the equatorial proton at C-3. This additional strong coupling is absent from the downfield ($\delta$ 5.51) part of the AB pattern corresponding to H-5. This is fully consistent with structure **27**, which should exist in the conformation **27c** having the hydrogen at C-6 pseudoaxially disposed and, thus, poorly oriented for coupling with H-5.




**27c**

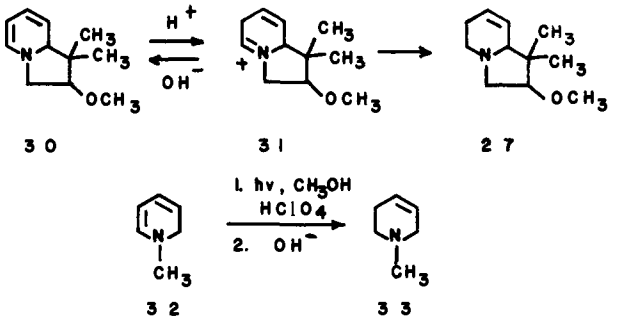
**Secondary Reduction Mechanism.** The production of indolizidine **27** by irradiation of methanolic solutions of **25** is remarkable since it suggests that an unusual process is involved in

(18) (a) Photofragmentations of related ammonium salts and substituted toluenes have been observed. (b) Jaeger, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 902. Cristol, S. J.; Schloemer, G. C. *Ibid.* **1972**, *94*, 5916. Cristol, S. J.; Strom, R. M. *Ibid.* **1979**, *101*, 5707. Laird, T.; Williams, H. *J. Chem. Soc. D* **1969**, 561. Maycock, A. L.; Berchtold, G. H. *J. Org. Chem.* **1970**, *35*, 2532.

(19) The exact reasons for the decreased yields of indolizidines **25** and **27** at high conversion remain obscure. Model studies conducted with 1-methyl-1,2,3,6-tetrahydropyridine (Experimental Section) suggest that this material undergoes decomposition upon irradiation in solutions containing 1-methyl-1,2-dihydropyridine and perchloric acid. Since compounds possessing the tetrahydropyridine ring system do not absorb light in the wavelength region of irradiation, the decomposition process must in some way involve the dihydropyridine as a catalyst. Importantly, control reactions demonstrate that both **25** and **27** are unstable when irradiated in methanol containing perchloric acid.

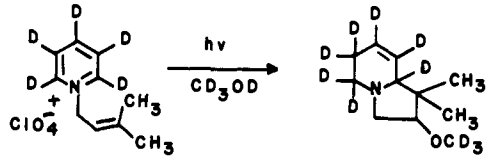
(20) For a discussion of mass spectrometer fragmentations of cyclic compounds of this type, see: McLafferty, F. W. "Interpretation of Mass Spectra"; University Science Books: Mill Valley, CA, 1980.

reduction of the 1,2-dihydropyridine ring system in the indolizidine **30** formed by an electron-transfer-initiated cyclization pathway.



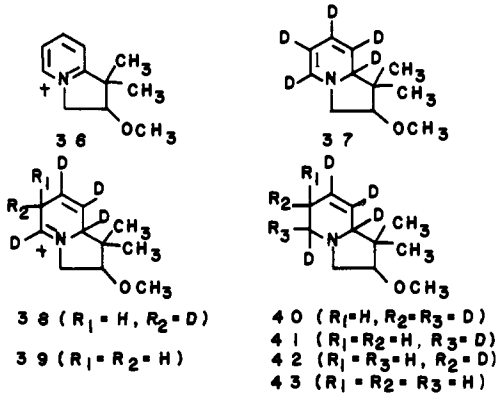

**30** **31** **27** **32** **33**

The observed photoreduction of 1-methyl-1,2-dihydropyridine (**32**) to produce 1-methyl-1,2,3,6-tetrahydropyridine (**33**) under similar conditions (Corex, $CH_3OH$, $HClO_4$) (see Experimental Section) provides precedent for and exemplifies the generality of this reduction process. The mechanism for this reduction has been subjected to detailed exploration. Several of the routes that can be envisaged for conversion of **30** to **27** include a Lukes-type[21] reduction by in situ formed formic acid on the C-3 protonated indolizidine **31**, a crossed-Cannizzaro reaction of formaldehyde with **31**, and disproportionation by hydride transfer from C-6 of the dihydropyridine ring in **30** to C-2 in **31**.[22] These possibilities were examined through studies with the pentadeuteriopyridinium salt **34**. Mass spectrometric analysis of the indolizidine products




**34** **35**

resulting from irradiation of perdeuteriomethanol ($CD_3OD$) solutions of **34** in the presence and absence of 2 molar equiv of either formic acid or formaldehyde indicated that the decadeuterioindolizidine **35** is produced exclusively in each case. These results enable us to clearly rule out the operation of reduction pathways in which formaldehyde or formic acid serves as the hydride donor. Additional experiments provide information dictating against the disproportionation mechanism for production of **27**. Hydride transfer from **30** to **31** would generate equimolar quantities of **27** and the indolizidinium salt **36**. Catalytic hydrogenation of



**36** **37**

**38** ($R_1$ = H, $R_2$ = D)
**39** ($R_1$ = $R_2$ = H)
**40** ($R_1$ = H, $R_2$ = $R_3$ = D)
**41** ($R_1$ = $R_2$ = H, $R_3$ = D)
**42** ($R_1$ = $R_3$ = H, $R_2$ = D)
**43** ($R_1$ = $R_2$ = $R_3$ = H)

**36** under the conditions employed in workup of the crude photolysates ($PtO_2$) is expected to yield the perhydroindolizidine **25**. Thus, the yield of **25**, formed from **26** by employing workup conditions that include hydrogenation, should be nearly twice that of indolizidine **27** arising under identical conditions without hydrogenation. However, the yields of **25** and **27** from parallel reactions run under carefully controlled condition were virtually equivalent.

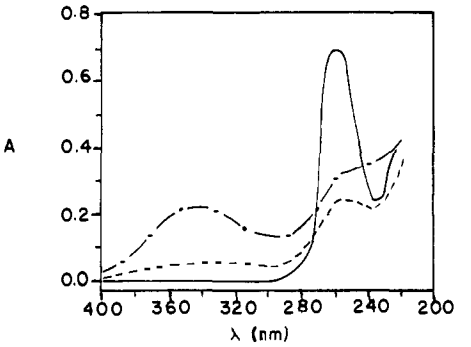



**Figure 3.** UV spectra in $CH_3OH$ of the *N*-prenylpyridinium perchlorate **26** (—), photolysate obtained by irradiation of **26** (---), and photolysate made basic by the addition of aqueous NaOH (-·-).

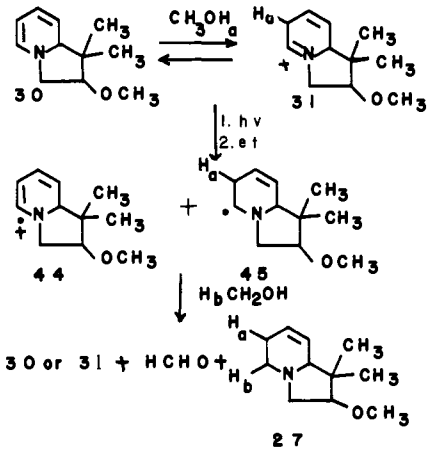
Likewise, indolizidine production by disproportionation would be reflected in the deuterium distribution in products arising by irradiation of **34** in methanol. Accordingly, deuteride transfer from dihydropyridine **37** to the C-3-protonated intermediate **38**, or **39** arising by multiple exchange with $CH_3OH$, would give the hexadeuterio- and pentadeuterioindolozidines **40** and **41** with geminal deuterium substitution at C-2. The experimental evidence indicates otherwise. Irradiation of **34** in methanol affords a product mixture containing the pentadeuterio- and tetradeuterioindolizidines **42** and **43** in a ca. 1:1 ratio. The isotopic distribution in these substances was determined by a combination of mass spectrometric and $^{13}C$ NMR methods. A significant observation is that the proton-decoupled $^{13}C$ NMR spectrum of the indolizidine mixture displays non-deuterium-coupled carbon resonance for C-3 as a singlet at $\delta$ 24.87 superimposed on a resonance for C-3 broadened by deuterium coupling. In addition, resonances for the remaining tetrahydropyridine ring carbons of **42** and **43** appear as broad, deuterium-coupled multiplets.

The results presented thus far appear to implicate a photochemical pathway for the extremely efficient conversion of **30** to **27** in which methanol serves as the hydrogen source. Furthermore, the intermediacy of the iminium salt **31** in this reduction is possible since C-3-protonated 1,2-dihydropyridines are known to exist at equilibrium under acidic conditions like those generated in the photolysis medium.[23] Deuterium distributions in the indolizidine products arising from irradiation of **34** in $CH_3OH$ and $CD_3OD$ are consistent with reduction mechanisms in which the C-3 and C-2 hydrogens of **27** derive from the OH and CH positions of methanol, respectively. A major question remaining about a photochemical pathway for this reduction concerns the nature of the light-absorbing species. The bicyclic iminium salt **31** cannot serve in this capacity due to the absence of UV absorption above 220 nm.[23c] On the other hand, the homoannular diene containing indolizidine **30** should absorb strongly in the 200–400-nm region.[23c] In fact, UV spectroscopic analysis of the photolysate arising by irradiation of **26** in methanol (Figure 3) revealed the presence of an absorption band with a maximum at 345 nm that underwent a significant and reversible increase in intensity when the pH of the medium was increased. The intensity of this absorption band corresponding to the dienamine chromophore[23c] gradually decreased when the basified photolysate was exposed to air, a result anticipated on the basis of the predicted instability of **30**.

The accumulated experimental data appear to be compatible with a mechanism for photoreduction involving initial electron transfer from excited **30** to the electron-accepting iminium salt **31** as depected in Scheme IV.[24] Sufficient precedent exists for

(21) Cervinka, O.; Kziz, O. *Collect. Czech. Chem. Commun.* **1965**, *30*, 1700.
(22) Abramovitch, R. A.; Poulton, G. A. *Chem. Commun.* **1967**, 274.
(23) (a) Opitz, G.; Merz, W. *Liebigs Ann. Chem.* **1962**, *652*, 139. (b) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; Cornell University Press: Ithica, NY, 1953; p 554. (c) Fry, E. M. *J. Org. Chem.* **1964**, *29*, 1647. (d) Lyle, R. E.; Anderson, P. S. *Adv. Heterocycl. Chem.* **1966**, *6*, 45.

Scheme IV



participation of dihydropyridines in photochemical electron-transfer-induced reactions. For example, the fluorescence of 1,4-dihydropyridine is known to be efficiently quenched by electron acceptors,[25] and it has been shown that excited dihydropyridines serve as one-electron donors in photoinitiated reduction of olefins.[26] Likewise, iminium salts are known to serve as efficient acceptors in electron-transfer quenching and reduction processes involving aromatic hydrocarbon singlet states as donors.[5] The ensuing mechanistic steps in this reduction pathway, including hydrogen atom abstraction from methanol by the $\alpha$-amino radical **45** and either electron or hydrogen atom transfer between the cation radical **44** and hydroxymethyl radical, furnish the reduced indolizidine **27**, starting indolizidine in neutral **30** or protonated **31** forms, and formaldehyde.

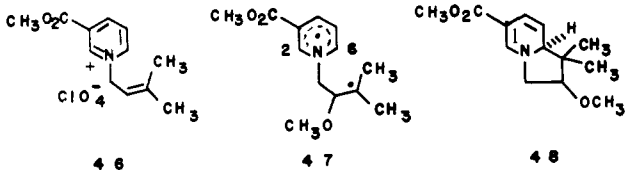
An important feature of this mechanism is related to the requirement that both the neutral and protonated dihydropyridine ring systems in indolizidines **30** and **31** be present for the light and electron-accepting steps. Thus, the efficiency of reduction should be minimal at pH extremes. This is completely consistent with our observation that irradiation of methanolic solutions of *N*-prenylpyridinium perchlorate (**26**) in the presence of potassium carbonate fails to produce the indolizidine **27**. Further information on this point has come from an investigation of the acid concentration dependence of the secondary phororeduction efficiency. Irradiations of methanolic solutions of **26** containing perchloric acid concentrations in the range $(1 \times 10^{-7})$-$(1 \times 10^{-1})$ M were conducted for fixed time periods. Equal portions of each photolysate were subjected to workup conditions that either exclude or include catalytic hydrogenation in order to determine the respective yields of photoreduced indolizidine **27** and total indolizidine products (**27** + **30** + **31**). The observed results, summarized in Table III, are totally consistent with the sequence outlined in Scheme IV. Accordingly, as acid concentration increases, the proportion of dihydropyridine containing indolizidine **30** should decrease, leading to a diminution in yield of reduced product **27**. Furthermore, the substantial increase in yield of total indolizidine observed at high acid concentrations is in complete harmony with the expectation that protonation protects indolizidine **30** from competitive oxidative decomposition. *It is important to note that the photocyclization–hydrogenation sequence converting pyridinium salt* **26** *to perhydroindolizidine* **27** *conducted in 1* $\times$ $10^{-1}$ *M methanolic perchloric acid occurs in a near-quantitative yield at conversions up to 50%.*

Table III. Acid Concentration Effects on Yields for Production of Indolizidines 25 and 27 by Irradiation of 26

| added $HClO_4$ concn,[a] M | relative yield of 27[b] | relative yield of 25[b] | ratio 25/27 |
|---|---|---|---|
| 0.0 | 1.0 | 0.9 | 0.9 |
| $1.0 \times 10^{-4}$ | 0.9 | 0.9 | 1.1 |
| $1.0 \times 10^{-3}$ | 0.5 | 0.9 | 1.9 |
| $1.0 \times 10^{-2}$ | 0.4 | 1.8 | 4.2 |
| $1.0 \times 10^{-1}$ | 0.4 | 1.8 | 4.6 |

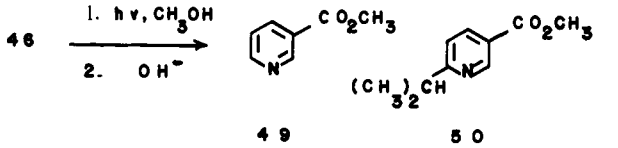
[a] Irradiations conducted on 100 mg of 26 in 50 mL of $CH_3OH$ to ca. 14% conversion. [b] Relative yields based upon formation of 27 from irradiations in the absence of added $HClO_4$ at ca. 14% conversion.

**Photocyclization of 1-Prenyl-3-(carbomethoxy)pyridinium Perchlorate.** Aspects of these processes were explored further through study of the substituted pyridinium salt **46** derived from



methyl nicotinate. Based upon considerations of spin density data[27] and steric effects, it is expected that cyclization of diradical **47**, which arises from **46**, would occur to generate the 3-carbomethoxy-substituted indolizidine **48**. Studies of borohydride reduction with nicotinate salts[28] have shown that electron-withdrawing-substituted ring systems like that present in **48** should resist protonation under conditions found in the photolysis medium. Thus, secondary photoreduction of **48** by the pathway outlined in Scheme IV should be inefficient for this system. Experimental observations support this hypothesis.

