Electron-Transfer Photochemistry of Iminium Salts. Olefin Photoadditions to 2-Phenyl-1-pyrrolinium Perchlorate

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Received October 10, 1980

Abstract: The photoaddition reactions of 2-phenyl-1-pyrrolinium perchlorate (**2**) and a variety of olefins have been investigated. Irradiation of methanolic solutions of **2** in the presence of the electron-rich olefins isobutylene, cyclohexene, butadiene, isopropenylcyclopropane, and methyl β,β-dimethylacrylate leads to formation of two types of addition products. One of these results from anti-Markovnikov addition of the components of methanol and the pyrrolinium salt across the olefinic π bond, generating a carbon–carbon bond to the pyrrolidine 2-position. The other corresponds to addition of the 2-phenylpyrrolidine unit across allylic C–H bonds of the olefins. Both reactions are explained by using electron-transfer mechanisms. Support for these mechanisms, which rationalize the nature of the reactions, their regiochemistry, and their stereochemistry, has come from studies with the electron-poor olefins methyl acrylate, acrylonitrile, and methyl methacrylate. Irradiation of **2** in the presence of these olefins leads to generation of 9-substituted 1-aza-6,7-benzospiro[4.4]non-6-ene products, results of [2 + 2] cycloadditions of the olefins to the C-1,C-2 π bond of the pyrrolinium salt phenyl ring. Fluorescence quenching studies have been conducted to gain further evidence in support of the mechanistic postulates.

Introduction

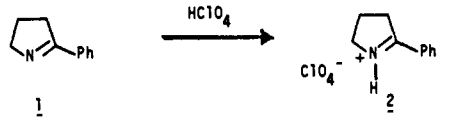
The photochemistry of organic substances containing carbonyl and olefinic chromophores has been the subject of intensive investigations over the years since studies in this area were initiated. Much of excited-state chemistry theory is based upon the interesting reactivity patterns displayed by systems containing these groupings. In contrast, exploratory and mechanistic investigations of the excited-state properties and chemical reactivity of imines and related substances containing the $RN{=}CR_2$ group have only more recently become the targets of detailed photochemical research efforts.[2] Despite this recent emphasis, the literature contains but a few summaries of work probing the photochemistry of systems containing the potentially related iminium salt function, $R_2N^+{=}CR_2$.[2c] Our survey has uncovered only a handful of isolated examples of studies of nonheteroaromatic iminium salts. These are restricted to additions of alcohols[3] and stilbene-like photocyclizations.[4] As a result of this apparent void in knowledge and our expectation that the excited-state reactivity of this chromophore might hold mechanistic, synthetic,[5] and biochemical[6] interest, we initiated an exploratory study in this area of organic photochemistry.

A brief and simplified look at the electronic characteristics of the iminium salt chromophore is instructive since it serves as a foundation for predictions about the potential chemical reactivity of the excited states of these systems. Iminium salts are isoelectronic with olefins and thus have only π–π^* excited states available for population. Yet, unlike olefins, the π bond in both their ground and π–π^* excited states should be polarized due to the electronegativity difference between nitrogen and carbon. Furthermore, since iminium salts are merely stabilized carbenium ions, both the ground and excited species should be electron deficient and, as a result, easily reduced in one-electron-transfer processes. These characteristics are summarized in Figure 1 in terms of comparable eigenfunctions and eigenvalues of olefinic, imine, and iminium salt chromophores calculated[7] for the parent systems. On the basis of this information, it might be expected that the reactive modes of iminium salt excited-state decay would resemble those of olefins (*EZ* isomerization[8] and [2 + 2] cycloaddition) and might include additional pathways resulting from electron transfer to the $R_2N^+{=}CR_2$ π–π^* excited state.[9]

Our preliminary investigations in this area have focused on the photochemistry of iminium salt–olefin systems. In this and the following paper we describe results of these efforts which demonstrate that electron-rich olefins undergo photoaddition to 2-phenyl-1-pyrrolinium perchlorate by pathways which involve electron transfer, that intramolecular versions of this process serve as useful methods for preparation of nitrogen heterocycles, and that 2-phenyl-1-pyrrolinium perchlorate and electron-poor olefins participate in [2 + 2] cycloadditions generating interesting 1-azaspiro[4.4]nonene systems.[10]

Results

Photoadditions of Electron-Rich Olefins to 2-Phenyl-1-pyrrolinium Perchlorate. Exploratory studies were conducted with the use of 2-phenyl-1-pyrrolinium perchlorate (**2**) as a model iminium salt. A number of factors contributed to this choice, including the high stability of **2**, its efficient fluorescence, and its constrained structure which prevents potential energy-wasting *EZ* and cis–trans isomerizations. Additionally, this iminium salt can be easily prepared in crystalline form (mp 116–117 °C) by the addition of 1 equiv of perchloric acid to 2-phenyl-1-pyrroline (**1**).[11]



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(1) To whom correspondence should be addressed at the University of Maryland.

(2) (a) Padwa, A. *Chem. Rev.* **1977**, *77*, 17. (b) Pratt, A. C. *Chem. Soc. Rev.* **1977**, *6*, 63. (c) Buchardt, O. "Photochemistry of Heterocyclic Compounds"; Wiley: New York, 1976.

(3) For example: (a) Cerutti, P.; Schmid, H. *Helv. Chim. Acta* **1964**, *47*, 203; Goth, H.; Cerruti, P.; Schmid, H. *Ibid.* **1967**, *50*, 1759; (b) Gault, R.; Meyers, A. I. *J. Chem. Soc., Chem. Commun.* **1971**, 778.

(4) Mallory, F. B.; Wood, C. S. *Tetrahedron Lett.* **1965**, 2643.

(5) Stavinoha, J. S.; Mariano, P. S.; Leone-Bay, A.; Swanson, R.; Bracken, C.; *J. Am. Chem. Soc.*, following paper in this issue.

(6) (a) The photochemistry of iminium salts could find its ultimate significance in relationship to the visual process which most probably involves photoisomerization of the protonated imine rhodopsin.[6b,c] (b) Reviews of this topic can be found in the following: *Acc. Chem. Res.* **1975**, *8*, 81–112. (c) Honig, B.; Dinur, U.; Nakanishi, K.; Balogh-Nair, V.; Gaivinowicz, M. A.; Arnaboldi, M.; Motto, M. G. *J. Am. Chem. Soc.* **1979**, *101*, 7084; Sheves, M.; Nakanishi, K.; Honig, B. *Ibid.* **1979**, *101*, 7086.

(7) Bohme, H.; Viehe, H. G. "Iminium Salts in Organic Chemistry"; Wiley: New York, **1976**.

(8) Dickie, B. D.; Childs, R. F.; "Abstracts of Papers", 63rd Canadian Chemical Conference, The Chemical Institute of Canada, Ottawa, Canada, 1980; OR-91.

(9) (a) Electron-transfer mechanisms have been invoked in the photochemistry of azaromatic systems.[9b-d] (b) Castellano, A.; Catteau, J. P.; La Blanche-Combier, A. *Tetrahedron* **1975**, *31*, 2255. (c) McCall, M. T.; Whitten, D. G. *J. Am. Chem. Soc.* **1969**, *91*, 5681. (d) Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1971**, 964; Hopkins, A. S.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, *2*, 80.

(10) Preliminary reports of these results have appeared in: Mariano, P. S.; Stavinoha, J. L.; Swanson, R. *J. Am. Chem. Soc.* **1977**, *99*, 6781; Mariano, P. S.; Stavinoha, J. L.; Pepe, G.; Meyer, E. F. *Ibid.* **1978**, *100*, 7714.

(11) Starr, D. F.; Bulbrook, H.; Hixon, *J. Am. Chem. Soc.* **1932**, *54*, 3971. Love, S. J.; Moore, J. A. *J. Org. Chem.* **1968**, *33*, 2361.