Irradiation (Corex) of **46** in methanol followed by neutralization and chromatographic separations gave trace quantities of methyl nicotinate (**49**, 7%) and 3-carbomethoxy-6-isopropylpyridine (**50**,



4%) as the only observable products. The structure of **50** is evidenced by spectroscopic data, including those from the $^1H$ NMR spectrum that are particularly useful in assigning the C-6 location of the isopropyl group (H-2, $\delta$ 9.2, d, $J$ = 2 Hz; H-4, $\delta$ 8.3, dd, $J$ = 2, 8 Hz; H-5, $\delta$ 7.3, *d*, $J$ = 8 Hz). The observed products appear to arise via either photofragmentation or secondary reaction pathways.[29] Importantly, an unprotonated indolizidine like **48** would not survive the conditions employed for product isolation. In contrast, two separable, stereoisomeric perhydroindolizidines **55** and **56** are isolated in modest yields (28% and 25%, respectively)[30] when the crude photolysate from irradiation of **46** is hydrogenated prior to base treatment. Trace

(24) On the basis of an approximate singlet excited state energy of 65 kcal/mol and oxidation potential of +0.7 V for 1,2-dihydropyridines and a reduction potential of −1.8 V for simple iminium salts,[5] the free energy for electron transfer from excited **30** to ground-state **31** should be in the range of ca. −0.3 V. Electron transfer from excited states of donors to ground states of iminium salts has been shown to be responsible for fluorescence quenching and excited-state addition reactions in model systems.[5]

(25) Martens, F. M.; Verhoeven, J. W.; Case, R. A.; Pandit, U. K.; de Boer, T. J. *Tetrahedron* **1978**, *34*, 443.

(26) (a) Ohnishi, Y.; Ohno, A. *Chem. Lett.* **1976**, 697. (b) Ohnishi, Y.; Kagami, M.; Ohno, A. *Ibid.* **1975**, 125.

(27) Dohrmann, J. K.; Becker, R. *J. Magn. Reson.* **1977**, *27*, 371.

(28) Kinoshita, N.; Hamana, M.; Kawasaki, J. *Chem. Pharm. Bull.* **1962**, *10*, 753.

(29) (a) The origin of methyl nicotinate (49) from irradiation of the pyridinium perchlorate **46** is, most probably, through the photoheterolytic cleavage pathway discussed earlier in regard to the photochemistry of the quinolinium salt **7**. The mechanism for production of methyl 6-isopropylnicotinate (**50**) is less clear. This material could arise via oxidation of the indolizidine **48** to a pyridinium salt followed by fragmentation during workup with base. The piperidine **53** appears to be formed by methanol addition to **46** through a route similar to those observed with related pyridinium[9b] and quinolinium[29b] salts. (b) Stermitz, F. R.; Wei, C. C.; Huang, W. H. *Chem. Commun.* **1968**, 482.

(30) Yields are based upon 60% conversion.

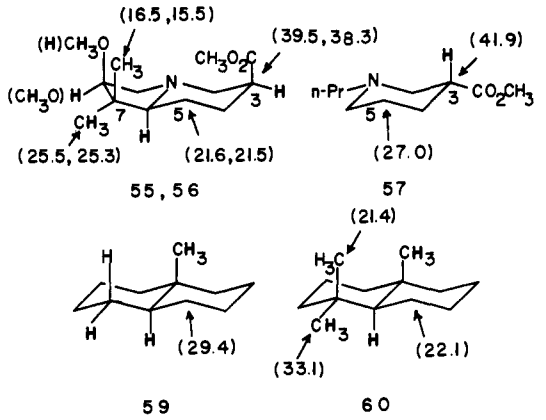
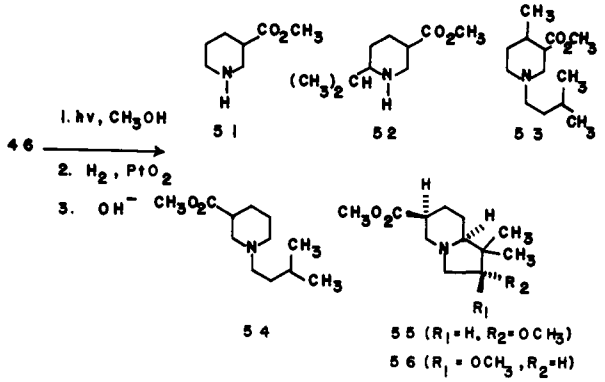


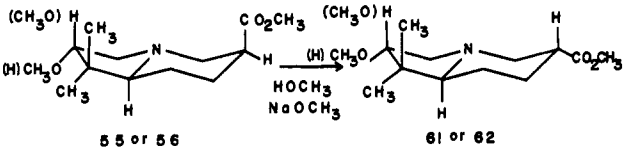

Figure 4. Characteristic $^{13}C$ NMR chemical shifts in ppm relative to $Me_4Si$ for indolizidines **55** and **56**, piperidine **57**, and model hydrocarbons **59** and **60**. Data for the latter come from ref 32.

quantities of the piperidines **51–53**[29] and the reduced starting material **54** (35%) were also formed in this process.



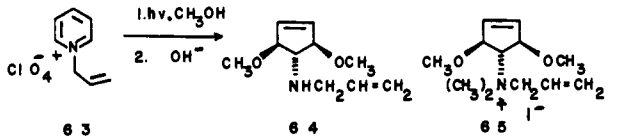

Structure and stereochemistry assignments to the indolizidine photoproducts **55** and **56** are based upon an assortment of theoretical, spectroscopic, and chemical data. The exceptionally close correspondence of the spectroscopic and mass spectrometric properties of these substances suggests their stereo- rather than regioisomeric relationship. The greater odd-electron density at C-6 over C-2 (ca. 8:1) in 3-electron-withdrawing-substituted pyridinyl radicals[27] and the general relationship between odd-electron density and site of free radical addition[31] combine to suggest that diradical **47** cyclization should favor formation of the 3-carbomethoxy-substituted indolizidine **48**. Support for this hypothesis derives from close inspection and comparison of selected $^{13}C$ NMR spectroscopic data for **55**, **56**, and the model 1-propyl-3-carbomethoxypiperidine (**57**) derived by reduction of the corresponding pyridinium salt **58** (Figure 4). The reasonably large upfield shifts for the C-5 and near invariance in C-3 resonances in **55** and **56** compared to **57** are in agreement with the assigned regiochemistry. Accordingly, the upfield shifts of C-5 are attributed to the familiar $\gamma$-gauche effect caused by interaction with the C-7 methyl groups (axial greater than equatorial) and seen in systems (e.g., **59** and **60**) containing closely related structural features.[32] The reciprocal nature of this effect is reflected in the large chemical shift differences seen between the axial and equatorial C-7 methyl carbons in **55** and **56**.

Chemical methods were employed to gain stereochemical information. The indolizidines **55** and **56** were found to undergo epimerization in methanolic sodium methoxide to produce independently different, stereoisomeric indolizidines **61** and **62**. Thus, the indolizidine photoproducts must be epimeric at the methoxyl-bearing carbon C-8 and have the thermodynamically less



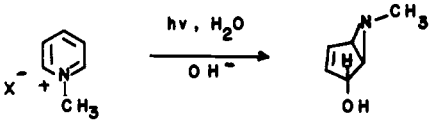

favored cis relative stereochemistry at C-3 and C-6. This is fully consistent with the expected $\alpha$-face approach of indolizidine **48** to the catalyst surface in the hydrogenation process.

**Photochemistry of *N*-Allylpyridinium Perchlorate.** Additional information about electron transfer in the photochemistry of *N*-alkenylheteroaromatic salts has been provided by the results from study of the simple *N*-allylpyridinium perchlorate (**63**). The

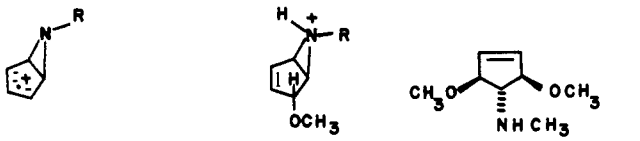



efficiencies for intramolecular electron transfer from olefinic to charged-heterocyclic excited moieties in these N-substituted salts should depend upon the degree of alkyl substitution on the alkene grouping owing to the general relationship between electron density and oxidation potential. This effect as it relates to fluorescence efficiency has been discussed above in the section dealing with the quinolinium and isoquinolinium perchlorates **6–9**. A chemical consequence of this feature is manifested in the photochemistry of **63**. Irradiation (Corex) of a methanolic solution of **63** followed by neutralization and molecular distillation gave the trans,trans aminocyclopentene **64** in surprisingly high chemical (86%) but low quantum (0.0024) efficiency. The structure of this photoproduct was unambiguously assigned by conversion to the dimethylammonium iodide **65**, characterized by X-ray crystallographic analysis (Figure 5).[33]

A mechanism, analogous to that proposed earlier by Wilzbach and his co-workers[34] to rationalize the photochemical transformation of *N*-methylpyridinium chloride to the bicyclic amino alcohol **67** under strongly basic conditions appears to be responsible




for the conversion of **63** to **64**. Accordingly, capture of the bicyclic allyl cation **68** (R = $-CH_2CH{=}CH_2$), formed by electrocyclization of **63**, would give the protonated aziridine **69** (R = $-CH_2CH{=}CH_2$). Methanolysis of this intermediate followed




by neutralization during workup furnishes the trisubstituted cyclopentene **64**. We have observed that *N*-methylpyridinium perchlorate (**66**, X = $-ClO_4$) undergoes a related ring contraction reaction to produce the aminocyclopentene **70** (80%) when irradiated in methanol. In this case, the intermediate bicyclic aziridine **69** (R = $CH_3$) could be detected by rapid neutralization and GLC analysis of the crude photolysate at low conversion.

The high chemical yields for the cyclopentene-forming reactions described above are unexpected in light of the previous results with *N*-prenyl salt systems. It appears that when the N substituent

(31) Hanson, P. *Adv. Heterocycl. Chem.* **1981**, *25*, 205.
(32) For an excellent review of the $\gamma$-gauche effect on $^{13}C$ NMR chemical shifts, see: Wehrli, F. W.; Wirthlin, T. "Interpretation of $^{13}C$-NMR Spectra"; Heyden: New York, 1976; pp 37–38.
(33) Results from the X-ray crystallographic analysis of **65** will be published elsewhere.
(34) Kaplan, L.; Pavlick, J. W.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1972**, *94*, 3283.

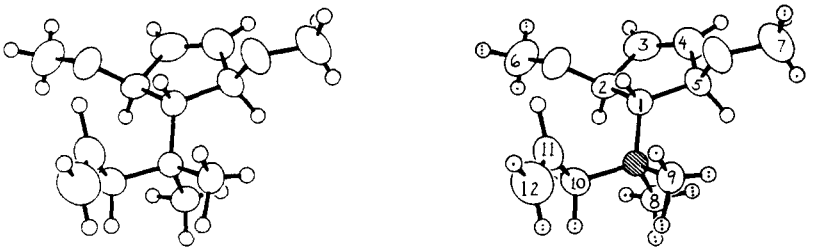
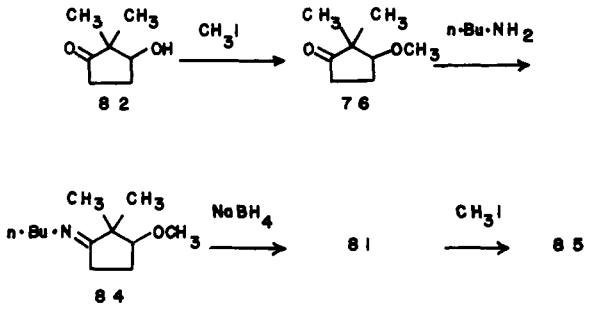
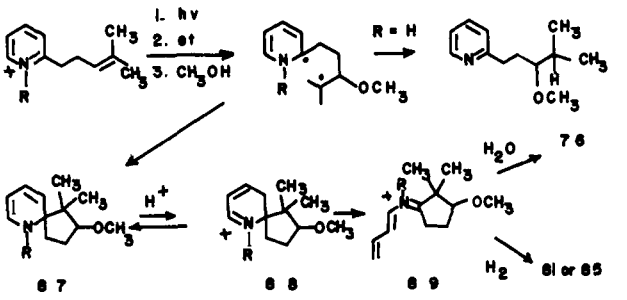


**Figure 5.** Stereoview of ammonium iodide **65** derived from X-ray crystallographic data.

Scheme V

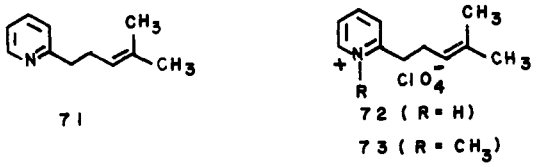


Scheme VI

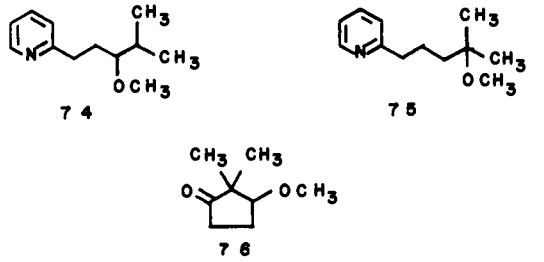


on the heteroaromatic ring system can serve as an efficient electron donor, the potential for competitive excited-state reactions of the pyridine nucleus is reduced. It is clear from a comparison of the quantum efficiencies that ring contraction ($\phi$ = 0.0024) would compete poorly with electron-transfer-induced cyclization ($\phi$ = 0.04) in cases where alkenyl-group substitution enables efficient one-electron donation to the heterocycle excited state.

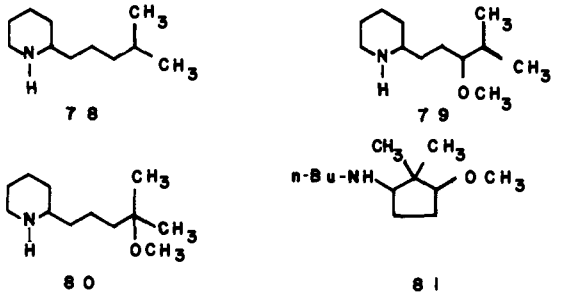
**Photochemistry of 2-(4-Methylpent-3-en-1-yl)pyridinium Perchlorates.** Our interest in extending the scope of investigations in this area has led to an exploration of the excited-state chemistry of other *N*-heteroaromatic cations having alkenyl side chains joined at positions other than nitrogen. As a result, we have conducted a limited photochemical study with the 2-alkenylpyridinium perchlorates **72** and **73**, systems which can potentially serve as



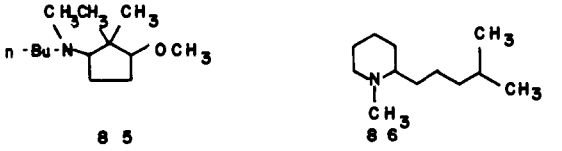
precursors for 1-aza[5,4]spiranes.[35] The salts are prepared from $\alpha$-picoline through the intermediate pyridine **71**. Irradiation of the N-protonated pyridine **72** prepared from **71** in a methanolic solution containing perchloric acid followed by neutralization and chromatographic separation gave a complex product mixture containing the (2-pyridyl)alkyl ethers **74** (20%) and **75** (2%) along with the methoxycyclopentanone **76** (6%).[36] A control reaction



demonstrated that the minor ether product **75** is formed by a ground-state, methanol addition pathway. The product mixture arising by irradiation of **72** followed by immediate hydrogenation ($PtO_2$) of the crude photolysate contained the cyclopentanone **76** and piperidine derivatives **78–80**, expected on the basis of the initial results. However, the isolation of the cyclopentyl amine **81** (13%) under the latter conditions provides an important clue to the origin of **76** and nature of the reaction pathways followed.



Structural characterizations of **81** and **76** were assisted by their independent synthesis from the known 2,2-dimethyl-3-hydroxycyclopentanone (**82**)[37] by the sequence outlined in Scheme V. The *N*-methylpyridinium perchlorate **73** displays similar photochemical reactivity. Thus, cyclopentanone **76** is the sole photoproduct isolated after irradiation in methanol followed by neutralization, while a mixture containing **76** (18%) and *N*-methylcyclopentylamine **85** (15%) along with reduced starting material **86** (10%)



are produced when the photolysate is hydrogenated prior to workup. The conversion of **81** to **85** by methylation provides evidence for their structural similarity.

(35) (a) Ring systems of this type have attracted recent, synthetic interest.[35b] (b) See, for instance: Venit, J. J.; Magnus, P. *Tetrahedron Lett.* **1980**, 4815.

(36) An addition product, tentatively identified as 7-methoxy-8,8-dimethyl-5,6,7,8-tetrahydroquinoline (**77**) (see Experimental Section) has also been isolated in an 8% yield.

(37) Hamon, A.; Lacoume, B.; Pasquet, G.; Pilgrim, W. R. *Tetrahedron Lett.* **1976**, 211.

Although details of the excited-state reaction pathways linking the 2-alkenylpyridinium salts with cyclopentanone and cyclopentylamine photoproducts are obscure, several gross features can be disected. Consideration of the excited- and ground-state electrochemical potentials for the key chromophores in the starting salts leads to the prediction that electron transfer should be efficient. Indeed, a process initiated in this fashion must be operable in the anti-Markovnikov addition of methanol to produce the ethers **74** and **79** (Scheme VI). This reasoning, along with precedent provided in earlier studies and thoughts about the origin of the five-membered-ring framework, enables speculation that the cyclopentanone and cyclopentylamine photoproducts arise through common 1,2-dihydropyridine and iminocyclopentane intermediates **87** and **89** (Scheme VI). The exact mechanisms for transformation of **87** to **89** are unclear, although electrocyclic opening of the C-5-protonated dihydropyridines **88**[38] seems reasonable.[39] If this is true, our studies in this area will have uncovered yet another interesting secondary reaction available to dihydropyridine ring systems generated by electron-transfer-induced cyclization pathways.

## Experimental Section

**General Procedures.** Nuclear magnetic resonance spectra were recorded by using Varian EM-360, XL-100, or XL-200 spectrometers, and chemical shifts are reported in $\delta$ values in parts per million downfield from tetramethylsilane employed as internal standard. Ultraviolet spectra were taken on a GCA McPherson EU-700-56 spectrometer. Infrared spectra were taken on a Perkin-Elmer 281-283 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tn, or by F. Kassler at the University of Maryland. Preparative photolyses were conducted with an apparatus consisting of 450-W Hanovia medium mercury vapor lamp surrounded by a glass filter in a quartz immersion well under inert atmospheres. Crude photolysates were subjected to the general workup procedure involving concentration in vacuo, basification with aqueous $NaHCO_3$, and $CHCl_3$ extraction. The $CHCl_3$ extracts were concentrated in vacuo to give residues. Gas chromatographic analyses were performed on a Varian-940 chromatograph with flame ionization detection. Preparative gas chromatographic work was done on a Varian-2700 chromatograph. Fluorescence and excitation spectra were recorded on a Perkin-Elmer MPF 44B spectrometer equipped with a Perkin-Elmer DCSU-1 differential corrected spectra unit. Fluorescence spectra were integrated with a LDC 308 digital integrator. Mass spectrometric data were recorded at 70 eV on a Du Pont 21-390 mass spectrometer. High-resolution mass spectra were taken on a CEC-21-110 double focusing mass spectrometer or at the Penn State Mass Spectrometer Facility. Melting points are reported uncorrected. Drying of organic layers obtained by workup of reaction mixtures was by washing with saturated NaCl and standing over anhydrous sodium sulfate. Preparative TLC was performed on 20 × 20 cm plates coated with E. Merck Silica gel 60 GF-254. Molecular distillations were performed at reduced pressure with a Kugelrohr apparatus.

**Quinolinium Perchlorate (1).** Perchloric acid (70%, 15 mL, 0.17 mol) was added dropwise to a stirred solution of quinoline (10.5 g, 0.081 mol) in anhydrous ether. The solution was stirred at 35 °C for 1 h under $N_2$ to yield the crystalline quinolinium salt. Recrystallization from absolute ethanol yielded 14.9 g (80%) of quinolinium perchlorate: mp 130–131 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 8.4–8.8 (d, 2 H, H-2 and H-4), 7.2–8.0 (m, 5 H), 2.9 (s, 1 H, NH); UV ($CH_3CN$) max 312 nm ($\epsilon$ 6530).

***N*-Methylquinolinium Perchlorate (2).** A solution of freshly distilled quinoline (10.0 g, 0.078 mol) and methyl iodide (11.2 g, 0.078 mol) in anhydrous ether was stirred for 2 h under $N_2$ to yield 13.1 g (62%) of *N*-methylquinolinium iodide. The iodide salt (1.0 g, 4 mmol) was eluted through a perchlorate ion exchange column (Dowex-1, mesh 50–100, 2.5 × 4.2 cm) with methanol. The product fraction was concentrated in vacuo to give the crsytalline perchlorate. Recrystallization from absolute ethanol gave 0.81 g (90%) of the perchlorate salt: mp 114–115 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 9–9.4 (2 d, $J_1$ = 12, $J_2$ = 10 Hz, 2 H, H-2 and H-4), 7.7–8.5 (m, 5 H), 4.9 (s, 3 H, $CH_3$); UV ($CH_3CN$) max 315 nm ($\epsilon$ 7230).

Anal. Calcd for $C_{10}H_{10}NClO_4$: C, 49.28; H, 4.12; N, 5.75; Cl, 14.58. Found: C, 49.38; H, 4.17; N, 5.54; Cl, 14.84.

**Isoquinolinium Perchlorate (3).** Perchloric acid (70%, 15 mL, 0.17 mol) was added dropwise to a stirred solution of isoquinoline (12.0 g, 0.093 mol) in anhydrous ether. The solution was stirred at 35 °C for 1 h under $N_2$ to yield the crystalline perchlorate salt. Recrystallization from absolute ethanol yielded 21.0 g (98%) of isoquinolinium perchlorate: mp 169–170 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 9.4 (s, 1 H, H-1), 7.3–8.2 (m, 6 H), 2.6 (s, 1 H, NH); UV ($CH_3CN$) max 336 nm ($\epsilon$ 3240).

***N*-Methylisoquinolinium Perchlorate (4).** A solution of isoquinoline (10.0 g, 0.078 mol) and methyl iodide (11.2 g, 0.078 mol) in anhydrous ether was stirred at 35 °C for 2 h under $N_2$ to yield 8.7 g (41%) of *N*-methylisoquinolinium iodide. The iodide salt (1.0 g, 4.0 mmol) was eluted through a perchlorate ion exchange column (Dowex-1, mesh 50–100, 2.5 × 4.2 cm) with methanol. The product fraction was concentrated in vacuo to give the crystalline perchlorate. Recrystallization with absolute ethanol gave 0.83 g (92%) of the perchlorate salt: mp 116–117 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 9.50 (s, 1 H, H-1), 7.5–8.2 (m, 6 H), 4.5 (s, 3 H, $CH_3$); UV ($CH_3CN$) max 334 nm ($\epsilon$ 4600).

Anal. Calcd for $C_{10}H_{10}NClO_4$: C, 49.28; H, 4.12; N, 5.75; Cl, 14.58. Found: C, 49.45; H, 4.12; N, 5.66; Cl, 14.80.

**2-Methoxyquinolinium Perchlorate (5).** A solution of 2-chloroquinoline (8.71 g, 0.053 mol) and sodium methoxide (from 5.7 g, 0.25 mol of Na) in 60 mL of methanol was stirred at 65 °C for 2 h under $N_2$. Concentration in vacuo gave a residue, which was diluted with water and extracted with ether. The ethereal extracts were dried, concentrated in vacuo, and subjected to molecular distillation to yield 7.59 g of 2-methoxyquinoline: bp 75 °C (1.5 torr) (lit.[40] bp 63–65 °C (0.03 torr)); $^1$H NMR ($CDCl_3$) $\delta$ 7.2–7.9 (m, 6 H), 4.1 (s, 3 H, $OCH_3$). Solutions of 2-methoxyquinolinium perchlorate used for fluorescence quenching experiments were obtained by the addition of 1.5 equiv of perchloric acid to acetonitrile solutions of 2-methoxyquinoline.

**1-(2-Propenyl)quinolinium Perchlorate (6).** A solution of quinoline (30 g, 0.23 mol) and 1-bromo-2-propene (29 g, 0.24 mol) in anhydrous ether was stirred at 35 °C for 48 h under $N_2$ to generate 27.3 g of 1-(2-propenyl)quinolinium bromide (47%). The bromide salt (1.04 g, 4.2 mmol) was eluted through a perchlorate anion exchange column (Dowex-1, mesh 50–100, 2.5 × 4.2 cm) with methanol to yield the crystalline salt. Recrystallization from absolute ethanol gave 0.80 g (72%) of the perchlorate salt: mp 96–97 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 9.2–9.6 (2 d, $J_1$ = 6, $J_2$ = 8 Hz, H-2 and H-4), 7.8–8.5 (m, 5 H), 6.0–6.4 (t of d of d, 1 H, vinyl CH), 5.8 (d, $J$ = 7 Hz, 2 H, allylic methylene), 5.2–5.5 (d of d, $J_1$ = 20, $J_2$ = 10 Hz, terminal $CH_2$); UV ($CH_3CN$) max 317 nm ($\epsilon$ 7450).

Anal. Calcd for $C_{12}H_{12}NClO_4$: C, 53.43; H, 4.45; N, 5.19; Cl, 13.17. Found: C, 53.36; H, 4.36; N, 5.19; Cl, 13.37.

**1-(3-Methyl-2-butenyl)quinolinium Perchlorate (7).** A solution of quinoline (5.0 g, 0.038 mol) and 1-bromo-3-methyl-2-butene in anhydrous ether was stirred at 35 °C for 48 h under $N_2$ to produce 7.53 g (71%) of 1-(3-methyl-2-butenyl)quinolinium bromide. The bromide salt (1.0 g, 3 mmol) was eluted through a perchlorate anion exchange column (Dowex-1, mesh 50–100, 2.5 × 4.2 cm) with methanol. The product fraction was concentrated in vacuo to give the crystalline perchlorate, which was recrystallized from absolute ethanol to yield 0.96 (90%) of the perchlorate salt: mp 110–111 °C; $^1$H NMR ($CDCl_3$) $\delta$ 9.1–9.4 (2 d, $J_1$ = 15, $J_2$ = 14 Hz, 2 H, H-2 and H-4), 8.0–8.5 (m, 5 H), 5.6 (s, 2 H, allylic methylene), 5.5–5.7 (t, 1 H, vinyl H), 1.9 (s, 3 H, $CH_3$), 1.8 (s, 3 H, $CH_3$); UV ($CH_3CN$) max 313 nm ($\epsilon$ 7860).

Anal. Calcd for $C_{14}H_{16}NClO_4$: C, 56.47; H, 5.38; N, 4.71; Cl, 11.93. Found: C, 56.18; H, 5.53; N, 4.62; Cl, 12.20.

**2-(2-Propenyl)isoquinolinium Perchlorate (8).** A solution of isoquinoline (17.1 g, 0.1328 mol) and 1-bromo-2-propene (16.1 g, 0.1328 mol) in anhydrous ether was stirred at 35 °C for 48 h under $N_2$ to produce 21.9 g of 2-(2-propenyl)isoquinolinium bromide. The bromide salt (2.58 g, 9.3 mmol) was eluted through a perchlorate anion exchange column (Dowex-1, mesh 50–100, 2.5 × 12 cm) with methanol. The product fraction was concentrated in vacuo to yield the crystalline salt, which was recrystallized from absolute ethanol to yield 1.92 g (77%) of the perchlorate salt: mp 107–108 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 10.1 (s, 1 H, H-1), 8.0–8.8 (m, 6 H), 6.1–6.6 (t of d of d, 1 H, vinyl CH), 5.7 (d, $J$ = 7 Hz, 2 H, allylic methylene), 5.4 (d, $J$ = 20 Hz, terminal $CH_2$); UV ($CH_3CN$) max 336 nm ($\epsilon$ 4280).

Anal. Calcd for $C_{12}H_{12}NClO_4$: C, 53.43; H, 4.45; N, 5.19; Cl, 13.17. Found: C, 53.42; H, 4.58; N, 5.09; Cl, 13.40.

**2-(3-Methyl-2-butenyl)isoquinolinium Perchlorate (9).** A solution of isoquinoline (22.4 g, 0.173 mol) and 1-bromo-3-methyl-2-butene (25.8 g, 0.173 mol) in anhydrous ether was stirred at 35 °C for 48 h under $N_2$ to yield 34.2 g of 2-(3-methyl-2-butenyl)isoquinolinium bromide (71%). The bromide salt (5.37 g, 4 mmol) was eluted through a perchlorate anion exchange column (Dowex-1, mesh 50–100, 2.5 × 12 cm) with

(38) Studies[23] have shown that subtle features control the kinetic and thermodynamic protonations of 1,2-dihydropyridines to produce either the C-3- or C-5-protonated iminium salts.

(39) The yields of **76** and **85** from irradiations of **73** appear to be enhanced by the addition of perchloric acid (see Experimental Section). The exact reasons for these phenomena are uncertain at this time.

(40) Beak, P.; Woods, T. S.; Mueller, D. S. *Tetrahedron Lett.* **1972**, 5507.

methanol. The product fraction was concentrated in vacuo to yield 3.83 g (66%) of the perchlorate salt: mp 117–118 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 10.0 (s, 1 H, H-1), 8.1–8.8 (m, 6 H), 5.4–5.7 (t, 1 H, vinyl H), 5.5 (s, 2 H, allylic $CH_2$), 2.1 (s, 3 H, $CH_3$), 1.9 (s, 3 H, $CH_3$); UV ($CH_3CN$) max 336 nm ($\epsilon$ 4150).

Anal. Calcd for $C_{14}H_{16}NClO_4$: C, 56.47; H, 5.38; N, 4.71; Cl, 11.93. Found: C, 55.35; H, 5.37; N, 4.38; Cl, 13.00.

**Measurement of Reduction Potentials.** Measurements were made by using a EG & E Princeton Applied Research Model 174 A Polarographic Analyzer and a Houston Instrument Omnigraphic 2000 recorder. The scan rate was 20 mV/s, current 0.1 mA, scan range 0 to −1.5 V. The electrodes were mercury (working), standard calomel (reference), and Pt wire (auxiliary). Solutions were made in $CH_3CN$ containing the heteroaromatic salts ($2 \times 10^{-3}$ M) and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte.

**Fluorescence Measurements.** Fluorescence spectra were recorded by using a Perkin-Elmer MPF 44 B fluorescence spectrophotometer equipped with a Differential Corrected Spectra Unit. The wavelength of excitation corresponded to the wavelength of maximum absorption in the UV absorption spectrum. Emission scans were typically run from 325 to 450 nm with an excitation band pass of 2 nm, emission band pass of 4 nm, and a scan rate of 120 nm/min. Solutions of the heteroaromatic salts ($1 \times 10^{-4}$ M) and varying concentrations of distilled quenchers in $CH_3CN$ were used. Stern–Volmer plots of the data were linear.

Fluorescence quantum yields were measured by comparing the relative fluorescence of solutions of a standard (anthracene, $\phi = 0.32$)[41] and of the perchlorate salts of equal absorbance. The rate constants for fluorescence ($k_f$) were estimated from the ultraviolet absorbance spectrum by using the standard method.[42] Fluorescence quantum yields and rate constants for fluorescence were used to determine radiative lifetimes.