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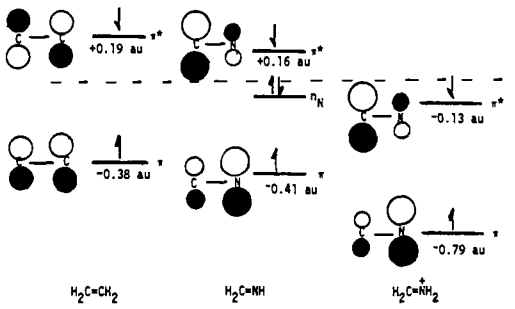
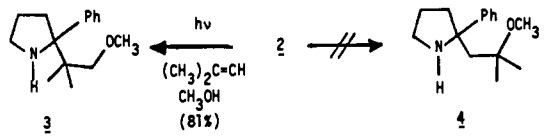


Figure 1. Eigenfunctions and eigenvalues for simple olefin, imine, and iminium salt chromophores.[7]

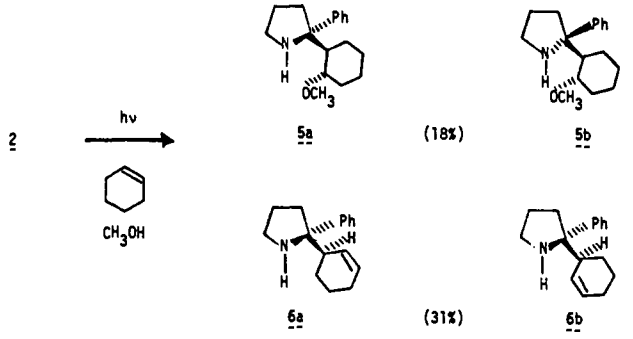
Alternatively, **2** is generated in situ prior to irradiation by the addition of 1.34 equiv of perchloric acid to a solution of **1** in either methanol or acetonitrile. Protonation of **1** in methanol is accompanied by a reversible (by addition of base) decrease in the UV absorption at 243 nm and an increase at 264 nm (ϵ 15 600). Solutions of **2** prepared in this way are stable for extended time periods.

Isobutylene. Irradiation of methanolic solutions of **2** (14 mM) containing isobutylene (0.8 M; −20 °C, Corex) followed by basic workup and molecular distillation gave an adduct (**3**, 81%) of

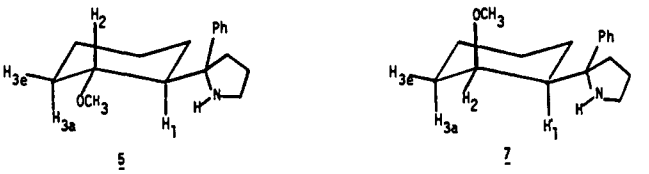


molecular composition $C_{15}H_{23}NO$, corresponding to a product incorporating the olefin, methoxy, and 2-phenylpyrrolidinyl units. Structure assignment to this photoaddition product is made on the basis of characteristic spectroscopic data. The ^1H NMR spectrum of **3** indicates the presence of diastereotopic methyl groups (δ 0.85 and 0.87) and methylene hydrogens (δ 2.86 and 3.00, J = 9 Hz). The base peak in the mass spectrum of **3** occurs at m/e 146 and is indicative of a charged 2-phenylpyrrolidin-2-yl cation arising by a fragmentation route expected to be highly efficient for 2-phenyl-2-alkylpyrrolidines.[12] Importantly, the ^{13}C NMR data accumulated for **3** support its structure assignment as the 2′-methoxy-1′-methyl-propylpyrrolidine **3** and provide firm evidence to rule out other structures such as **4** with the regioisomeric side chain. Accordingly the resonances at 80.8 (t) and 40.3 ppm (s) are characteristic for the side-chain composition of $(CH_3)_2CCH_2OCH_3$.

Cyclohexene. Similar types of photoaddition reactions occur when 2-phenyl-1-pyrrolinium perchlorate is irradiated in methanolic solutions containing a variety of electron-rich olefins. For example, a separable mixture of two diastereomeric (methoxycyclohexyl)pyrrolidines **5** (ca. 1:1) are obtained from irradiation

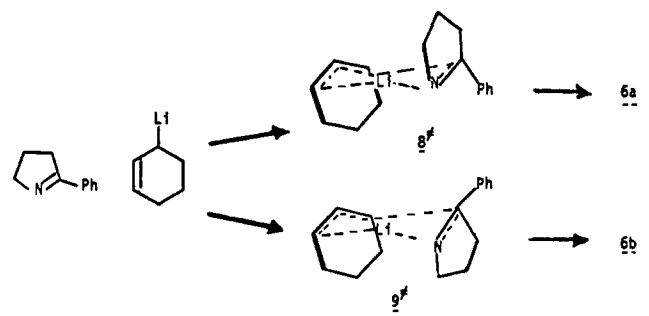


of **2** in methanol (25 °C, Corex) containing cyclohexene (0.74 M) followed by basic workup and silica gel TLC. The structure assignments to both diastereomers of **5** are made on the basis of an analysis of spectroscopic data and comparisons to those obtained for related compounds in the series. The presence of the 2-phenylpyrrolidine and 2-methoxy-2-substituted cyclohexane moieties in the stereoisomeric ethers are characterized by the mass spectrum base peak at m/e 146 and ^{13}C NMR resonances at 52.8 and 53.4 ppm (doublets) and at 81.3 and 81.8 ppm (doublets). The cyclohexane ring stereochemistry in both diastereomers of **5** is difficult to determine with a great degree of certainty in the absence of X-ray data. However, the 220-MHz ^1H NMR spectra of both epimers contain multiplets (δ 2.94 and 2.90) with chemical shifts expected for the methine protons at the methoxy-substituted cyclohexane ring carbon. The conformation of the cyclohexane ring in each epimer should be a chair with the large phenylpyrrolidine group equatorial. The relative chirality at C-1 and C-2 of the cyclohexane ring can then be elucidated since the protons at C-2 will be either axial in the trans isomers **5** or equatorial in the cis isomers **7**. The multiplet for H-2 in the



chromatographically slower moving stereoisomer (R_f 0.10) can be disected into a doublet of triplets with coupling constants ($J_{2,1} = J_{2,3a}$ = 9.5 Hz; $J_{2,3e}$ = 4.9 Hz) in the range expected ($J_{aa} \approx$ 8–13 Hz; J_{ae} − 2–6 Hz) for a proton oriented axially. Additionally, the width of the multiplet at half-height (W_H) is ca. 24 Hz, highly characteristic of an axial proton coupled to two adjacent axial hydrogens.[13] The H-2 resonance in the faster moving diastereomer (R_f 0.26) is not well resolved and, thus, does not yield coupling constant data. However, the value of 28 Hz for W_H is indicative of an axial proton at C-2. It appears that both stereoisomers of the (methoxycyclohexyl)pyrrolidines **5** have the methoxy and pyrrolidyl groups trans disposed and, therefore, that they are epimers differing in the chirality at the pyrrolidine α-carbon.

The major products (31%) generated by irradiation of **2** in the presence of cyclohexene are the separable (1:1, R_f 0.39 and 0.47) isomeric 3-cyclohexenylpyrrolidines **6**. Although the structures of these materials and their stereoisomeric relationship could be clearly elucidated by use of spectroscopic data, unambiguous assignment was made through independent synthesis. This was achieved by the addition of cyclohexen-3-yllithium[14] to 2-phenyl-1-pyrroline[15] which yielded an adduct identical with only one (**6a**, R_f 0.39) of the two epimers produced photochemically. The formation of a single stereoisomer in the alkyllithium reaction is interesting and possibly rationalized by use of transition-state arguments. In transition state **8**‡, nonbonded interactions are



minimized, and maximum stabilization of the incipient negative

(12) McLafferty, F. W. "Interpretation of Mass Spectra;" W. A. Benjamin: New York, 1967; pp 99–149.