**Irradiation ($CH_3OH$) of 1-(3-Methyl-2-butenyl)quinolinium Perchlorate.** A $N_2$-purged solution of absolute methanol (200 mL) and 1-(3-methyl-2-butenyl)quinolinium perchlorate (150 mg, 0.5 mmol) was irradiated in a preparative apparatus with flint-glass-filtered light for 15 min (ca. 60% conversion by UV monitoring). The photosylate was immediately hydrogenated (8 h, 55 psi, 50 mg $PtO_2$), filtered, and subjected to the normal workup procedure to give an oil, which was subjected to preparative TLC (silica gel, 4:1 pentane–ether) to yield 31.3 mg (27%) of the benzoindolizidine **19** ($R_f$ 0.7) and 15.3 mg (23%) of 1,2,3,4-tetrahydroquinoline ($R_f$ 0.5). Spectroscopic data for **19**: $^1$H NMR ($CDCl_3$) $\delta$ 6.2–7.0 (m, 4 H), 3.6 (s, 3 H, $OCH_3$), 3.0–3.2 (t, 2 H, benzylic $CH_2$), 2.7–2.9 (t, 2 H, $CH_2$), 1.0–1.9 (m, 4 H), 0.9 (2 s, 6 H, 2 $CH_3$); IR (neat) 2900, 1600, 1500, 1470, 1450, 1340, 1320, 1090, 740 cm$^{-1}$; UV ($CH_3CN$) max 263 nm ($\epsilon$ 5560); mass spectrum, *m/e* (rel intensity) 231 (1, $M^+$), 200 (16), 194 (33), 146 (100, $M^+ - (CH_3)_2C{=}CHOCH_3$), 132 (75), 130 (50), 117 (30), 91 (25); high-resolution mass spectrum, *m/e* 231.1616 ($C_{15}H_{21}NO$ requires 231.1623).

**Irradiation ($H_2O$–$CH_3CN$) of 1-(3-Methyl-2-butenyl)quinolinium Perchlorate.** A $N_2$-purged solution of 3:1 $CH_3CN$–$H_2O$ and 1-(3-methyl-2-butenyl)quinolinium perchlorate (150 mg, 0.5 mmol) was irradiated in a preparative apparatus with flint-glass-filtered light for 15 min. The photosylate was immediately hydrogenated (8 h, 55 psi, 50 mg $PtO_2$), filtered, and subjected to the normal workup procedure to give an oil, which was subjected to preparative TLC (silica gel, 4:1 pentane–ether) to yield 22.8 mg (21%) of the benzoindolizidine **20** ($R_f$ 0.7) and 24.6 mg (37%) of 1,2,3,4-tetrahydroquinoline. Spectroscopic data for **20**: $^1$H NMR ($CDCl_3$) $\delta$ 6.4–7.2 (m, 4 H), 3.1–3.3 (t, 2 H, benzylic $CH_2$), 2.6–2.8 (t, 2 H, $CH_2$), 2.2 (s, 1 H, OH), 1.1–1.9 (m, 4 H), 0.9 (2 s, 6 H, 2 $CH_3$); IR (neat) 3400, 2930, 2860, 1610, 1510, 1470, 1460, 1350, 1320, 1100, 810, 750 cm$^{-1}$; UV ($CH_3CN$) max 257 nm ($\epsilon$ 5620); mass spectrum, *m/e* (rel intensity) 217 (1.7, $M^+$), 203 (53), 200 (48), 199 (13.4), 146 (100, $M^+ - (CH_3)_2C{=}CHOH$), 130 (37), 97 (19), 83 (21), 69 (45), 57 (45); high-resolution mass spectrum, *m/e* 199.1379 ($C_{14}H_{19}NO - H_2O$ requires 199.1361).

**Dark Reaction To Determine Origin of Tetrahydroquinoline.** A solution of 1-(3-methyl-2-butenyl)quinolinium perchlorate (150 mg, 0.50 mmol) in methanol (200 mL) was heated at 40 °C for 15 min, hydrogenated (8 h, 55 psi, 50 mg $PtO_2$), filtered, and subjected to the normal workup procedure to give an oil that did not contain tetrahydroquinoline ($^1$H NMR and TLC).

**1-Methoxy-3-methyl-2-butene (21).** A solution of 3-methyl-2-buten-1-ol (1.00 g, 0.0116 mol) and NaH (0.417 g, 0.0176 mol) in pentane (10 mL) was stirred at 36 °C for 2 h. Methyl iodide (3.29 g, 0.0232 mol) was added, and the solution refluxed for an additional 2 h. The reaction mixture was poured into water and extracted with pentane. The extracts were concentrated in vacuo to give a residue, which was subjected to molecular distillation to yield 1.04 g (90%) of 1-methoxy-3-methyl-2-butene: bp 104 °C (lit.[43] bp 101–103 °C, 740 torr).

**1-Methoxy-3-methyl-2-butene (21) and 3-Methoxy-3-methyl-1-butene (22).** A solution of 1-bromo-3-methyl-2-butene (5.0 g, 0.034 mol) and $Na_2HPO_4$ (4.77 g, 0.034 mol) in anhydrous methanol (25 mL) was stirred at reflux for 12 h. The solution was poured into water and extracted with pentane. The extracts were subjected to molecular distillation to yield 0.941 g (28%) of 1-methoxy-3-methyl-2-butene (bp 104 °C (760 torr) (lit.[44] bp 101–103 °C)); and 0.403 g (12%) 3-methoxy-3-methyl-1-butene (bp 80 °C (760 torr) (lit.[43] bp 80–83 °C)). The methyl ethers, **21** and **22**, could be separated by GLC (10 ft × $^1/_8$ in. diameter, 5% OV-101 on 100–120-mesh Chromosorb GHP, 30 °C, 10 mL/min flow rate). The retention time of 1-methoxy-3-methyl-2-butene was 21.9 min and of 3-methoxy-3-methyl-1-butene was 9.8 min.

**Photolysis of 7. Detection of Methyl Ethers 21 and 22.** A $N_2$-purged solution of absolute methanol (200 mL) and 1-(3-methyl-2-butenyl)-quinolinium perchlorate (150 mg, 0.50 mmol) was irradiated in a preparative apparatus for 15 min. The photosylate was poured into water (100 mL) and extracted with pentane. Back extraction with water served to remove methanol. The resulting pentane solution was analyzed for **21** and **22** by GLC with the conditions described above. The two cleavage products **21** and **22** were detected with retention times identical with the independently prepared compounds. The ratio of 1-methoxy-3-methyl-2-butene and 3-methoxy-3-methyl-1-butene was 1.4:1.

**1-(3-Methyl-2-butenyl)pyridinium Perchlorate (26).** A solution of pyridine (30 g, 0.38 mol) and 1-bromo-3-methyl-2-butene (56.6 g, 0.38 mol) in anhydrous ether was stirred at 25 °C for 12 h. The formed crystalline salt was collected by filtration, washed with ether, dried to yield 64.5 g of 1-(3-methyl-2-butenyl)pyridinium bromide (74%). The bromide salt (7.0 g, 0.0283 mol) was eluted through a perchlorate anion exchange column (Dowex-1, mesh 50–100, 2.5 × 12 cm) with methanol. The product fraction was concentrated under reduced pressure and recrystallized from absolute ethanol to yield 5.9 g of the perchlorate salt **26** (75%): mp 93–95 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 1.85 (s, 3 H, $CH_3$), 1.90 (s, 3 H, $CH_3$), 5.34 (s, 2 H, allylic $CH_2$), 5.2–5.7 (m, 1 H, vinyl H), 8.23 (d of d, $J$ = 8, 8 Hz, 2 H, H-3 and H-5), 8.71 (t, $J$ = 8 Hz, 1 H, H-4), 9.08 (d, $J$ = 8 Hz, 2 H, H-2 and H-6); UV (methanol) max 259 nm ($\epsilon$ 4300).

Anal. Calcd for $C_{10}H_{14}NClO_4$: C, 48.48; H, 5.66; N, 5.66; Cl, 14.34. Found: C, 48.82; H, 5.97; N, 5.47; Cl, 14.39.

**Irradiation of 1-(3-methyl-2-butenyl)pyridinium Perchlorate (26).** A nitrogen-purged solution of 1-(3-methyl-2-butenyl)pyridinium perchlorate (**26**) (124 mg, 0.5 mmol) in 100 mL of absolute methanol was irradiated with Corex-filtered light for 15 min. The photolysate was subjected to the general workup procedure to give a residue that was subjected to molecular distillation (95 °C, 2 torr), yielding 33 mg of 1,1-dimethylhexahydro-2-methoxyindolizidine (**27**) (60% yield at 60% conversion): $^1$H NMR ($CCl_4$) $\delta$ 0.83 (s, 3 H, $CH_3$) 0.92 (s, 3 H, $CH_3$), 1.9–3.1 (m, 8 H), 3.18 (s, 3 H, $OCH_3$), 5.51 (s, 2 H, -CH=CH-); $^{13}$C NMR ($CDCl_3$) $\delta$ 20.27 (q, $CH_3$), 24.25 (q, $CH_3$), 25.23 (t, C-6), 42.36 (s, C-1), 48.47 (t, C-5), 57.79 (q, $OCH_3$), 58.20 (t, C-3), 68.39 (d, C-8a), 87.46 (d, C-2), 125.61 (d, C-7 or C-8), 126.43 (d, C-8 or C-7); IR (neat) 3025, 2920, 1468, 1230, 1161, 1109, 850 cm$^{-1}$; mass spectrum, *m/e* (rel intensity) 181 ($M^+$, 5), 95 ($M^+ - (CH_3)_2{=}CHOCH_3$, 100), 80 (4), high-resolution mass spectrum, *m/e* 181.1461 ($C_{11}H_{19}NO$ requires 181.1467).

**1,1-Dimethyloctahydro-2-methoxyindolizidine (25).** A solution of 80 mg (0.44 mmol) of 1,1-dimethylhexahydro-2-methoxyindolizidine in 50 mL of methanol was hydrogenated (100 mg $PtO_2$, 55 psi, 14 h). The reaction mixture was filtered and concentrated in vacuo to yield 75 mg of the octahydroindolizidine **25** (93%): $^1$H NMR ($CCl_4$) $\delta$ 0.87 (s, 6 H, 2 $CH_3$), 1.0–2.6 (m, 7 H), 3.18 (s, 3 H, $OCH_3$), 3.0–3.5 (m, 5 H); IR (neat) 2980, 1460, 1370, 1230, 1100, 850 cm$^{-1}$.

Anal. Calcd for $C_{11}H_{21}NO$: C, 72.13; H, 11.48; N, 7.65. Found: C, 71.95; H, 11.65; N, 7.26.

**Hydrogenation of Crude Photolysate from 1-(3-Methyl-2-butenyl)-pyridinium Perchlorate (26).** A nitrogen-purged solution of 1-(3-methyl-2-butenyl)pyridinium perchlorate (120 mg, 0.48 mmol) in 100 mL of absolute methanol was irradiated with Corex-filtered light for 15 min. The crude photolysate was immediately hydrogenated (100 mg $PtO_2$, 55 psi, 2 h). The solution was filtered and concentrated in vacuo to give a residue, which was stirred with 5 mL of saturated sodium bicarbonate and extracted with ether. The ethereal extracts were dried and concentrated in vacuo to give a residue, which was subjected to molecular distillation, to yield 32 mg of 1,1-dimethyloctahydro-2-methoxyindolizidine (**25**) (37%). This material was identical in all respects

(41) Berlman, I. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1971; p 356.

(42) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin: Menlo Park, CA, 1978; pp 176–179.

(43) Grob, C.; Fisher, W. *Helv. Chim. Acta* **1978**, *61*, 2336.

(44) Nazarou, I.; Azerbaef, I. N.; Rakcheeva, U. N. *Zh. Obsch. Khim.* **1948**, *18*, 407.

with the material obtained upon catalytic hydrogenation of the photoproduct **27** isolated after irradiation of **26** in methanol.

**Quantum Yield Measurements.** Quantum yields were measured by using a "linear optical bench" system described earlier[4] employing the filter solution combination 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) colbalt sulfate heptahydrate in 5% sulfuric acid, and 0.0001 M (0.0315 g/L) bismuth cloride in 10% hydrochloric acid. The UV transmission of this filter system was 250–310 nm, with a maximum at 280 nm. Product analyses were performed by GLC (5 ft × $^1/_8$ in., 2% OV-101 on 100–200-mesh Chromosorb GHP, 10 mL/min flow rate) of reaction mixtures; workup as in the preparative runs by using biphenyl as an internal standard. Conversions in quantum yield runs were in the range 0.3–2%.

**Summary of Quantum Yield Results.** The data are listed as follows: iminium salt; run number (mmol of iminium salt); light absorbed; product (mmol); quantum yield of formation; percent conversion; column temperature. 1-(3-Methyl-2-butenyl)pyridinium perchlorate (**26**): run 1 (0.82 mmol; 0.30 mEinstein; **27** (0.0144 mmol); $\Phi$ = 0.048; 1.3%; 120 °C. Run 2 (0.65 mmol); 0.20 mEinstein; **27** (0.0083 mmol); $\Phi$ = 0.042; 0.94%; 120 °C. Run 3 (0.58 mmol); 0.23 mEinstein; **27** (0.0089 mmol); $\Phi$ = 0.039; 1.08%; 120 °C.

1-(2-Propenyl)pyridinium perchlorate (**63**): run 1 (0.93 mmol); 1.69 mEinstein; **64** (0.0036 mmol); $\Phi$ = 0.0021; 0.32%; 120 °C. Run 2 (0.92 mmol); 1.58 mEinstein; **64** (0.0034 mmol); $\Phi$ = 0.0022; 0.39%; 120 °C.

1-(3-Methyl-2-butenyl)quinolinium perchlorate (**7**): run 1 (0.38 mmol); 0.30 mEinstein; **19** (0.00148 mmol); $\Phi$ = 0.0044; 0.38%; 120 °C. Run 2 (0.38 mmol); 0.69 mEinstein; 19 (0.00279 mmol); $\Phi$ = 0.0041; 0.73%, 120 °C. Run 3 (0.38 mmol); 0.99 mEinstein; **19** (0.0041 mmol); $\Phi$ = 0.0041; 1.14%; 120 °C.

**Direct Comparison of Product (27) Yield from Photolysis of 1-(3-Methyl-2-butenyl)pyridinium Perchlorate (26) with Product (25) Yield from Photolysis Followed by Hydrogenation.** A nitrogen-purged solution of 0.5 g (2.02 mmol) of 1-(3-methyl-2-butenyl)pyridinium perchlorate (**26**) in 600 mL of methanol was irradiated with Corex-filtered light for 30 min. An acidified ($HClO_4$, pH 4) aliquot (200 mL) of the photolysate was hydrogenated (200 mg $PtO_2$, 55 psi, 40 h). The solution was filtered and subjected to the general workup procedure, giving a residue that was diluted to 25 mL. To a 2-mL aliquot of the diluted solution was added 1 mL of biphenyl standard solution (56 mg/50 mL of $CHCl_3$).

Another 200-mL aliquot of the photolysate was worked up in the same way but without hydrogenation as described above and diluted to 25 mL in a volumetric flask. To a 2-mL aliquot of the diluted solution was added 1 mL of biphenyl standard solution (56 mg/50 mL of $CHCl_3$).

Both solutions were subjected to GLC analysis (5% OV 101, 10 ft × $^1/_8$ in., 150 °C, 12 mL/min flow rate) for direct comparison of product yields. The ratio of response factor of the product (**27**) to that of product (**25**) was 1.90. The yields of the tetrahydro **27** and hexahydro **25** products were identical to within experimental error.

**Product (27) Yields for Irradiation of 1-(3-Methyl-2-butenyl)pyridinium Perchlorate (26) at Varying Conversion.** Nitrogen-purged solutions of 1-(3-methyl-2-butenyl)pyridinium perchlorate (**26**) (62 mg, 0.25 mmol) in absolute methanol (100 mL) were irradiated with Corex-filtered light for 5 min, 10 min, 15 min, 30 min, and 1 h. An aliquot (3 mL) from each solution was diluted to 50 mL with methanol and analyzed by UV to determine the extent of conversion of starting material. The remaining photolysate was subjected to the general workup procedure to give a residue that was dissolved in $CHCl_3$. To the $CHCl_3$ solution was added biphenyl standard. The solution was subjected to GLC analysis (5 ft × $^1/_8$ in., 5% OV 101 on 100–120-mesh Chromosorb GHP, 150 °C, 10 mL/min flow rate) to determine the product yields.