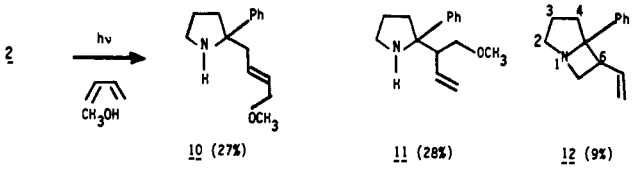
(13) Lemieux, R. U.; Kullnig, R. K.; Bernstein, H. J.; Schneider, W. G. *J. Am. Chem. Soc.* **1958**, *80*, 6098.

(14) The cyclohexenyl anion was prepared by using the method of: Crawford, R. J.; Erman, W. F.; Broaddus, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 4298.

(15) This reaction proceeded in low yield (8%) most probably due to competitive proton abstraction from the 3-position of the pyrroline. Indeed, the pyrroline was recovered from this reaction in a 66% yield.

charge on nitrogen occurs through simultaneous complexation of the lithium cation by the heteroatom and alkyl anion fragment.[16] Reaction via $8^{\ddagger}$ would produce the *R,S* and *S,R* enantiomeric pair **6a**. A head to head approach of reactants via $9^{\ddagger}$ seems more energetic due to an increased degree of steric repulsion. Thus, if this reasoning is correct, the stereochemistry of the cyclohexenylpyrrolidine photoadducts can be assigned as follows: *RS/SR* to the epimer at R_f 0.39 (**6a**) and *SS/RR* to the epimer at R_f 0.47 (**6b**).

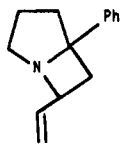
Butadiene. Three photoproducts, the methoxybutenyl ether **10** (27%), (methoxymethyl)propenyl ethers **11** (28%, 1:1 mixture of diastereomers), and the vinyl-azabicycloheptane **12** (9%), were



formed by irradiation of a methanolic solution of **2** and butadiene (0.85 M, −20 °C, Corex). Isolation and purification of these materials was accomplished after basic workup of the crude photolysate by molecular distillation and silica gel TLC. The ether **10** (R_f 0.18) and one epimer of **11** (R_f 0.31) were obtained in pure form by this procedure. However, preparative GLC of the band at R_f 0.45 was required in order to separate the second diastereomer of **11** and azetidine **12**.

Structure assignments to **11**, products arising from formal anti-Markovnikov 1,2-addition of methanol and pyrrolinium salt to butadiene, were made simple by the first-order nature of their ^{1}H NMR spectra which revealed the presence of methoxy, vinyl, phenyl, and 2,2-disubstituted pyrrolidinyl moieties. Data from the ^{13}C NMR spectra, especially the doublets at 53.7 and 52.9 ppm and triplets at 74.0 and 73.6 ppm for the respective fast and slow moving isomers, lend support for the regiochemistry represented in **11** in which methoxy is located at the butenyl methylene carbon.

Elucidation of the structure of **10**, resulting from formal 1,4-addition, was accomplished by using similar methods. The disubstituted olefin stereochemistry is assigned as trans from IR spectroscopic data. A strong band is present at 980 cm^{-1} while no bands appear in the 730–665-cm^{-1} range except for those due to the aromatic ring (755 and 670 cm^{-1}). A molecular formula of $C_{14}H_{17}N$, resonances in the ^{1}H NMR spectrum corresponding to protons of the vinyl group, and the absence of a strong peak at *m/e* 146 in the mass spectrum combine to suggest that the minor photoproduct **12**, obtained from irradiation of **2** in the presence of butadiene, does not possess a structure similar to that of products observed to this point. The resonances in the ^{13}C NMR spectrum at 56.2 (t) and 54.8 ppm (t) are suggestive of a structure which contains two N–CH_2 groups and are assigned to the C-2 and C-7 carbons of **12**, while the resonance at 46.8 ppm (d) is due to C-6. The chemical shifts for the C-2, C-7, C-6, and C-4 (41.1 ppm) signals are in fact very close to those predicted by using empirical relationships.[17] The alternative regiochemistry found in **13** is less probable since carbon NMR assignments would be much less satisfactory. It should be pointed out that the data gathered thus far is not sufficient to allow a determination of the C-6 stereochemistry of **12**.



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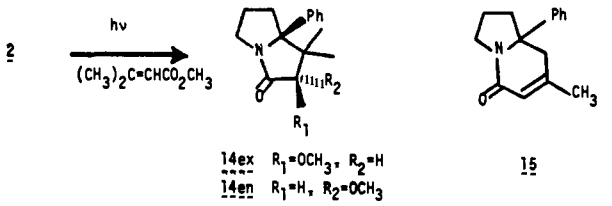
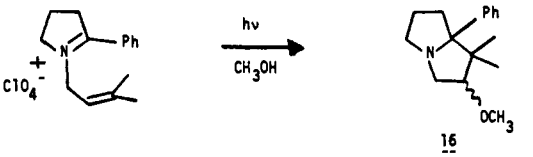
(16) (a) Transition states similar to $8^{\ddagger}$ have been used by Heathcock[16b] to rationalize preferred stereochemistry in the addition of lithium enolates to aldehydes. (b) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Larupe, J. *J. Org. Chem.* **1980**, *45*, 1066.

(17) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: New York, 1976; pp 36–48.

Methyl β,β-Dimethylacrylate. Substances containing bicyclic lactam ring systems are generated by photoaddition of methyl β,β-dimethylacrylate to **2**. Accordingly, irradiation of **2** in methanol solution containing this olefinic ester gave after workup and chromatographic purification a separable mixture (1:1) of the epimeric pyrrolizidinones **14** and the indolizidinone **15**.



Spectroscopic data for each of the stereoisomers of **14** are consistent with the assigned γ-lactam structures (IR 1695 cm^{-1}; ^{13}C NMR 172.7 and 175.2 ppm), containing nonequivalent methyls (^{1}H NMR δ 0.81 and 0.59, and 1.05 and 1.24), one of which is located in a strong shielding region of the phenyl group, and methoxy-substituted methine carbons (doublets at 86.8 and 89.3 ppm). The stereochemistry at C-3 is elucidated by use of base-catalyzed epimerization ($NaOCH_3$, CH_3OH) which yielded a 5.9:1 ratio of isomers on starting with either one. Inspection of CPK models indicates that the *endo*-methoxy stereoisomer **14en** should be the thermodynamically more stable since it avoids severe steric interactions with the *exo*-methyl and angular phenyl moieties. The structures of the bicyclic lactams were further revealed by chemical correlation with the pyrrolizidines **16**, prepared independently[5]



by photocyclization of 1-isopentenyl-2-phenyl-1-pyrrolinium perchlorate in methanol. The chemical and physical properties of materials produced in this way were identical with those determined for the product formed upon treatment of **14** with lithium aluminum hydride.

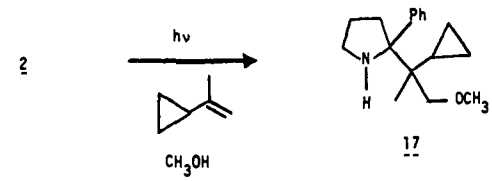
The minor product from irradiation of **2** in methanol solution containing methyl β,β-dimethylacrylate is the indolizidinene **15**. Characteristic spectroscopic data aided this assignment. For example, the proton NMR spectrum indicates that allylic methyl (δ 1.66) and methylene (δ 2.75) groups, both being long-range coupled (J = 0.5 Hz) to the vinyl proton (δ 5.72), are present. The strong IR band at 1660 cm^{-1} is fully consistent with a conjugated δ-lactam chromophore.

Isopropenylcyclopropane. Thus far in our exploratory studies of iminium salt–olefin photoaddition processes, we have used simple olefins in order to gain information about the overall nature of the processes occurring and their regiochemical and stereochemical outcomes. We have extended this study to include an electron-rich olefin with properties potentially capable of reflecting the identity and lifetimes of intermediates in mechanistic pathways followed. Accordingly, 2-phenyl-1-pyrrolinium perchlorate was irradiated in a methanolic solution of isopropenylcyclopropane (25 °C, Corex). Reaction occurred to afford an inseparable mixture (1:1) of the diastereomeric (1-cyclopropylethyl)-pyrrolidines **17** in an isolated yield of 50%. The presence of the

18 19

cyclopropyl group in **17** is evidenced by IR absorption bands at 3080 and 1020 cm^{-1}, ^{1}H NMR resonances in the region δ 0.08–0.40, and a ^{13}C NMR spectrtum which contains sets of

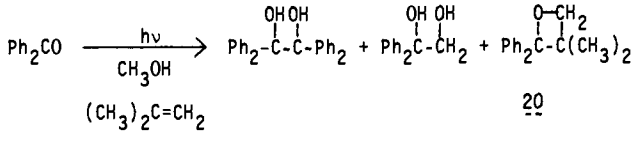
triplets for the diastereotopic methylene carbons at 2.3 and 1.3 ppm and at 1.8 and 0.1 ppm. Furthermore, the key carbon resonances at 80.1 (t) and 41.9 ppm (s) establish that side-chain structure in the photoadduct is that found in **17** and not that in the corresponding (2-cyclopropylethyl)- or pentenylpyrrolidines **18** and **19**, respectively.



State and Multiplicity Studies. Dark control experiments, in which all pyrrolinium salt–olefin systems were subjected to a variety of potential reaction conditions in the absence of light, demonstrated that the processes described above result from the excited state of 2-phenyl-1-pyrrolinium perchlorate. In all of these cases, **2** was recovered quantitatively, attesting to the stability of this material in methanolic solutions containing olefin.

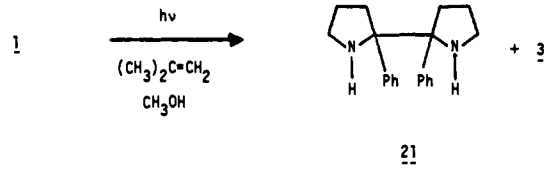
In an attempt to gain information about the multiplicity of the excited state of **2** responsible for the observed photoaddition reactions, experiments were conducted with benzophenone as a triplet sensitizer and irradiation conditions (uranium-glass filter) which guaranteed selective light absorption by the ketone. Triplet-sensitized reactions of **2** run in the presence of isobutylene did not produce detectable quantities of the photoaddition product **3**.

Benzpinacol and benzophenone–methanol mixed pinacol formation were quenched when methanolic solutions of benzophenone containing **2** were irradiated. Likewise, the oxetane **20** producing reaction between benzophenone triplet and isobutylene[18] is 26%



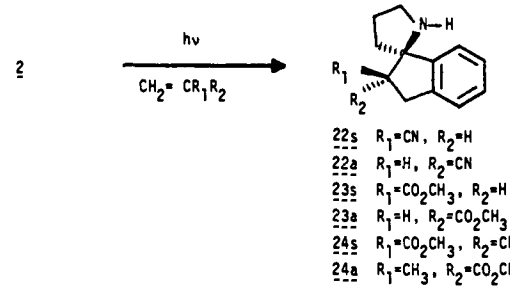
less efficient and the disappearance of benzophenone 25% less efficient when irradiations are conducted in the presence of **2**. Finally, only 47% of the pyrroline **1** is recovered, and none of the photoadduct **3** is detected after basic workup of the photolysates obtained from benzophenone-sensitized runs.

The photochemistry of the neutral 2-phenyl-1-pyrroline (**1**) was explored briefly. Irradiations of **1** in methanol, containing potassium carbonate and isobutylene, through a Vycor filter for time periods exceeding those used in experiments with the perchlorate salt caused inefficient reaction. The starting material was recovered in large quantities (53%). ^{1}H NMR analysis of the crude photolysate after removal of unreacted **1** indicated that small quantities of the 2-phenyl-1-pyrroline dimer **21** (18%) and the photoaddition product **3** (10%) had been generated. Photodimerization of **1** yielding **21** has been reported previously by



Hornback.[19] The small quantity of **3** obtained under these conditions may result from photoaddition of isobutylene to the neutral imine. However, a more reasonable rationalization is that the pyrrolinium cation **2** is generated in its excited state by proton transfer from methanol to **1**[51] under these reaction conditions. Excited-state proton transfer such as this has been invoked to explain phenomena observed in pyridine photochemistry where the excited state K_b is found to be ca. 10^5–10^6 times larger than that for its ground state.[20]

Photoadditions of Electron-Poor Olefins to 2-Phenyl-1-pyrrolinium Perchlorate. In order to investigate the effect of substituents on the nature and efficiency of the olefin-iminium salt photoaddition processes, we explored the photochemistry of 2-phenyl-1-pyrrolinium perchlorate and electron-deficient olefins. Interestingly, no pyrrolidine ether or olefinic products analogous to those described above are produced when methanolic solutions of **2** containing acrylonitrile, methyl acrylate, or methyl methacrylate are irradiated. Instead, products arising from remarkably different reaction pathways are produced in reasonably high yield. For example, a separable mixture (1.5:1) of the epimeric benzospirocyclic amino nitriles **22s** and **22a** are isolated after basic workup and molecular distillation of the photolysate obtained from irradiation of **2** (14 mM) in either acetonitrile or methanolic



acrylonitrile (1.2 M) solutions. The yield of this process is slightly higher in acetonitrile (44%) than in methanol (37%). Similar results are obtained when **2** is irradiated in methyl acrylate containing solutions. The spirocyclic amino esters **23s** and **23a** are produced in nearly equal quantities in an overall yield that is invariant (50–52%) with the solvent (methanol or acetonitrile) used. Finally, a separable mixture of the epimeric amines **24** are formed (54% in methanol, 47% in acetonitrile) when methyl methacrylate is used as the olefinic addend.

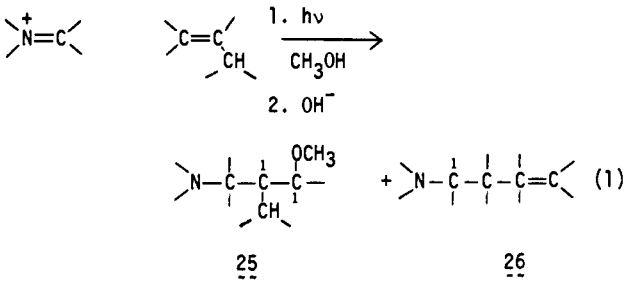
Structural and stereochemical assignments to the nitriles **22** and esters **23** were made on the basis of characteristic spectroscopic data and with the use of equilibration and interconversion reactions which served to relate these substances to the anti nitrile epimer **22a**. Treatment of either **22s** or **22a** with sodium methoxide in methanol resulted in formation of a mixture of the two substances. In addition, the selective transformations of **22s** to **23s** and **22a** to **23a** by use of methanolic sulfuric acid interrelates the stereochemical counterparts in the ester and nitrile series. Finally, single-crystal X-ray diffraction data[21] accumulated for the ammonium perchlorate derivative of **22a** yields unambiguous structural and stereochemical characterizations of the isomeric esters and nitriles. The very close correspondence of the spectroscopic data for the *C*-methyl spirocyclic amines **24** with that of their ester and nitrile counterparts is consistent with the assignment of the benzospirocyclic amine structures to these materials.

Photoaddition Quantum Yields. Quantum efficiencies for selected photoadditions of olefins to 2-phenyl-1-pyrrolinium perchlorate (**2**) were measured at low conversion (e.g., 1–4%) with the use of an optical bench apparatus described in the Experimental Section. The data are collected in Table I.