**Irradiation of 1-Methyl-1,2-dihydropyridinium Perchlorate (32).** To carefully degassed absolute methanol (100 mL, boiled for 10 min and nitrogen purged while cooling) was added 70.1% perchloric acid (0.3 g, 2.1 mmol) and 1-methyl-1,2-dihydropyridine[45] (200 mg, 2.1 mmol). Care was taken to minimize exposure of the dihydropyridine to air. The methanolic solution was irradiated until the dihydropyridine was completely consumed, as monitored by the disappearance of the 330-nm band in the UV spectrum of aliquots removed from the solution. The photolysis was monitored by GLC (5% OV-101, 5 ft × $^1/_8$ in., 50 °C, 10 mL/min flow rate and 10% SE-30, 10 ft × $^1/_8$ in., 78 °C, 10 mL/min flow rate), which showed the appearance of 1-methyl-1,2,5,6-tetrahydropyridine (**33**) occurring simultaneously with the disappearance of starting dihydropyridine **32**. The tetrahydropyridine **32** was identified by comparing the photolysate with an authentic sample of 1-methyl-1,2,5,6-tetrahydropyridine prepared independently. The tetrahydropyridine **32** was not detected in the starting dihydropyridine or in a control consisting of a methanolic solution of the dihydropyridine kept under dark conditions.

**1-(3-Methyl-2-butenyl)pyridinium-$d_5$ Perchlorate (34).** A solution of pyridine-$d_5$ (5.0 g, 0.06 mol, 99 atom % D) and 1-bromo-3-methyl-2-butene (8.9 g, 0.06 mol) in anhydrous ether was stirred at 25 °C for 12 h. The formed crystalline salt was collected by filtration, washed with anhydrous ether, and dried to yield 9.8 g of 1-(3-methyl-2-butenyl)-pyridinium bromide (70%). The bromide salt (7.0 g, 0.03 mol) was eluted through a perchlorate anion exchange column (Dowex-1, mesh 50–100, 2.5 × 12 cm) with methanol. Concentration of the product fraction and crystallization from absolute ethanol yielded 5.9 g of the perchlorate salt **34** (75%): mp 93–95 °C; $^1$H NMR (acetone-$d_6$) $\delta$ 1.89 (s, 3 H, $CH_3$) 1.96 (s, 3 H, $CH_3$), 5.54 (s, 2 H, allylic $CH_2$), 5.3–5.9 (m, 1 H, vinyl H); $^{13}$C NMR (acetone-$d_6$) 18.37 ($CH_3$), 25.86 ($CH_3$), 59.51 ($CH_2$), 116.78 (—CH=), 144.70 ppm (=C=).

**Irradiation of 1-(3-Methyl-2-butenyl)pyridinium-$d_5$ Perchlorate (34) in Methanol-$d_4$ ($CD_3OD$).** A solution of 12.5 mg (0.05 mmol) of 1-(3-methyl-2-butenyl)pyridinium-$d_5$ perchlorate (**34**) in 1.5 mL of methanol-$d_4$ (99.5 atom % D, Aldrich) in a quartz tube (19 × 0.4 cm in diameter) was irradiated with Corex-filtered light for 15 min. The photolysate was subjected to the general workup procedure to give a residue that contained the deuteriohexahydro indolizidine product (**35**). The mass spectrum of the product was obtained without further purification: $m/e$ (rel intensity) 191 ($M^+$, 4.4), 190 (3.0), 189 (5.8), 188 (3.3), 157 ($M^+ - \cdot OD_3$, 4.2) 102 ($M^+ - (CH_3)_2$=CHOCD$_3$, 100), 101 (16.2), 100 (11.6), 99 (5.6).

**Irradiation of 1-(3-Methyl-2-butenyl)pyridinium-$d_5$ Perchlorate (34) in Methanol-$d_4$ ($CD_3OD$) in the Presence of Formic Acid.** A solution of 12.5 mg (0.05 mmol) of 1-(3-methyl-2-butenyl)pyridinium perchlorate (**34**) and 5.2 mg (0.1 mmol) of formic acid (88%) in 1.5 mL of methanol-$d_4$ (99.5 atom % D) in a quartz tube (19 × 0.4 cm in diameter) was irradiated with Corex-filtered light for 15 min. The photolysate was subjected to the general workup procedure. The mass spectrum of the product was obtained without further purification: $m/e$ 191 ($M^+$, 4.4), 190 (2.6), 189 (10.9), 188 (4.7), 157 ($M^+ - \cdot OD_3$, 4.0), 102 ($M^+ - (CH_3)_2$=CHOCD$_3$, 100), 101 (15.2), 100 (16.4), 99 (3.4).

**Irradiation of 1-(3-Methyl-2-butenyl)pyridinium-$d_5$ Perchlorate (34) in Methanol-$d_4$ ($CD_3OD$) in the Presence of Formaldehyde.** A solution of 12.5 mg (0.05 mmol) of 1-(3-methyl-2-butenyl)pyridinium perchlorate (**34**) and 3 mg (2 molar equiv) of paraformaldehyde in 1.5 mL of methanol-$d_4$ (99.5 atom % D) in a quartz tube (19 × 0.4 cm in diameter) was irradiated with Corex-filtered light for 15 min. After workup by using the general procedure, the mass spectrum of the product was obtained: $m/e$ (rel intensity) 191 ($M^+$, 5.0), 190 (4.3), 189 (17.3), 188 (5.4) 157 ($M^+ - \cdot OD_3$, 4.5), 102 ($M^+ - (CH_3)_2$=CHOCD$_3$, 100), 101 (16.2), 100 (11.6), 99 (5.6).

**Irradiation of 1-(3-Methyl-2-butenyl)pyridinium-$d_5$ Perchlorate (34) in Methanol ($CH_3OH$).** A nitrogen-purged solution of 1-(3-methyl)-2-butenyl)pyridinium-$d_5$ perchlorate (**34**) (127 mg, 0.5 mmol) in 100 mL of absolute methanol was irradiated with Corex-filtered light for 15 min. The photolysate was subjected to the general workup procedure to yield 33 mg of product (36%), which contained an ca. 1:1 mixture of penta- and tetradeuterioindolizidines **42** and **43** as determined by mass spectroscopy and $^{13}$C NMR analysis (vide supra): $^1$H NMR ($CDCl_3$) $\delta$ 0.92 (s, 3 H, $CH_3$), 1.03 (s, 3 H, $CH_3$), 1.83–2.33 (m, ca. 1.5 H, H-5 and H-6), 2.33–2.54 (m, 1 H, H-2), 3.35 (s, 3 H, $OCH_3$), 3.24–3.48 (m, 2 H, H-3); $^{13}$C NMR ($CDCl_3$) 20.27 ($CH_3$), 24.27 ($CH_3$), 24.87 (C-6), 42.85 (C-1), 47.56 (br, C-5), 52.75 ($OCH_3$), 58.08 (C-3), 67.49 (br, C-8a), 87.65 (C-2), 124–127 ppm (br, C-7 and C-8); mass spectrum, $m/e$ (rel intensity) 187 (6.4), 186 (11.5), 185 (22.5), 184 (5.5).

**Irradiation of 1-Methyl-1,2,5,6-tetrahydropyridinium Perchlorate in the Presence of 1-Methyl-1,2-dihydropyridinium Perchlorate.** To carefully degassed absolute methanol (100 mL, degassed by boiling for 10 min and nitrogen purged while cooling) was added 70.1% perchloric acid (0.6 g, 4.2 mmol), 1-methyl-1,2,5,6-tetrahydropyridine (204 mg, 2.1 mmol), and 1-methyl-1,2-dihydropyridine (200 mg, 2.1 mmol). Irradiation with Corex-filtered light for 15 min led to a 25% reduction in the quantity of 1-methyl-1,2,5,6-tetrahydropyridinium perchlorate as determined by GLC analysis (5% OV 101, 5 ft × $^1/_8$ in., 50 °C, 10 mL/min flow rate) of basified aliquots taken during the course of the irradiation. None of 1-methyl-1,2-dihydropyridinium perchlorate was present at the end of irradiation, as determined by UV analysis (complete disappearance of the 328-nm band).

**Irradiation of 1-Methyl-1,2,5,6-tetrahydropyridinium Perchlorate in the Presence of 1-Methylpyridinium Perchlorate.** A nitrogen-purged solution of 1-methyl-1,2,5,6-tetrahydropyridine (50.1 mg, 0.5 mmol), 1-methylpyridinium perchlorate (100 mg, 0.5 mmol), and 70.1% perchloric acid (74.1 mg, 0.5 mmol) in absolute methanol (100 mL) was irradiated for 20 min through a Corex filter. 1-Methylpyridinium perchlorate was ca. 80% reacted after this period, as determined by UV analysis (decrease

(45) Fowler, F. W. *J. Org. Chem.* **1972**, *37*, 1321.

in the 259-nm band). The quantity of 1-methyl-1,2,5,6-tetrahydropyridine remaining in the reaction mixture was unchanged, as determined by GLC analysis of basified samples taken during the course of reaction.

**Yield Comparison of Hexahydroindolizidine 27 and Octahydroindolizidine 25 from Irradiation of 1-(3-Methyl-2-butenyl)pyridinium Perchlorate (26) at Various Acid Concentrations.** Nitrogen-purged solutions of 1-(3-methyl-2-butenyl)pyridinium perchlorate (**26**) (250 mg) in 125 mL of methanol with different perchloric acid concentrations (no acid; $1 \times 10^{-4}$; $1 \times 10^{-3}$; $1 \times 10^{-2}$; $1 \times 10^{-1}$ M) were irradiated with Corex-filtered light for 30 min. Aliquots (50 mL) of the photolysates were concentrated, dissolved in 70 mL of chloroform, and extracted with 10 mL of saturated $NaHCO_3$ solution and 20 mL of water. The water phases were reextracted with 10 mL of chloroform. The combined chloroform extracts were washed with 15 mL of water twice, concentrated to ca. 5 mL, and then diluted to 10 mL with chloroform in volumetric flasks. Aliquots (50 mL) from the crude photolysates were also transferred into Parr medium-pressure reaction bombs containing 50 mg of platinum oxide, acidified to ca. pH2 with perchloric acid, and shaken for 15 h under hydrogen atmospheres (55 psi). The solutions were filtered, worked up in the same manner as those without hydrogenation, and diluted to 10 mL with chloroform. All solutions were analyzed by GLC (5 ft × $^1/_8$ in., 5% OV 101, 150 °C, 10 mL/min) with biphenyl as the internal standard to determine product yields.

**1-(3-Methyl-2-butenyl)-3-carbomethoxypyridinium Perchlorate (46).** 1-(3-Methyl-2-butenyl)-3-carbomethoxypyridinium perchlorate (**46**) was prepared in 73% yield by the same procedure as described above: mp 75–76.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.89 (s, 6 H, $(CH_3)_2C$=), 3.98 (s, 3 H, $OCH_3$), 5.2–5.6 (m, 3 H, $-CH_2CH$=), 8.13 (d of d, 1 H, $J$ = 7.5, 7.5 Hz, aromatic H-5), 8.82 (d, 1 H, $J$ = 7.5 Hz, aromatic H-6), 8.98 (d, 1 H, $J$ = 7.5 Hz, aromatic H-4), 9.13 (s, 1 H, aromatic H-2); UV (methanol) max 264 nm ($\epsilon$ 4890).

Anal. Calcd for $C_{12}H_{16}NClO_6$: C, 47.15; H, 5.28; N, 4.58. Found: C, 47.21; H, 5.28; N, 4.31.

**Irradiation of 1-(3-Methyl-2-butenyl)-3-carbomethoxypyridinium Perchlorate (46).** A nitrogen-purged solution of 1.0 g (3.27 mmol) of 1-(3-methyl-2-butenyl)-3-carbomethoxypyridinium perchlorate (**46**) in 600 mL of absolute methanol was irradiated with Corex-filtered light for 90 min. The reaction process was monitored by UV. The photolysate was subjected to the general workup procedure, yielding 0.62 g of brown oily residue. Molecular distillation (90 °C (0.05 torr)) of the residue afforded 98 mg of a mixture of products. Preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 130 °C, 75 mL/min flow rate) gave 29 mg (6.5%) of methylnicotinate **49** and 23 mg (4%) of methyl 6-isopropylnicotinate (**50**). The physical properties of **49** were the same as those of commercially available methyl nicotinate. For 6-isopropylnicotinate (**50**): $^1$H NMR ($CDCl_3$) $\delta$ 1.34 (d, 6 H, $J$ = 7.0 Hz, $(CH_3)_2$), 3.15 (septet, $J$ = 7.0 Hz, $(CH_3)_2CH$), 3.97 (s, 3 H, $OCH_3$), 7.29 (d, 1 H, $J$ = 8.0 Hz, aromatic H-5), 8.25 (d of d, 1 H, $J$ = 8.0, 2.0 Hz, aromatic H-4), 9.19 (d, 1 H, $J$ = 2.0 Hz, aromatic H-2); IR (neat) 2960, 1725, 1598, 1454, 1432, 1385, 1374, 1289, 1272, 1115 cm$^{-1}$; mass spectrum, $m/e$ (rel intensity) 179 ($M^+$, 19), 164 ($M^+$ – -$CH_3$, 100), 151 (26), 113 (32), 85 (35), 83 (53), 75 (53), high-resolution mass spectrum, $m/e$ 179.0938 ($C_{10}H_{13}NO_2$ requires 179.09462).

A dark control experiment was run in the following manner. A solution of 1 g (3.27 mmol) of 1-(3-methyl-2-butenyl)-3-carbomethoxypyridinium perchlorate in 600 mL of methanol was stirred for 2 h and worked up in the same manner as for the photochemical reaction. GLC analysis (2% OV-101, 5 ft × $^1/_8$ in., 125 °C, 10 mL/min, flow rate) showed the presence of a trace amount (0.005%) of methylnicotinate (**49**) and no formation of its 6-isopropyl derivative **50**.

**Irradition of 1-(3-Methyl-2-butenyl)-3-carbomethoxypyridinium Perchlorate (46) Followed by Hydrogenation.** A nitrogen-purged solution of 1.0 g (3.27 mmol) of 1-(3-methyl-2-butenyl)-3-carbomethoxypyridinium perchlorate (**46**) in 600 mL of absolute methanol was irradiated with Corex-filtered light for 90 min, and the photolysate was concentrated to 200 mL in vacuo. The solution was made acidic (pH 4) with concentrated perchloric acid (70%) and hydrogenated (100 mg $PtO_2$, 55 psi, 12 h). The solution was filtered and subjected to the general workup procedure to yield 860 mg of residue that was subjected to molecular distillation (110 °C (0.05 torr)) to give 740 mg of a mixture of products. Preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 150 °C, 80 mL/min flow rate) gave 245 mg (35%) of 1-(3-methylbutyl)-3-carbomethoxypiperidine (**54**), 20.8 mg (3.5%) of 3-carbomethoxypiperidine (**51**), 20.8 mg (2.8%) of 1-(3-methylbutyl)-3-carbomethoxy-4-methylpiperidine (**53**), 94.8 mg (12.0%) of one of the diastereomers (A) of 1,1-dimethyl-2-methoxy-6-carbomethoxyoctahydroindolizidine (**55**), and 89.7 mg (11.4%) of diastereomer B of 1,1-dimethyl-2-methoxy-6-carbomethoxyoctahydroindolizidine (**56**).

**1-(3-Methylbutyl)-3-carbomethoxypiperidine (54):** $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (d, 6 H, $J$ = 6.0 Hz), 1.11–3.51 (m, 14 H), 3.68 (s, 3 H, $CO_2CH_3$); $^{13}$C NMR ($CDCl_3$) 22.70, 24.61, 26.57, 27.04, 35.81, 41.77, 51.36, 53.86, 55.49, 57.14, 174.23 ppm; IR (neat) 2948, 2862, 2800, 2764, 1735, 1465, 1430, 1150 cm$^{-1}$; mass spectrum, $m/e$ (rel intensity) 213 ($M^+$, 6.4), 198 ($M^+$ – -$CH_3$, 1.0), 182 ($M^+$ – -$OCH_3$, 5.4), 156 ($M^+$ – -$C_4H_9$, 100), 142 (6.5), 113 (13.0); high-resolution mass spectrum, $m/e$ 213.1718 ($C_{12}H_{23}NO_2$ requires 213.1729). All physical properties of the isolated **54** were identical with those of the authentic compound prepared independently (vide infra).

**1-(3-Methylbutyl)-3-carbomethoxy-4-methylpiperidine (53):** $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (d, 6 H, $J$ = 6.0 Hz, 2 $CH_3$) 0.92 (d, 3 H, $J$ = 6.9 Hz, $CH_3$), 1.2–3.6 (m, 13 H), 3.67 (s, 3 H, $OCH_3$); $^{13}$C NMR ($CDCl_3$) 14.47 ($CH_3$ at C-4), 22.71 ($CH_3$), 26.69 ($CH_3$), 29.5 (C-4), 31.38 (C-5), 35.87 (—$CH$=$(CH_3)_2$), 45.23 (C-3), 49.59 ($NCH_2CH_2CH$=), 50.73 (C-6), 51.19 ($CO_2CH_3$), 57.18 (C-2), 173.77 ppm (C=O); IR (neat) 2940, 2905, 2860, 2800, 2762, 1730, (C=O stretching), 1460, 1428, 1374, 1359 cm$^{-1}$; mass spectrum, $m/e$ (rel intensity) 227 ($M^+$, 4.1), 212 ($M^+$ – -$CH_3$, 1.5), 196 ($M^+$ – $OCH_3$-, 4.9), 170 ($M^+$ – -$CH_2CH$=$(CH_3)_2$, 100), high-resolution mass spectrum, $m/e$ 227.1892 ($C_{13}H_{25}NO_2$ requires 227.1885).

**Diastereomer A of 1,1-Dimethyl-2-methoxy-6-carboxymethoxyoctahydroindolizidine (55):** $^1$H NMR ($CDCl_3$) $\delta$ 0.84 (s, 3 H, $CH_3$), 1.00 (s, 3 H, $CH_3$), 1.2–3.6 (m, 11 H), 3.31 (s, 3 H, $OCH_3$), 3.68 (s, 3 H, $CO_2CH_3$); $^{13}$C NMR ($CDCl_3$) 16.53 (q, $CH_3$), 21.64 (t, C-8), 24.74 (t, C-7), 25.51 (q, $CH_3$), 39.52 (d, C-6), 43.14 (s, C-1), 51.50 (q, $CO_2CH_3$), 54.56 (t, C-3), 58.35 (t and q, C-5 and $OCH_3$), 72.4 (d, C-8a), 87.38 (d, C-2), 174.08 ppm (s, C=O); IR (neat) 2950, 2820, 2790, 1734 (C=O stretching), 1464, 1440, 1382, 1362, 1259, and 1210 cm$^{-1}$; mass spectrum, $m/e$ (rel intensity) 241 ($M^+$, 15.7), 210 ($M^+$ – -$OCH_3$, 41.1), 155 (100), 142 (30.2), 96 (79.5), high-resolution mass spectrum, $m/e$ 241.1673 ($C_{13}H_{23}NO_3$ requires 241.1678).

**Diastereomer B of 1,1-Dimethyl-2-methoxy-6-carbomethoxyoctahydroindolizidine (56):** $^1$H NMR ($CDCl_3$) $\delta$ 0.86 (s, 3 H, $CH_3$), 1.08 (s, 3 H, $CH_3$), 1.2–3.6 (m, 11 H), 3.31 (s, 3 H, $OCH_3$), 3.65 (s, 3 H, $CO_2CH_3$); $^{13}$C NMR ($CDCl_3$) 15.46 (q, $CH_3$), 21.45 (t, C-8), 25.33 (q, $CH_3$), 28.00 (t, C-7), 38.29 (d, C-6), 43.02 (s, C-1), 51.12 (q, $CO_2CH_3$), 54.87 (t, C-3), 57.73 (t, C-5), 58.16 (q, $OCH_3$), 73.78 (d, C-8a), 86.51 (d, C-2), 174.17 ppm (C=O); IR (neat) 2920, 2820, 2760, 1742 (C=O stretching), 1464, 1434, 1375, 1360, 1320, 1297, 1225, 1145, 1100 cm$^{-1}$; mass spectrum, $m/e$ (rel intensity) 241 ($M^+$, 7.3), 210 ($M^+$ – -$OCH_3$, 19.2), 200 (16.1), 170 (18.0), 155 (46.6), 142 (21.0), 96 (100); high-resolution mass spectrum, $m/e$ 241.1685 ($C_{13}H_{23}NO_3$ requires 241.1678).

**1-(3-Methylbutyl)-3-carbomethoxypiperidine (54).** A solution of 300 mg (0.98 mmol) of 1-(3-methyl-2-butenyl)-3-carbomethoxypyridinium perchlorate (**46**) in 30 mL of methanol containing platinum oxide (50 mg) was shaken under a hydrogen atmosphere (55 psi) in a Parr medium-pressure apparatus for 15 h. The reaction mixture was filtered and subjected to the general workup procedure yielding 143 mg (76%) of the reduced product **54**.

**3-Carbomethoxypiperidine (51).** An acidic methanolic solution (30 mL, pH 4/$HClO_4$) of 300 mg (2.2 mmol) of methyl nicotinate (**49**) was hydrogenated (50 mg $PtO_2$, 55 psi, 15 h). The reaction mixture was filtered through Celite and subjected to the general workup procedure, yielding 145 mg of 3-carbomethoxypiperidine (45%): $^1$H NMR ($CDCl_3$) $\delta$ 1.2–3.5 (m, 9 H), 1.26 (s, 1 H, NH), 3.66 (s, 3 H, $CO_2CH_3$); IR (neat) 2937, 2845, 1730 (C=O stretching), 1430 cm$^{-1}$; mass spectrum, $m/e$ (rel intensity) 143 ($M^+$, 11), 128 ($M^+$ – -$CH_3$, 9), 112 ($M^+$ – -$OCH_3$, 14), 84 (41), 57 (87), 56 (100), high-resolution mass spectrum, $m/e$ 143.0934 ($C_7H_{13}NO_2$ requires 143.09462).

**Hydrogenation of Methyl 6-Isopropylnicotinate.** An acidic solution (pH 4/$HClO_4$) of 8 mg (0.045 mmol) of methyl 6-isopropylnicotinate in 15 mL of methanol containing 20 mg of platinum oxide was shaken under a hydrogen atmosphere (55 psi) in a Parr medium-pressure apparatus for 6 h. The solution was worked up as in the hydrogenation of photolysate of 1-(3-methyl-2-butenyl)-3-carbomethoxypyridinium perchlorate (**46**) (vide supra). GLC analysis (5% OV 101, 10 ft × $^1/_8$ in., 150 °C, 10 mL/min flow rate) showed the presence of two products ($t_R$ = 9, 10 min) in a 2:1 ratio, which were identified as the diastereomer **52** by their identical spectroscopic properties with material from hydrogenation of the photolysate from 1-(3-methyl-2-butenyl)-3-carbomethoxypyridinium perchlorate.

**Epimerization of Indolizidines 55 and 56.** A solution of the indolizidine **55** (62 mg, 0.26 mmol) and 150 mg (3 mmol) of sodium methoxide in 4 mL of methanol was refluxed for 80 min. The reaction was monitored by GLC (5% OV 101, 5 ft × $^1/_8$ in., 150 °C, 10 mL/min flow rate). A new product ($t_R$ = 27.5 min) appeared after 30 min at reflux while starting material ($t_R$ = 21 min) disappeared and slowly decomposed on prolonged reaction. The solution was diluted with water and extracted with chloroform. The extracts were washed with water, dried, and concentrated in vacuo to yield 23 mg of a residue that contains the epimeric **61** and starting indolizidine **55**. The epimer **61** was separated by pre-

parative GLC (20% SE 30, 5 ft × $^5/_{16}$ in., 140 °C, 80 mL/min flow rate): $^1$H NMR ($CDCl_3$) δ 0.89 (s, 3 H, $CH_3$), 1.02 (s, 3 H, $CH_3$), 1.2–3.5 (m, 11 H), 3.32 (s, 3 H, $OCH_3$), 3.66 (s, 3 H, $CO_2CH_3$); high-resolution mass spectrum, *m/e* 241.1685 ($C_{13}H_{23}NO_3$ requires 241.1678).

A solution of the indolizidine **56** (22 mg, 0.091 mmol) and 100 mg (2 mmol) of sodium methoxide in 4 mL of methanol was refluxed for 20 h. The same workup procedure as used for **61** gave 16.5 mg of the residue, which was shown to contain a 7:1 mixture of the epimeric ($t_R$ = 22 min) and starting indolizidines ($t_R$ = 25 min) by GLC analysis (5% OV 101, the same conditions as above). The new product **62** was separated by preparative GLC (20% SE-30, the same conditions as above): $^1$H NMR ($CDCl_3$) δ 0.96 (s, 3 H, $CH_3$), 0.97 (s, 3 H, $CH_3$), 1.43–3.3 (m, 11 H), 3.31 (s, 3 H, $OCH_3$), 3.67 (s, 3 H, $CO_2CH_3$); high-resolution mass spectrum, *m/e* 241.1678 ($C_{13}H_{23}NO_3$ requires 241.1678).

**1-(2-Propenyl)-3-carbomethoxypyridinium Perchlorate (58).** A solution of 12 g (0.088 mol) of methyl nicotinate and 12.8 g (0.106 mol) of allylbromide in 100 mL of anhydrous ether was refluxed for 24 h. The formed crystalline salt was collected by filtration, washed with anhydrous ether several times, and dried in vacuo to yield 15.3 g of 1-(2-propenyl)-3-carbomethoxypyridinium bromide (68%). The bromide salt (7.5 g, 0.0293 mol) was eluted through a perchlorate anion exchange column (Dowex-1, mesh 50–100, 2.5 × 12 cm) with methanol. The product fraction was concentrated under reduced pressure to yield 8.0 g of the perchlorate salt **58**: $^1$H NMR (acetone-$d_6$) δ 4.0 (s, 3 H, $OCH_3$), 5.44–6.93 (m, 4 H, allylic $CH_2$ and vinyl $CH_2$), 6.09–6.77 (m, 1 H, vinyl CH), 8.49 (d of d, 1 H, *J* = 7, 7 Hz, aromatic H-5), 9.18 (d, 1 H, *J* = 7 Hz, aromatic H-6), 9.70 (d, 1 H, *J* = 7 Hz, aromatic H-4), 9.79 (s, 1 H, aromatic H-2); UV (methanol) max 266 nm (ε 4060).

Anal. Calcd for $C_{10}H_{12}NClO_6$: C, 43.23; H, 4.36; N, 5.04. Found: C, 44.19; H, 4.54; N, 5.09.

**1-Propyl-3 carbomethoxypiperidine (57).** A solution of 500 mg (1.80 mmol) of 1-(2-propenyl)-3-carbomethoxypyridinium perchlorate in 50 mL of methanol was acidified to pH 4 with concentrated perchloric acid (70%) and hydrogenated (50 mg $PtO_2$, 55 psi, 20 h), filtered, and concentrated in vacuo. The residue was basified with 10 mL of saturated sodium bicarbonate and extracted with $CHCl_3$. The extracts were washed with water, dried, and concentrated in vacuo to yield 239 mg (72%) of the reduced product **57**: $^1$H NMR ($CDCl_3$) δ 0.89 (t, 3 H, $CH_2CH_2CH_3$), 1.28–3.10 (m, 13 H), 3.70 (s, 3 H, $OCH_3$); $^{13}$C NMR ($CDCl_3$) 11.96 (q, $CH_3$), 20.12 (t), 24.65 (t), 27.09 (t), 41.87 (d, C-3), 51.57 (q, $CH_3O$), 53.84 (t), 55.46 (t), 60.97 (t), 174.76 ppm (s, C=O); mass spectrum, *m/e* (rel intensity) 185 ($M^+$, 5.9), 170 ($M^+$ – $-CH_3$, 1.1), 156 ($M^+$ – $-CH_2CH_3$, 100), 154 ($M^+$ – $-CH_3O$, 9.0), 126 ($M^+$ – $-CO_2CH_3$, 3.5); high-resolution mass spectrum, *m/e* 185.1407 ($C_{10}H_{19}NO_2$ requires 185.14157).

**1-(2-Propenyl)pyridinium Perchlorate (63).** 1-(2-propenyl)pyridinium perchlorate (**63**) was prepared in 81% yield by use of the same procedure as described above for compound **26**: mp 69–70.5 °C (lit.[46] mp 69–71 °C); $^1$H NMR (acetone-$d_6$) δ 5.39–5.75 (m, 4 H, $CH_2$= and allylic $CH_2$), 6.05–6.75 (m, 1 H, —CH=), 8.30 (t, 2 H, aromatic), 8.85 (t, 1 H, aromatic), 9.21 (d, 2 H, aromatic); UV (methanol) max 258 nm (ε 4000).

**Irradiation of 1-(2-Propenyl)pyridinium Perchlorate (63).** A nitrogen-purged solution of 1-(2-propenyl)pyridinium perchlorate (100 mg, 0.46 mmol) in 100 mL of absolute methanol was irradiated with Corex-filtered light for 45 min. The reaction course was monitored by UV. The photolysate was concentrated in vacuo, made basic by addition of 5 mL of saturated sodium bicarbonate, and extracted with ether. The ethereal extracts were dried, concentrated in vacuo, and subjected to molecular distillation (90 °C, 0.05 torr) to yield 25.3 mg of the cyclopentene **64** as an oil (30% at 35% conversion determined by UV analysis): $^1$H NMR ($CDCl_3$) δ 1.56 (s, 1 H, NH), 3.17 (t, 1 H *J* = 4.5 Hz, CH(NH)), 3.28–3.39 (m, 2 H, allylic $CH_2$), 3.36 (s, 6H, $2CH_3O$), 4.00 (d, 1 H, *J* = 4.5 Hz, H-1), 4.92–5.25 (m, 2 H, $CH_2$=CH), 5.65–6.08 (m, 1 H, $CH_2$=C*H*), 6.00 (s, 2 H, —CH=CH—); $^{13}$C NMR ($CDCl_3$) 50.74 (t, $NHCH_2CH$=), 56.06 (q, $CH_3O$), 69.41 (d, C-4), 88.97 (d, C-3), 115.89 (t, —CH=$CH_2$), 132.267 (d, C-1), 136.54 ppm (d, —*C*H=$CH_2$); IR (neat) 3300 (NH stretch), 3060, 2980, 2925, 2895, 2820, 1460, 1370, 1190, 1095, 990, 960, 912, 750 $cm^{-1}$; mass spectrum, *m/e* (rel intensity) 183 ($M^+$, 7.2), 168 ($M^+$ – $-CH_3$, 3.2), 152 ($M^+$ – $-OCH_3$, 100), 120 (44), 110 (10.2), 108 (11.6), 94 (12.0), 80 (23.2); high-resolution mass spectrum, *m/e* 183.1256 ($C_{10}H_{17}NO_2$ requires 183.1259).