Discussion

General Features. The observations outlined above demonstrate that 2-phenyl-1-pyrrolinium perchlorate undergoes efficient photoaddition to a series of electron-rich olefins when irradiated in methanol. These reactions, summarized in eq 1, lead to production of both amino ether and olefin adducts having general

(18) Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum Press: New York, 1976; p 182.
(19) Hornback, J. M.; Proehl, G. S.; Starner, I. J. *J. Org. Chem.* **1975**, *40*, 1077.
(20) Van Bergen, T. J.; Kellog, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8451.
(21) Meyers, E.; Pepe, G.; Stavinoha, J. L.; Mariano, P. S. *Cryst. Struct. Commun.* **1981**, in press.



structures represented by **25** and **26**. A number of results have stimulated thought about the mechanistic details of these novel processes. These include the regiochemistry for ether adduct formation, the stereochemical course of cyclohexene photoadditions, and the dependence of the reaction course on the nature of the olefin. Several mechanisms which are consistent with some but not all of the observations made require brief discussion. For example, sequences involving ionic additions of olefins to a twisted singlet excited state of the iminium salt with diminished delocalization of the positive charge would be attractive in rationalizing the reactivity of olefin-nitrogen-stabilized carbenium ion system. However, routes of this type are inconsistent with the regiochemistry for isobutylene, isopropenylcyclopropene, and methyl β,β-dimethylacrylate additions. Likewise, stepwise free radical mechanisms involving addition of photogenerated methoxy radicals ($CH_3O\cdot$) to olefin followed by alkyl radical coupling to the iminium salt carbon would find precedent in studies by Ledwith[22] in which methoxy radicals were indirectly identified as secondary products from irradiations of methanolic solutions of pyridinium salts. Analogous processes could be operative in methanol–pyrrolinium salt systems. Importantly, the radical addition route is expected to display regiochemical results which are equivalent with those observed.[23] Mechanisms of this type require the interaction of methanol with pyrrolinium salt singlet excited states in the initial step following excitation. The rate constant for quenching of pyrrolinium fluorescence by electron-rich olefins such as cyclohexene is close to the diffusion-controlled limit. On the other hand, fluorescence quenching by methanol is approximately 2 orders of magnitude slower.[24]

Another mechanism more difficult to dismiss on the basis of the experimental findings involves [$_\pi$2 + $_\pi$2] photocycloaddition of olefins across the C=N π bond of the pyrrolinium perchlorate, resulting in production of intermediate azetidinium cations **27** in bicyclo[3.2.0]heptane frameworks. Indeed, cycloadditions of olefins to the neutral imine grouping have been observed in *N*-acyl imine,[25] azapyrimidine,[26] benzonitrile,[27] and conjugated imine[28] systems. Collapse of the intermediate azonium ions **27** by heterolytic cleavage of the external CN bond followed by or in concert with nucleophilic addition of methanol (required to be rapid if carbenium ion **30** is an intermediate) would generate the β-amino ether adducts **28** (Scheme I). Similarly, deprotonation of **30** or E_2 elimination directly from the bicyclic azetidinium salt **27** could give rise to the amino olefin photoproducts. The cycloaddition pathways possess additional attractiveness since they are useful in analyzing the observed regiochemistry. Specifically, consideration of both the HOMO–HOMO′ and LUMO–LUMO′ orbital interactions (Figure 2) leads to the predictions that cycloadditions of these olefins to the CN bond of 2^{S1} should yield the bicyclic intermediates **27** rather than the regioisomeric **28** through bonding

Table I. Quantum Yields for Photoaddition of Olefins to 2-Phenyl-1-pyrrolinium Perchlorate (2)

olefin[a]	solvent	product (ϕ of formation)
cyclohexene	CH_3OH	6[b] (0.020)
		5[b] (0.012)
$(CH_3)_2C{=}CHCO_2CH_3$	CH_3OH	15 (0.003)
		16[b] (0.008)
$CH_2{=}CHCN$	CH_3OH	22[b] (0.007)
	CH_3CN	22[b] (0.021)
$CH_2{=}C(CH_3)CO_2CH_3$	CH_3OH	24[b] (0.007)
	CH_3CN	24[b] (0.029)

[a] Olefin concentrations were 1.0 M and iminium salt concentration was 6.9×10^{-3} M. [b] Quantum yields for total of mixture of diastereomers.

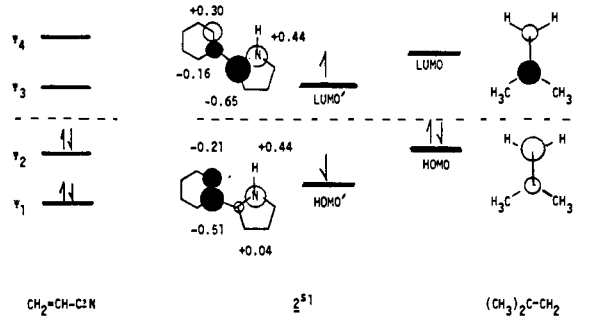
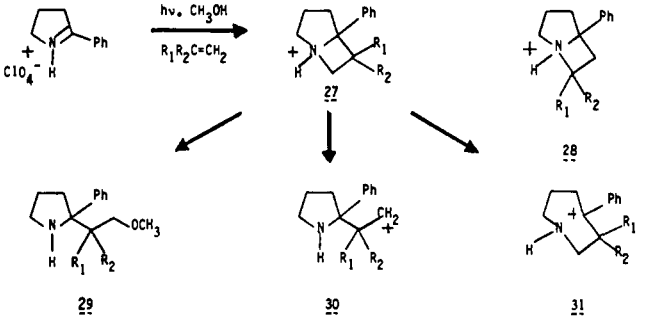


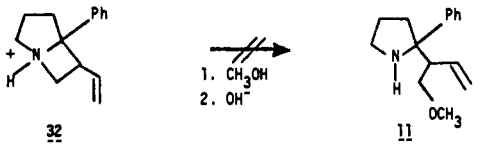
Figure 2. Frontier molecular orbitals for olefin and pyrrolinium salt systems undergoing cycloaddition.

Scheme I



of the most substituted olefinic carbon to C-2 of the pyrroline ring. Koch[25] has found that additions of isobutylene and other electron-rich olefins to 3-ethoxyisoindolone follow regiochemical courses which are consistent with these predictions.[30]

The azetidinium salts which would be produced as intermediates in the [$_\pi$2 + $_\pi$2] cycloaddition mechanisms are expected to display greatly different patterns of chemical reactivity than those required to rationalize production of the observed amino ethers and amino olefins. First, protonated 1-azabicyclo[3.2.0]heptanes such as **27** should be resistant to thermally activated ring-opening reactions in methanol at room temperature.[29a] Indeed, the salt **32**, derived by protonation of the vinylazetidine **12** is stable indefinitely in refluxing methanol solution and, thus, cannot be the precursor of the adduct **11** obtained by irradiation of **2** in the presence of butadiene. Second ring-opening reactions of bicyclic azetidines



(22) Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *Proc. R. Soc. London, Ser. A* **1973**, *332*, 151.
(23) Photocyclization of *N*-allyliminium salts,[5] an analogous process, occurs in water. No possibility for electron-transfer generation of hydroxyl radicals exists under these conditions.
(24) Stavinoha, J. L.; Mariano, P. S.; Bay, E.; Leone, A. A. *Tetrahedron Lett.* **1980**, 3455.
(25) Howard, A.; Koch, T. H. *J. Am. Chem. Soc.* **1975**, *97*, 7288.
(26) Swenton, J. S.; Hyatt, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4879.
(27) Cantrell, T. S. *J. Org. Chem.* **1977**, *42*, 4238 and references therein.
(28) Margaretha, P. *Helv. Chim. Acta* **1978**, *61*, 1025.
(29) (a) Leonard, N. J.; Aurand, D. A. *J. Org. Chem.* **1968**, *33*, 1322. (b) Kohn, M.; Giaconi, *J. Chem. Mh.* **1907**, *28*, 461.

(30) Cycloaddition of isobutylene to 6-azapyrimidines[26] which give azetidine products shows a regiochemical outcome different from predictions based upon the FMO consideration presented here. The effect of donating substituents such as are present in the N—N=C linkage on frontier orbital coefficients and energies might be the source of this difference.