**3,5-Dimethoxy-4-(2-propenyldimethylamino)-1-cyclopentene Iodide (65).** A solution of 150 mg (0.82 mmol) of 3,5-dimethoxy-4-(2-propenylamino)-1-cyclopentene (**64**) and excess $CH_3I$ (4.92 mmol) in 5 mL of anhydrous ether was refluxed for 2 days. The formed crystals were collected on a filter, washed with $CHCl_3$–ether (1:9, v/v), and dried at room temperature to yield 29 mg (16%) of the crystalline iodide salt **65**. Recrystallization from $CHCl_3$–ether (1:5) afforded colorless crystals: mp 162–163 °C; $^1$H NMR ($CDCl_3$) δ 3.49 (s, 6 H, 2 $CH_3O$), 3.56 (s, 6 H, 2 $CH_3N$), 3.66 (t, 1 H, *J* = 5 Hz, C*H*(NH)), 4.48 (d, 2 H, *J* = 5 Hz, $^+NCH_2CH$= or 2 *CH*($OCH_3$)), 5.08 (d, 2 H, *J* = 5 Hz, $^+NCH_2CH$= or 2 *CH*($OCH_3$)), 5.68–6.34 (m, 3 H, —CH=$CH_2$), 6.22 (s, 2 H, —CH=$CH_2$). This material was characterized by X-ray crystallographic analysis.

**Irradiation of 1-Methylpyridinium Perchlorate (66) and 3,5-Dimethoxy-4-(methylamino)-1-cyclopentene (70).** A nitrogen-purged solution of 1 g (5.57 mmol) of 1-methylpyridinium perchlorate in 600 mL of methanol was irradiated with Corex-filtered light for 2.5 h. The reaction course was monitored by UV and GLC (5% OV 101, 10 ft × $^1/_8$ in., 115 °C, 10 mL/min flow rate). For GLC analysis, 3 mL of aliquot was removed and immediately concentrated in vacuo (30 °C, 20 torr) to yield a residue that was stirred with 0.5 mL of water and 0.05 mL of saturated sodium bicarbonate and extracted with 0.5 mL of chloroform. GLC analysis of the chloroform extracts showed the presence of two products ($t_R$ = 3.5, 8.5 min), one of which was 3,5-dimethoxy-4-(methylamino)-1-cyclopentene (**70**) ($t_R$ = 8.5 min). On standing in the dark, the amount of 3,5-dimethoxy-4-(methylamino)-1-cyclopentene (**70**) in the mixture increased while the other product, not identified, ($t_R$ = 3.5 min) slowly disappeared.

The photolysate was concentrated in vacuo, giving a residue that was made basic with 40 mL of saturated sodium bicarbonate and extracted with $CHCl_3$. The extract was washed with water, dried, and concentrated to yield 220 mg of 3,5-dimethoxy-4-(methylamino)-1-cyclopenetene (**70**) (22.5% at 27% conversion determined by UV analysis): $^1$H NMR ($CDCl_3$) δ 1.56 (s, 1 H, NH), 2.54 (s, 3 H, $NHCH_3$), 3.03 (t, 1 H, *J* = 4.2 Hz), 3.39 (s, 6 H, 2 $CH_3O$), 4.02 (d, 2 H, *J* = 4.2 Hz, 2 C*H*($OCH_3$)), 6.0 (s, 2 H, —CH=CH—); mass spectrum, *m/e* (rel intensity) 157 ($M^+$, 2.3), 142 ($M^+$ – $-CH_3$, 3.8), 126 ($M^+$ – $-OCH_3$, 100), 110 (13.2), 94 (63.0), 82 (19.0); high-resolution mass spectrum, *m/e* 157.1096 ($C_8H_{15}NO_2$ requires 157.11027).

**2-(4-Methyl-3-pentenyl)pyridine (71).** A solution of 20.0 g (0.22 mol) of 2-picoline in 30 mL of ether was added to preformed lithium diisopropylamide solution (21.78 g, 0.22 mol diisopropyl amine, and 137.5 mL of 1.6 M *n*-butyllithium in 60 mL of ether) at 0 °C. After 15 min of stirring at 0 °C, a solution of 17.6 g (0.22 mol) of 1-bromo-3-methyl-2-butene) in 30 mL of ether was added, followed by water quenching. The ethereal layer was separated, washed with water, dried, and concentrated in vacuo to give an oil, which upon distillation gave 25.6 g (72.3%) of the desired pyridine product: bp 110–123 °C (11 torr); $^1$H NMR ($CDCl_3$) δ 1.52 (s, 3 H, $CH_3$), 1.64 (s, 3 H, $CH_3$), 2.22–2.50 (m, 2 H, allylic), 2.65–2.85 (m, 2 H, $CH_2CH_2CH$=), 5.06 (t, *J* = 6 Hz, 1 H, vinyl) 6.91 (t, *J* = 6 Hz, 1 H, aromatic), 6.98 (d, *J* = 7 Hz, 1 H, aromatic), 7.41 (t, *J* = 7 Hz, 1 H, aromatic), 8.36 (d, *J* = 6 Hz, 1 H, aromatic); $^{13}$C NMR ($CDCl_3$) δ 17.6 (q, $CH_3$), 25.6 (q, $CH_3$), 28.4 (t, allylic), 38.5 (t, *C*$H_2$ $CH_2CH$=), 120.6 (d, C-5 aromatic), 122.6 (d, C-3 aromatic), 123.4 (d, *C*H=$C(CH_3)_2$, vinyl), 131.7 (s, CH=*C*$(CH_3)_2$ vinyl), 135.8 (d, C-4, aromatic), 149.0 (d, C-6, aromatic), 161.7 (s, C-2, aromatic).

Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 82.15; H, 9.40; N, 8.80.

**1-Methyl-2-(4-methyl-3-pentenyl)pyridinium Perchlorate (73).** A solution of 8.0 g of 2-(4-methyl-3-pentenyl)pyridine (**71**) (0.049 mol) and methyl iodide (0.148 mol, 21.0 g) in 30 mL of ether was stirred at reflux for 3 days. The formed crystalline material was separated by filtration, washed with ether, and dried to yield 12.7 g of 1-methyl-2-(4-methyl-3-pentenyl)pyridinium iodide (85%): mp 112–113.5 °C; $^1$H NMR (acetone-$d_6$) δ 1.61 (s, 3 H, $CH_3$), 1.70 (s, 3 H, $CH_3$), 2.48–2.73 (m, 2 H, allylic), 3.37 (t, *J* = 7 Hz, —$CH_2CH_2CH$=), 4.61 (s, 3 H, $NCH_3$), 5.30 (t, *J* = 7 Hz, 1 H, vinyl), 8.06 (t, *J* = 7 Hz, 1 H, aromatic), 8.19 (d, *J* = 8 Hz, 1 H, aromatic), 8.65 (t, *J* = 8 Hz, 1 H, aromatic), 9.30 (d, *J* = 7 Hz, 1 H, aromatic). The iodide salt (6.0 g, 0.0198 mol) was subjected to perchlorate anion exchange (Dowex-1, mesh 50–100, 2.5 × 12 cm), with methanol as eluant. Concentration of the product fraction under reduced pressure and recrystallization (ethanol) yielded 3.8 g of the perchlorate (**73**) (69%): mp 59.5–61.0 °C; $^1$H NMR (acetone-$d_6$) δ 1.61 (s, 3 H, $CH_3$), 1.69 (s, 3 H, $CH_3$), 2.46–2.71 (m, 2 H, allylic), 4.53 (s, 3 H, $NCH_3$), 5.28 (t, *J* = 7.5 Hz, 1 H, vinyl), 8.02 (t, *J* = 7 Hz, 1 H, aromatic), 8.13 (d, *J* = 7 Hz, 1 H, aromatic), 8.61 (t, *J* = 7 Hz, 1 H, aromatic), 8.99 (d, *J* = 7 Hz, aromatic); UV ($CH_3OH$) max 268 nm (ε 7290).

Anal. Calcd for $C_{12}H_{18}NO_4Cl$: C, 52.27; H, 6.58; N, 5.08. Found: C, 51.99, H, 6.76; N, 4.95.

**Irradiation of 2-(4-Methyl-3-pentenyl)pyridinium Perchlorate (72) without Hydrogenation.** A nitrogen-purged solution of 700 mg of 2-(4-methyl-3-pentenyl)pyridine (4.32 mmol) and 621 mg of 70% perchloric acid (4.32 mmol) in 200 mL of methanol was irradiated with Corex-

(46) Duling, I. N.; Price, C. C. *J. Am. Chem. Soc.* **1962**, *84*, 578.

filtered light for 3 h. The photolysate was subjected to the general workup procedure to give a residue that was subjected to molecular distillation (100 °C, 0.05 torr), yielding 445 mg of a mixture of products that contained 28.4 mg (6.3% yield based on conversion) of 2,2-dimethyl-3-methoxycyclopentanone (**76**), 185 mg (26.5%) of the starting material (**71**), 163.4 mg (19.6% yield based on conversion) of 2-(3-methoxy-4-methylpentyl)pyridine (**74**), 17.5 mg (2.1% yield based on conversion) of 2-(4-methyl-4-methoxypentyl)pyridine (**75**), and 62.7 mg (7.6%) of 7-methoxy-8,8-dimethyl-5,6,7,8-tetrahydroquinoline (**77**) (yields were determined by GLC analysis). Product separation was performed by preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 150 °C, 130 mL/min flow rate).

**2,2-Dimethyl-3-methoxycyclopentanone (76)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.00 (s, 3 H, $CH_3$), 1.07 (s, 3 H, $CH_3$), 1.72–2.56 (m, 4 H, $—CH_2CH_2—$), 3.40 (s, 3 H, $OCH_3$), 3.53 (t, $J$ = 6 Hz, 1 H, $CHOCH_3$); IR (neat) 2962, 2913, 2822, 1740, (C=O stretching), 1469, 1410, 1383, 1362, 1204, 1120, 1094, 1067 cm$^{-1}$; $^{13}$C NMR ($CDCl_3$) $\delta$ 17.3 (q, $CH_3$), 22.9 (q, $CH_3$), 23.8 (t), 34.2 (t), 49.6 (s, C-2), 57.3 (q, $OCH_3$), 87.0 (d, C-3), 120.8 (s, C=O); mass spectrum, $m/e$ (rel intensity) 142 ($M^+$, 38.5), 127 ($M^+ - \cdot CH_3$, 4.0), 110 (8.7), 95 (14.4), 82 (100), 71 (34.0); high-resolution mass spectrum , $m/e$ 142.0986 ($C_8H_{14}O_2$ requires 142.09937).

**2-(3-Methoxy-4-methylpentyl)pyridine (74)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.92 (d, $J$ = 7 Hz, 6 H, 2 $CH_3$), 1.62–2.20 (m, 3 H), 2.72–3.25 (m, 3 H), 3.37 (s, 3 H, $OCH_3$), 7.12 (t, 1 H, aromatic), 7.18 (d, 1 H, aromatic), 7.67 (t, 1 H, aromatic), 8.53 (d, 1 H, aromatic); $^{13}$C NMR ($CDCl_3$) $\delta$ 17.7 (q, $CH_3$), 18.3 (q, $CH_3$), 30.2 (t and d, C-1 and C-4), 34.5 (t, C-2′), 57.5 (q, $OCH_3$), 85.5 (d, C-3′), 120.7 (d, C-5, aromatic), 122.6 (d, C-3, aromatic), 136.0 (d, C-4, aromatic), 149.0 (d, C-6, aromatic), 162.1 (s, C-2, aromatic); mass spectrum $m/e$ (rel intensity) 193 ($M^+$, 0.17), 178 ($M^+ - \cdot CH_3$, 5.6), 162 ($M^+ - \cdot OCH_3$, 13.3), 151 (15.5), 150 ($M^+ - \cdot C_3H_7$, 100), 118 (11.2), 106 ($C_7H_8N^+$, 25.5), 93 (57.7), 92 (11.9), 87 ($CH_3{}^+O{=}CCH(CH_3)_2$, 16.2), high-resolution mass spectrum, $m/e$ 193.1450 ($C_{12}H_{19}NO$ requires 193.14665).

**2-(4-Methyl-4-methoxypentyl)pyridine (75)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.13 (s, 6 H, 2$CH_3$), 1.30–2.20 (m, 4 H, $—CH_2CH_2—$), 2.79 (br t, 2 H, $CH_2$), 3.13 (s, 3 H, $OCH_3$), 7.09 (t, 1 H, aromatic), 7.15 (d, 1 H, aromatic), 7.61 (t, 1 H, aromatic), 8.55 (d, 1 H, aromatic); $^{13}$C NMR ($CDCl_3$) $\delta$ 23.9 (t, C-2′), 24.5 (q, 2 $CH_3$), 38.4 (t), 39.1 (t), 48.6 (q, $OCH_3$), 73.9 (s, C-4′, aromatic), 148.6 (d, C-6, aromatic).

**7-Methoxy-8,8-dimethyl-5,6,7,8-tetrahydroquinoline (77)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.30 (s, 6 H, 2$CH_3$), 2.11 (t, $J$ = 6.5 Hz, 2 H, H-8), 2.80–3.40 (m, 3 H, H-7 and H-6), 3.47 (s, 3 H, $OCH_3$), 6.92–8.50 (m, 3 H, aromatic); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.4 (t, C-5), 25.3 (q, $CH_3$), 29.4 (q, $CH_3$), 29.7 (t, C-6), 38.8 (s, C-5), 57.1 (q, $OCH_3$), 83.8 (d, C-6), 121.2 (d, C-3), 134.3 (d, C-4), 146.4 (d, C-2), 154.9 (s, C-10); mass spectrum, $m/e$ (rel intensity) 191 ($M^+$, 100), 176 ($M^+ - \cdot CH_3$, 89.0), 160 ($M^+ - \cdot OCH_3$, 26.4), 150 (16.2), 146 (14.7), 144 (12.6), 132 (13.8), 118 (8.6), 93 (17.3), 84 (43.3); high-resolution mass spectrum, $m/e$ 191.1310 ($C_{12}H_{17}NO$ requires 191.1306).

A dark control experiment was run in the following manner. A solution of 200 mg of 2-(4-methyl-3-pentenyl)pyridine and 177 mg of 70% perchloric acid in 60 mL of methanol was stirred for 3 h and worked up in the same manner as for the photochemical reaction except the molecular distillation step. GLC analysis (5% OV 101, 10 ft × $^1/_8$ in., 135 °C, 20 mL/min flow rate) showed that 2-(4-methyl-4-methoxypentyl)-pyridine (**75**) was the only product produced.

**Irradiation of 2-(4-Methyl-3-pentenyl)pyridinium Perchlorate (72) Followed by Hydrogenation.** A nitrogen-purged solution of 700 mg of 2-(4-methyl-3-pentenyl)pyridine (4.32 mmol) and 621 mg of 70% perchloric acid (4.32 mmol) in 200 mL of methanol was irradiated with Corex-filtered light for 3 h. The crude photolysate was hydrogenated (100 mg $PtO_2$, 55 psi, 24 h), filtered, and subjected to the general workup procedure to give a residue that was subjected to molecular distillation (100 °C, 0.05 torr), giving 440 mg of a mixture of products that contained 34.3 mg (7.0% based on conversion) of 2,2-dimethyl-3-methoxycyclopentanone (**76**), 153.6 mg (20.9%) of 2-(4-methylpentyl)piperidine (**78**), 80.9 mg (12.7%) of 1-(*N*-butylamino)-2,2-dimethyl-3-methoxycyclopentane (**81**), 67.9 mg (10.5%) of 2-(3-methoxy-4-methylpentyl)-piperidine (**79**), and 12.4 mg (1.9%) of 2-(4-methoxy-4-methylpentyl)-piperidine (**80**). The products were separated by preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 150 °C, 130 mL/min flow rate).