Scheme II

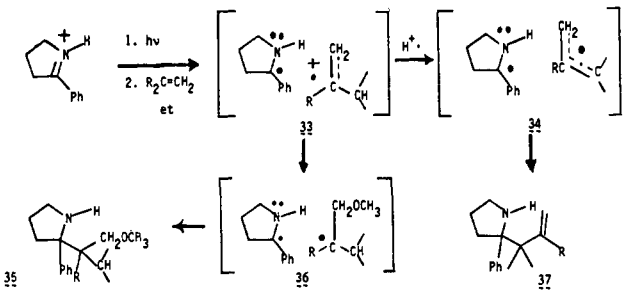


Table II. Calculated Rates of Electron Transfer from Olefins to the Singlet Excited State of 2-Phenyl-1-pyrrolinium Perchlorate (2)

olefin	$E_{1/2}(+)$,[a] V vs. SCE	G°_{et},[b] kcal/mol	$G^{\ddagger}_{et}$, kcal/mol	k_{et} (CH_3CN, 25 °C), M^{-1} s^{-1}
$(CH_3)_2C{=}CH_2$	2.29	−13.4	0.42	1.3×10^{10}
cyclohexene	2.03	−19.4	0.29	1.4×10^{10}
butadiene	2.17	−16.1	0.35	1.4×10^{10}
$(CH_3)_2C{=}CHCO_2CH_3$[c]	2.70	−3.9	1.14	7.5×10^{9}
$CH_2{=}C(CH_3)CO_2CH_3$	3.37	+11.5	12.0	1.1×10^{2}
$CH_2{=}CHCO_2CH_3$	3.80	+21.5	21.8	8.5×10^{-6}
$CH_2{=}CHCN$	3.97	+25.4	25.6	1.37×10^{-8}

[a] $E_{1/2}$ values of olefins were calculated from known ionization potentials[33] by using the relationship of Miller.[34] [b] Experimentally determined $E_{1/2}(-)$ of 2 is ca. 0.99 V (CH_3CN) vs. SCE as expected on the basis of previous measurements.[35] [c] Ionization potentials, and thus $E_{1/2}(+)$, were estimated by using a cumulative methyl substituent effect.

27 having phenyl substitution at the bridgehead carbon adjacent to nitrogen should proceed via S_N1 reaction mechanisms in polar media.[29a,31] Accordingly, ring opening by rupture of the internal CN bond to produce the tertiary benzylic cation **31** should occur most rapidly. Importantly, no products containing the hydroazepine structure which would arise from **31** were detected in any of the product mixtures.

Electron-Transfer Mechanisms. The structural, regiochemical, and stereochemical characteristics of the pyrrolinium salt–olefin photoadditions are best rationalized by mechanisms involving electron transfer[32] as outlined in Scheme II. One electron transfer from alkyl-substituted olefins to 2^{S_1} in methanol solution should be energetically feasible (Table II, vide infra). The direction of nucleophilic attack by methanol on the radical cation **33** derived from the olefin should be controlled by steric and electronic factors. The pathway involving bonding of methanol to the less substituted carbon of the unsymmetric cation radical would be of lower energy due to the avoidance of steric interference, the more favorable frontier orbital interactions between the low-lying oxygen nonbonded AO of methanol and the HOMO of the cation radical,[36] and the greater stability of the developing alkyl radical. Collapse of the radical pair **36** formed in this way by carbon–carbon bond formation gives rise to the amino ether products **35**. Alternatively, deprotonation of the radical cation **33** generates the radical pair **34** serving as the precursor for olefin adducts **37**. It is important to note that the regiochemistry of these processes, corresponding to anti-Markovnikov addition of pyrrolinium salt and methanol to the olefin, is reminiscent of that observed for the related electron-transfer-sensitized photohydration, -alcoholation, and -hydrocyanation processes of unsymmetric olefins elegantly investigated by Arnold and his coworkers.[32b]

Table III. Rate Constants for Fluorescence Quenching of 2[a] by a Variety of Olefins and Methanol in Acetonitrile[b-d]

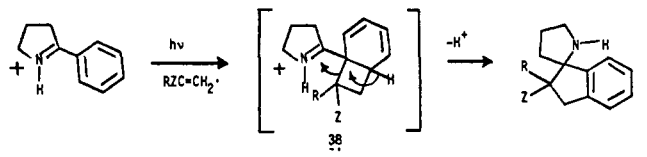
quencher	k_q (25 °C), M^{-1} s^{-1}	k_{et} (calcd), M^{-1} s^{-1}
cyclohexene	6.0×10^{9}	1.4×10^{10}
$(CH_3)_2C{=}CHCO_2CH_3$	3.7×10^{9}	7.5×10^{9}
$CH_2{=}CHCN$	6.6×10^{8}	1.4×10^{-8}
CH_3OH	7.4×10^{7}	1.2×10^{-6}

[a] Photophysical data for 2 in acetonitrile include $\phi_f = 0.16$, $\tau = 16$ ns, $k_f = \phi_f/\tau = 9.7 \times 10^{6}$ s^{-1}, λ_{max} emission = 375 nm, and $k_d = 5.0 \times 10^{7}$ s^{-1}. [b] See ref 39. [c] Estimated by comparison to *p*-dioxane. [d] Calculated by using Miller's relationship.[34]

A qualitative test has been employed to gain preliminary information to support the electron-transfer mechanistic rationale presented above. The efficiency of electron transfer from olefins to the excited iminium cation and, thus, of the photoaddition reactions of **2** should be dependent upon the relative energies of the olefin and iminium salt HOMOs. Importantly, the criteria for rapid excited-state electron transfer based upon the respective oxidation ($E_{1/2}(+)$) and reduction ($E_{1/2}(-)$) potentials of donor and acceptor and acceptor singlet energy ($E_{0,0}$) have been outlined by Rehm and Weller[37] in the semiempirically derived relationships which are supported by theoretical calculations.[38] The rates of electron transfer from a series of olefins observed to undergo photoaddition to **2** are calculated by use of the Weller equations to be near the diffusion controlled limit of 1×10^{10} M^{-1} s^{-1} in acetonitrile or methanol solution (Table II). Although methyl β,β-dimethylacrylate is expected to transfer an electron to 2^{S_1} rapidly, less alkyl-substituted, more electron-deficient olefins such as methyl methacrylate, methyl acrylate, and acrylonitrile should be poorer donors (Table II). Fluorescence quenching rate constants are useful in evaluating the potential relationship between the oxidation potential of donor olefins and electron-transfer rates. Stern–Volmer analysis of fluorescence quenching has yielded rate constants for quenching (k_q) of 2^{S_1} by an assortment of olefins (Table III). The relative magnitudes of k_q appear to follow the trend predicted on the basis of estimated k_{et} values. Surprisingly, contrary to expectations, the electron-poor olefins which should be unable to interact with 2^{S_1} by electron transfer or energy transfer, serve as reasonable quenchers. Thus, either alternative pathways are operative in the electron-poor olefin induced deactivation of the singlet excited pyrrolinium salt or quenching by both electron-rich and electron-poor olefins occurs prior to electron transfer by a common mechanism.

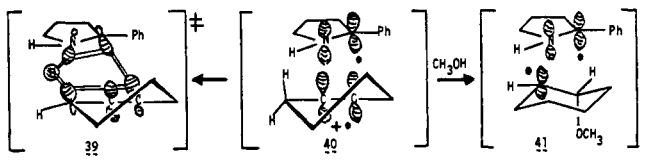
Irradiation of methanol or acetonitrile solutions of **2** containing the electron-poor olefins, acrylonitrile, methyl methacrylate, and methyl acrylate does not lead to the production of amino ether or olefin adducts. Instead, the epimeric spirocyclic amines **22–24** are generated in reasonably high yields. Formation of these materials most probably takes place through a mechanism involving initial $[_{\pi}2 + _{\pi}2]$ arene–olefin cycloaddition to produce the bicyclic diene **38**. Rearrangement by ring expansion of the cyclobutylcarbinyl cationic systems followed by, or in concert with, deprotonation would then generate the spirocyclic amine system. Precedent for the initial step of this process is found in several literature examples describing olefin–aromatic ring cycloadditions.[27,40] Thus, quenching of 2^{S_1} by electron-poor olefins could

(31) Crist, D. R.; Leonard, N. J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 962.
(32) Numerous photochemical processes initiated by electron transfer to or from excited-state species are summarized in an excellent review[32a] and paper.[32b] (a) Davidson, R. S. "Molecular Association"; Foster, R., Ed.; Academic Press: London, 1975; Vol. 1, 215. (b) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535 and references therein.
(33) Houk, K. N.; Munchhausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937.
(34) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.
(35) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1970**, *26*, 223.
(36) Since the nonbonded atomic orbitals on oxygen are of low energy, they should interact more strongly with the HOMO rather than LUMO orbitals of the cation radicals which in the case of alkyl substituted systems are largest at the unsubstituted carbon. Interestingly, this reasoning suggests that if soft nucleophiles (having higher energy nonbonded AOs) are employed and FMO interactions are controlling, the regiochemistry of addition could be the reverse of that seen in these reactions.
(37) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(38) Scandola, F. S.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140.
(39) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970.



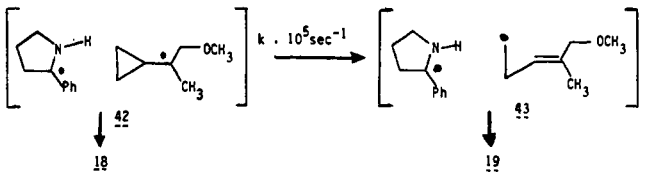
very well involve reversible formation of an exciplex which serves as a precursor for [$_{\pi}2 + _{\pi}2$] cycloaddition.

Mechanistic Details. Radical-Pair Lifetimes. Several of the subtle mechanistic details of these photoaddition reactions require more detailed discussion. Electron transfer from electron-rich olefins to the pyrrolinium salt most probably occurs through the intermediacy of an encounter complex (exciplex). No emission has been detected from these exciplexes, a result perhaps of their short lifetime due to the large rate of electron transfer in polar solvents such as methanol and acetonitrile. The narrow solubility range of the pyrrolinium salt has prevented a search for exciplex emission in nonpolar solvent systems. In a similar way, the radical cation pairs formed by electron transfer are likely to be strongly associated in solvent cages due to the mutually beneficial stabilizing interactions existing between the electron-rich amino radical and electron-deficient cation radicals. Several results appear to be in agreement with this postulate. First, cyclohexene photoaddition to **2** produces only two of the four possible diastereomeric ether adducts. The products obtained (**5a** and **5b**) are epimeric at the pyrrolidine C-2 position and both have the methoxy and pyrrolidine substituents trans about the cyclohexane ring. These stereochemical findings are in accord with an electron-transfer mechanism in which methanol attack occurs on the radical cation pair **40**, held rigidly in a solvent cage, from a sterically more accessible



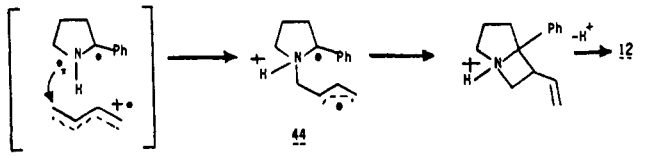
direction anti to the pyrrolidinyl ring. Another important requirement of a reaction having stereochemistry governed in this way is that carbon–carbon bond formation from the ultimate radical pair **41** be fast relative to reorganization of or diffusion from the cage. If this were not the case, product stereochemistry might not necessarily be controlled by nucleophilic attack but rather by preferences in carbon–carbon bond formation. Evidence which suggests that radical pair coupling is fast relative to other available processes will be discussed below. However, on the basis of information available at this time, we cannot rule out alternative sources of stereochemical control in the cyclohexene–pyrrolinium salt photoadditions. Finally, formation of olefin adducts should also proceed via cation radical pairs analogous to **40**. Transformation of these pairs to olefin could take place through a stepwise process involving proton transfer to the amino radical or solvent, generating allyl radical pairs. Alternatively, a concerted, pericyclic pathway (via **39**) of the type, $_{\pi}3_s + _{\sigma}2_s + _{\pi}1_s$, might intervene.

The reasonably high yields of products from the intermolecular olefin–iminium salt additions and the absence of detectable quantities of cross-over coupling products serve to reinforce the postulate that the individual processes following the electron-transfer step occur rapidly compared to diffusion from the initially formed cage. In an attempt to gain a qualitative estimate of the rate of these radical coupling processes, we have explored the photoaddition reactions of isopropenylcyclopropane to **2** in methanol. The rates of cyclopropyl to homallyl radical conversions are known to be fast at room temperature.[41] For example, a rate constant of 1×10^8 s^{-1} has been measured by Ingold for transformation of the unsubstituted system. No rate constants for conversion of tertiary cyclopropylcarbinyl to homoallyl radicals have been yet determined. However, a rough estimate of 3×10^5 s^{-1} can be made, with $A = 10^3$ s^{-1} obtained from the simple system and an approximated E_a of 13 kcal/mol, for the rate of conversion of the tertiary radical **42** derived from isopropenylcyclopropane to its butenyl radical counterpart **43**. Thus, if the lifetime of the



final radical pairs arising by addition of nucleophile to the initially formed cation radical pair is longer than 10^{-5} s, addition products **19**, resulting from coupling of the 2-pyrrolidinyl radical to the ring-opened radical, should be produced. Since the ring-opened amino ethers **19** are not generated in these photoprocesses, the radical coupling step following solvent capture of the cation radical pair as expected must be fast.

Alternative Reaction Pathways. The major reaction pathways adopted by the cation radical pair generated by electron transfer involve addition of a nucleophile and deprotonation. The latter route leads to the same radical pair which would have arisen through allylic hydrogen atom abstraction by the singlet excited state of the pyrrolinium salt. Although no hard evidence is available to support either mechanistic postulate, it is unlikely that hydrogen atom abstraction would be competitive with electron transfer in iminium salt systems which lack n–π^* excited states.[43,44] In this regard, the behavior of pyrrolinium salts differs from their neutral imine counterparts which are known to undergo photodimerizations[45] and photoadditions[46] by hydrogen atom abstraction mechanisms. Another pathway open to cation radical pairs is reversible C–N bond formation resulting in production of 2-aza-1,4-diradicals. The vinylazetidine **12** which arises by irradiation of **2** in the presence of butadiene might derive by a route of this type through the diradical **44**. It should be noted that



this mechanism smoothly rationalizes the observed regiochemistry for cycloadduct formation in terms of the relative stability of intermediate diradicals. Importantly, the regiochemistry expected from the alternative [$_{\pi}2 + _{\pi}2$] concerted cycloaddition mechanism would be opposite that observed. Thus, the results accumulated thus far suggest that the processes followed in the photochemistry of olefin–pyrrolinium salt systems might all have a common mechanistic origin.

A final aspect of this investigation warranting discussion concerns the factors which control the nature of the reaction pathways which are ultimately followed in the electron-transfer excited-state chemistry of olefins. Specifically, electron-transfer-photosensitized

(40) The chemoselectivities (C=C vs. C=N) and regioselectivities of these processes have been discussed in FMO terms: Leone-Bay, A. A.; Mariano, P. S. *Tetrahedron Lett.* **1980**, 4581.

(41) Kochi, J.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1879.