**2-(4-Methylpentyl)piperidine (78)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.86 (d, $J$ = 6 Hz, 6 H, 2 $CH_3$), 1.10–3.30 (m, 17 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.2 (q, $CH_3$), 23.3 (t, C-2′), 24.6 (t, C-4), 26.3 (t, C-5), 27.5 (d, C-4′), 32.7 (t, C-3), 37.4 (t, C-3′), 38.8 (t, C-1′), 46.9 (t, C-6), 56.2 (d, C-2); mass spectrum, $m/e$ (rel intensity) 169 ($M^+$, 3.3), 168 ($M^+ - 1$, 1.9), 154 ($M^+ - \cdot CH_3$, 1.4), 112 (0.7), 98 (5.68), 84 ($C_5H_{10}N^+$, 100); high-resolution mass spectrum, $m/e$ 169.1828 ($C_{11}H_{23}N$ requires 169.18304). This material was also produced by catalytic hydrogenation ($PtO_2$) of the pyridine derivative **71**, which provided a substance with identical spectroscopic properties.

**1-(Butylamino)-2,2-dimethyl-3-methoxycyclopentane (81)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.80 (s, 3 H, $CH_3$), 0.88 (t, 3 H, $CH_3(CH_2)_3$-), 1.05 (s, 3 H, $CH_3$), 1.12–2.20 (m, 9 H), 2.30–2.75 (m, 3 H), 3.33 (s, 3 H, $CH_3O$); mass spectrum, $m/e$ (rel intensity) 142 ($M^+$, 38.5), 127 ($M^+ - \cdot CH_3$, 4.0), 110 (8.7), 95 (14.4), 82 (100), 71 (34.0); high-resolution mass spectrum, $m/e$ 142.0986 ($C_8H_{14}O_2$ requires 142.09937). The physical and spectroscopic properties of the isolated material were identical with those of the compound prepared by independent synthesis (vide infra).

**2-(3-Methoxy-4-methylpentyl)piperidine (79)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (d, $J$ = 6 Hz, 2 $CH_3$), 1.15–3.20 (m, 16 H), 3.35 (s, 3 H, $OCH_3$); mass spectrum, $m/e$ (rel intensity) 199 ($M^+$, 3.7), 198 ($M^+ - 1$, 25.4), 184 ($M^+ - \cdot CH_3$, 19.0), 168 ($M^+ - \cdot OCH_3$, 11.8), 156 (2.5), 142 (10.5), 124 (10.0), 112 (2.6), 84 ($C_5H_{10}N^+$, 100); high-resolution mass spectrum, $m/e$ 199.1932 ($C_{12}H_{25}NO$ requires 199.19360). The physical and spectroscopic properties of the isolated material were identical with those of the compound prepared by hydrogenation ($PtO_2$, $CH_3OH$, pH2, 55 psi) of 2-(3-methoxy-4-methylpentyl)piperidine (**74**) (vide supra).

**2-(4-Methoxy-4-methylpentyl)piperidine (80)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.16 (s, 6 H, 2 $CH_3$), 1.20–3.20 (m, 16 H), 3.27 (s, 3 H, $OCH_3$); mass spectrum, $m/e$ (rel intensity) 199 ($M^+$, 3.0), 198 ($M^+ - 1$, 17.6), 168 ($M^+ - \cdot OCH_3$, 15.4), 142 (5.9), 126 (1.8), 84 ($C_5H_{10}N^+$, 100); high-resolution mass spectrum, $m/e$ 199.1935 ($C_{12}H_{25}NO$ requires 199.19360). The physical and spectroscopic properties of the isolated material were identical with those of the substance prepared by hydrogenation ($PtO_2$, $CH_3OH$, pH2, 55 psi) of 2-(4-methoxy-4-methylpentyl)pyridine (**75**), which was isolated from the photolysate of 2-(4-methyl-3-pentenyl)pyridinium perchlorate (**72**) (vide supra).

A dark control experiment using the same procedure followed in the photochemical reaction except without irradiation indicated that 2-(4-methoxy-4-methylpentyl)piperidine (**80**) is produced and that none of the other products form.

**Irradiation of 1-Methyl-2-(4-methyl-3-pentenyl)pyridinium Perchlorate (73).** A nitrogen-purged solution of 700 mg (2.57 mmol) of 1-methyl-2-(4-methyl-3-pentenyl)pyridinium perchlorate (**73**) in 200 mL of methanol was irradiated with Corex-filtered light for 2 h. The photolysate was subjected to the normal workup procedure to give a residue that was subjected to molecular distillation (100 °C, 0.05 torr), yielding 39.5 mg of oily residue shown to contain 3-methoxy-2,2-dimethylcyclopentanone (**76**) as the sole product by GLC analysis. Pure 2,2-dimethyl-3-methoxycyclopentanone (**76**) (27 mg, 7.4%) was obtained by preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 120 °C, 100 mL/min flow rate).

**Irradiation of 1-Methyl-2-(4-methyl-3-pentenyl)pyridinium Perchlorate (73) Followed by Hydrogenation.** A nitrogen-purged solution of 700 mg (2.57 mmol) of 1-methyl-2-(4-methyl-3-pentenyl)pyridinium perchlorate (**73**) in 200 mL of methanol was irradiated with Corex-filtered light for 2 h. The photolysate was immediately hydrogenated by using a Parr medium-pressure reaction bomb containing 200 mg of platinum oxide and shaking under a hydrogen atmosphere (55 psi) for 18 h. The solution was filtered and concentrated in vacuo to yield a residue that was stirred with 10 mL of saturated $NaHCO_3$ and extracted with chloroform. The $CHCl_3$ extracts were washed with water, dried, concentrated in vacuo, and subjected to molecular distillation (100 °C, 0.05 torr), giving 285 mg of a mixture of products. GLC analysis showed that the mixture contained 57.2 mg (18.1% based on conversion) of 2,2-dimethyl-3-methoxycyclopentanone (**76**), 46.9 mg (10.1%) of 1-methyl-2-(4-methylpentyl)piperidine (**86**), and 69.6 mg (14.8%) of 1-(*N*-butyl-*N*-methylamino)-2,2-dimethyl-3-methoxycyclopentane (**85**) as major products. The products were separated by preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 145 °C, 130 mL/min flow rate).

**1-Methyl-2-(4-methylpentyl)piperidine (86)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.95 (d, $J$ = 6 Hz, 6 H, 2 $CH_3$), 1.09–2.60 (m, 15 H), 2.24 (s, 3 H, $NCH_3$), 2.80–3.10 (m, 1 H, NCH, methine; $^{13}$C NMR ($CDCl_3$) $\delta$ 22.6 (q, $CH_3$), 22.8 (q, $CH_3$), 23.0 (t), 24.6 (t, C-4), 26.0 (t), 28.0 (d, C-4′), 30.9 (t), 33.3 (t, C-3), 39.6 (t, C-1′), 43.1 (q, $NCH_3$), 57.4 (t, C-6), 64.0 (d, C-2); mass spectrum, $m/e$ (rel intensity) 183, ($M^+$, 1.26), 182 ($M^+ - 1$, 1.48), 168 ($M^+ - \cdot CH_3$, 0.98), 98 ($C_6H_{12}N^+$, 100); high-resolution mass spectrum, $m/e$ 183.1977 ($C_{12}H_{25}N$ requires 183.19869). This material was independently synthesized by catalytic ($PtO_2$) hydrogenation of the pyridinium perchlorate (**73**), which provided a substance with identical physical and spectroscopic properties with those of the material obtained in the photoreaction.

**1-(Butylmethylamino)-2,2-dimethyl-3-methoxycyclopentane (86)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.83 (s, 3 H, $CH_3$), 0.90 (t, $J$ = 7 Hz, 3 H, $CH_3(CH_2)_3N$), 1.10 (s, 3 H, $CH_3$), 1.20–2.1 (m, 8 H), 2.24 (s, 3 H, $NCH_3$), 2.10–2.70 (m, 3 H), 3.13 (t, $J$ = 8 Hz, 1 H), 3.33 (s, 3 H, $OCH_3$); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.2 (q, $CH_3$), 14.9 (q, $CH_3$), 20.7 (t), 23.7 (t), 25.5 (t), 27.7 (q, $CH_3(CH_2)_3N$), 28.4 (t), 40.6 (q, $NCH_3$), 44.2 (s, C-2), 56.4

(t), 57.6 (q, $OCH_3$), 70.6 (C-1), 88.5 (C-3); mass spectrum, *m/e* (rel intensity) 213 ($M^+$, 24.2), 182 ($M^+ - -OCH_3$, 91.7), 170 ($M^+ - -C_3H_7$, 13.6) 168 (8.8), 126 (100), 114 (28.5), 98 (24.5); high-resolution mass spectrum, *m/e* 213.2086 ($C_{13}H_{27}NO$ requires 213.20925). This substance was prepared independently by methylation of **81** by using $CH_3I$ (1.2 equiv, $Et_2O$, reflux, 10 h). The synthetic and photochemically generated materials had identical physical and spectroscopic properties.

A dark control experiment was run in the following manner. A solution of 200 mg (0.73 mmol) of 1-methyl-2-(4-methyl-3-pentenyl)-pyridinium perchlorate (**73**) in 60 mL of $CH_3OH$ was stirred for 2 h and hydrogenated (60 mg of $PtO_2$, 55 psi, 12 h). The solution was worked up in the same manner as for the photochemical reaction except for the molecular distillation step. GLC analysis (5% OV 101, 10 ft × $^1/_8$ in., 150 °C, 20 mL/min flow rate) indicated the presence of the reduced starting material **86** and the complete absence of other substances arising in the irradiation experiment.

**2,2-Dimethyl-3-methoxycyclopentanone (76).** A solution of 200 mg (1.57 mmol) of 2,2-dimethyl-3-hydroxycyclopentanone (**82**) and 1.1 g (4.80 mmol) of $Ag_2O$ in 5 mL of $CH_3I$ containing 0.5 mL of DMF was heated at 55 °C for 3 h. The solution was diluted with 300 mL of ether, filtered, and washed with water. The ethereal solution was dried and concentrated in vacuo to yield 127 mg (57.1% yield) of keto ether **76**. All physical and spectroscopic properties of this substance were identical with those of the material generated photochemically.

**1-(Butylimino)-2,2-dimethyl-3-methoxycyclopentane (84).** A solution of 120 mg (0.85 mmol) of 2,2-dimethyl-3-methoxycyclopentanone (**76**) and 373 mg (2.55 mmol) of *n*-butylamine in 45 mL of benzene containing 60 mg of *p*-toluenesulfonic acid was stirred at reflux with water removal through a molecular sieve (4 Å) column for 40 h. The solution was diluted with ether and extracted with 0.15% aqueous $K_2CO_3$. The ethereal solution was washed with water, dried, and concentrated in vacuo to yield 153 mg (78%) of the imine (**84**). For spectroscopic analysis, a portion of this material was further purified by preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 135 °C, 120 mL/min flow rate) (36.7% yield): $^1H$ NMR ($CDCl_3$) $\delta$ 1.03 (s, 3 H, $CH_3$), 1.03 (t, 3 H, $CH_3(CH_2)_3N=$), 1.11 (s, 3 H, $CH_3$), 1.2-2.55 (m, 8 H), 3.15-3.55 (m, 3 H), 3.40 (s, 3 H, $OCH_3$); IR (neat) 1680 (C=N stretching), 1460, 1379, 1359, 1270, 1205, 1120, 1100, 990, 947 $cm^{-1}$; mass spectrum, *m/e* (rel intensity) 197 ($M^+$, 18), 182 ($M^+ - -CH_3$, 19), 166 ($M^+ - -OCH_3$, 28), 154 ($M^+ - -C_3H_7$, 23), 124 (30), 110 (68), 73 (90), 69 (100); high-resolution mass spectrum, *m/e* 197.1767 ($C_{12}H_{23}NO$ requires 197.1781).

**1-(Butylamino)-2,2-dimethyl-3-methoxycyclopentane (81).** To a solution of 100 mg (0.51 mmol) of 1-(1-butylimino)-2,2-dimethyl-3-methoxycyclopentane in 4 mL of 1:1 methanol-THF was added 100 mg of $NaBH_4$. The resulting mixture was stirred for 30 min. The solution was concentrated in vacuo to yield a residue that was diluted with chloroform. The chloroform solution was washed with water, dried, and concentrated in vacuo to yield 95 mg (94%) of 1-(*N*-butylamino)-2,2-dimethyl-3-methoxycyclopentane. This material possesses physical and spectroscopic properties identical with those of the substance produced photochemically.

**Effect of Acid on the Yield of 3-Methoxy-2,2-dimethylcyclopentanone (76) and 1-(Butylmethylamino)-2,2-dimethyl-3-methoxycyclopentane (85).** Solutions of 200 mg (0.73 mmol) of 1-methyl-2-(4-methyl-3-pentenyl)pyridinium perchlorate (**73**) in 125 mL of methanol containing 0.0, $1 \times 10^{-4}$, and $1 \times 10^{-2}$ M $HClO_4$ were irradiated with Corex-filtered light for 30 min. The crude photolysate derived by irradiation in methanol with no acid was acidified to ca. pH 2 with concentrated perchloric acid. The crude photolysates were then transferred to Parr medium-pressure reaction bombs and shaken under hydrogen atmospheres (55 psi) for 18 h. The solutions were filtered and concentrated in vacuo, yielding residues that were stirred with 70 mL of chloroform, 10 mL of saturated sodium bicarbonate, and 20 mL of water. The chloroform layers were separated, and the water layers were extracted again with 10 mL of chloroform. Each of the combined chloroform layers were washed with water, dried, and concentrated in vacuo to ca. 5 mL. To each of the concentrated solutions was added the biphenyl standard. GLC analysis (5% OV 101, 10 ft × $^1/_8$ in., 135 °C, 20 mL/min flow rate) give the relative yields of 2,2-dimethyl-3-methoxycyclopentanone (**76**) and 1-(butylmethylamino)-2,2-dimethyl-3-methoxycyclopentane (**85**) as follows: no acid, 1.0:1.0; $1 \times 10^{-4}$ M $HClO_4$, 2.2:1.2; $1 \times 10^{-2}$ M $HClO_4$, 2.9:1.3.

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# Photochemical Transformations. 32. Stereochemical Course and Stereochemical Requirement for Activation of Photosolvolysis and Photorearrangements in a Chlorobenzobicyclo[2.2.2]octadienyl System[1,2]

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**Abstract:** The epimers 6-*anti*- and 6-*syn*-7-dichloro-2,3-benzobicyclo[2.2.2]octa-2,5-diene (**7**-Cl and **8**-Cl) have been subjected to irradiation in wet acetonitrile at 254 nm. The epimer **7**-Cl with chlorine anti to the benzene ring chromophore is photoactive, giving photo-Wagner-Meerwein isomerization and photosolvolysis to Wagner-Meerwein rearranged acetamides. Both the isomerization and the solvolysis (photo-Ritter reaction) are nonstereospecific, although migration of the syn chloroethenyl group occurs in modest preference to that of the anti benzo group. The syn chloride **8**-Cl is relatively photoinert, and no products attributable to photosolvolysis or photo-Wagner-Meerwein isomerization are produced.

A recent communication[3a] from this laboratory described the direct irradiation in acetonitrile or in acetic acid of some 7-chloro derivatives of dibenzobicyclo[2.2.2]octadienes (**1**) and of 6-chloro and 6-methanesulfonoxy derivatives of 7-chloro-3,4-benzotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**2** and **3**). These are all homobenzyl systems; that is, they have nucleofugal groups $\beta$ to aromatic rings.

(1) Paper 31: Cristol, S. J.; Graf, G. A. *J. Org. Chem.* **1982**, *47*, 5186.
(2) A portion of this work was described at the Spring 1981 meeting of the American Chemical Society in Atlanta, Georgia, and at the Tenth International Conference on Photochemistry in Iraklion, Crete, Greece, in September 1981.

(3) (a) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977. (b) Morrison, H.; Miller, A. *Ibid.* **1980**, *102*, 372.

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