(42) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

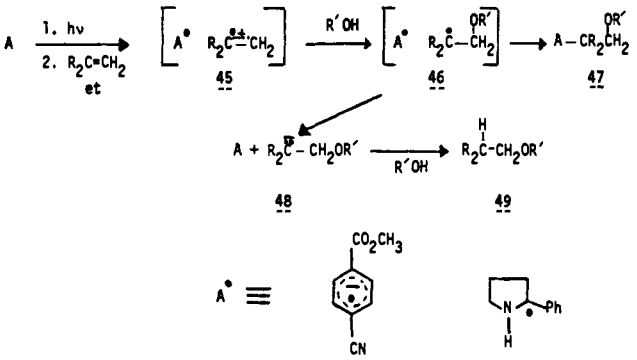
(43) In an analogous situation (e.g., acetophenone vs. trifluoroacetophenone) electron transfer occurs more efficiently than hydrogen atom abstraction even when the reactive excited state is of n–π^* configuration: Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669; Godfrey, T. S.; Porter, G.; Suppan, P. *Discuss. Farad. Soc.* **1965**, *39*, 194; Hoshino, M.; Koizumi, M. *Chem. Lett.* **1972**, 189.

(44) We have found that electron-transfer mechanisms operate in fluorescence quenching and photoaddition processes occurring in pyrrolinium salt–toluene systems: Klinglier, L.; Mariano, P. S., unpublished results.

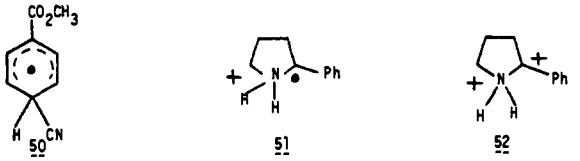
(45) 2-Phenyl-1-pyrroline undergoes efficient photodimerization to generate the bipyrrolidine products when irradiated in hydrogen atom donating solvents.[19]

(46) Toshima, N.; Asao, K.; Takada, K.; Hirai, H. *Tetrahedron Lett.* **1970**, 5123.

Scheme III



additions of water or alcohols to olefins[32b] and the amino ether forming addition reactions described herein are closely related processes with common mechanistic roots. In both cases an acceptor singlet excited state undergoes ready one-electron reduction through interaction with an electron-rich olefin donor. In addition, the cation radicals produced are captured by nucleophiles. It is clear that the divergent behavior of these systems stems from the variable reactivity of the final radical pairs formed in this sequence. Whether photosensitized reactions or photoadditions predominate is controlled at this stage by factors which govern the relative rates of back-electron-transfer to produce alkyl anions **48** vs. bond formation to generate the coupling products **46**. The results suggest that back-electron-transfer in the pyrrolinium salt reaction is not as efficient as coupling by carbon–carbon bond formation. When neutral acceptors such as 1-cyanonaphthalene and methyl *p*-cyanobenzoate are employed, back-electron-transfer generating the ground state of the aromatic sensitizer occurs rapidly. This difference might be due to a combination of factors including the ability of the radical A· (Scheme III) to serve as a reducing agent in reduction of the alkyl radical neighbor. The comparative reduction potentials of the acceptors A can be used to estimate the energetics and, thus, the rate for the back-electron-transfer processes. As expected, one-electron oxidation of the anion radicals ($E_{1/2}$(+) ca. +1.6)[47] should be more exergonic than when the amino radicals ($E_{1/2}$(+) ca. +0.9) are donors. The conclusion drawn above concerning the abilities of radical and radical anions to undergo electron transfer to alkyl radicals or coupling would remain unaltered if proton reorganization in the radical pair following methanol attack occurs to generate the acceptor-derived radicals **50** and **51**. Here again, electron transfer from **51** to generate the dication **52** would be less competitive with radical coupling than for the case of the corresponding neutral radical **50**.



Summary

The observations outlined above suggest that olefin–iminium salt systems undergo novel photoaddition reactions resulting in the production of amino ether and olefin adducts. Electron-transfer mechanisms appear to be useful in rationalizing all of the features of these processes. Further studies are necessary, however, to solidify these mechanistic postulates and to explore the synthetic versatility of the processes.

Experimental Section

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

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

Protonation of 2-Phenyl-1-pyrroline (1). To 2-phenyl-1-pyrroline (3.00 mL of a 6.621×10^{-5} M solution in methanol) was added small increments of $HClO_4$ (3.33×10^{-3} M solution in methanol). This caused a simultaneous decrease in the UV maximum at 243 nm and an appearance of a new absorption at 264 nm (ϵ 15 570) with an isosbestic point at 251 nm. Protonation was complete after the addition of 1.34 equiv of $HClO_4$. Complete reversal of the above change was noted upon addition of NaOH.

2-Phenyl-1-pyrrolinium Perchlorate (2). The iminium salt was prepared by the following general method. To 2-phenyl-1-pyrroline (**1**) were added 1.0 equiv of perchloric acid and enough methanol to effect solution. Benzene was added and removed successively in vacuo until all the water had been removed and the salt crystallized. Recrystallization for an analytical sample was performed by passing a stream of argon over a solution of the salt in chloroform until the crystals of pure 2-phenyl-1-pyrrolinium perchlorate (**2**) formed: mp 116–117 °C; ^{1}H NMR (acetone-d_6) δ 2.49 (m, 2 H, C-4 CH_2), 3.74 (m, 2 H, C-3 CH_2), 4.32 (m, 2 H, C-5 CH_2), 5.21 (br s, 1 H, NH), 7.7 (m, 2 H, aromatic), ,.1 (m, 3 H, aromatic); ^{13}C NMR (acetone-d_6) δ 207.3 (s, C=N), 137.2 (s, C-1, aromatic), 131.1, 130.3, 129.0, 126.5 (d, aromatics), 54.6 (t, C-5), 35.8 (t, C-3), 20.3 (t, C-4).

Anal. Calcd for $C_{10}H_{12}NO_4Cl$: C, 48.89; H, 4.92; N, 5.70; Cl, 14.43. Found: C, 48.76; H, 4.98; N, 5.59; Cl, 14.29.

Photolysis of 2-Phenylpyrrolinium Perchlorate with Isobutylene. Preparation of 2-Phenyl-2-(1-methoxy-2-methylprop-2-yl)pyrrolidine (3). An argon-purged solution containing 2-phenyl-1-pyrroline (400 mg, 2.76 mmol), 70% (w/w) perchloric acid (530 mg, 3.69 mmol), and ca. 15 mL of isobutylene (0.165 mmol) in 200 mL of freshly distilled methanol was irradiated below −5 °C for 1.75 h in a preparative photolysis apparatus consisting of a water–ethylene glycol-cooled quartz immersion well containing a 450-W Hanovia medium-pressure lamp and a Corex filter. Solid K_2CO_3 was then added, and the mixture was stirred for 3 min before the K_2CO_3 was filtered and the photolysate was concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo giving the photoadduct **3** which was further purified by molecular distillation (55–60 °C, 0.025 torr) to give 0.518 g (81%) of **3** as an oil. An analytical sample was obtained by GLC on 4% SE-30 (5 ft × $^3/_8$ in.): IR ($CHCl_3$) 3030, 2940, 2860, 1475, 1460, 1115, 970 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.85 (s, 3 H, *gem*-CH_3), 0.87 (s, 3 H, *gem*-CH_3), 1.0–3.0 (m, 7 H, ring protons), 3.00 (d, J = 9 Hz, 1 H, diast H α to OCH_3), 2.86 (d, J = 9 Hz, 1 H, diast H α to OCH_3), 3.20 (s, 3 H, OCH_3), 7.1–7.5 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 233 (≪1, M$^+$), 163 (2), 147 (13), 146 (100), 145 (18), 144 (11), 91 (6), 87 (10), 77 (5), 45 (5); UV (EtOH) λ_{max} 251 nm (ϵ 633), 257 (544), 264 (441); ^{13}C NMR ($CDCl_3$) δ 143.9 (s, C-1 aromatic), 128.5 (d, meta aromatic), 27.1 (d, ortho aromatic), 126.0 (d, para aromatic), 80.8 (t, CH_2 α to OCH_3), 73.6 (s, C-2 of ring), 58.8 (q, OCH_3), 44.8 (t, C-5 of ring), 40.3 (s, quaternary of *gem*-dimethyl), 33.4 (t, C-3 of ring), 24.6 (t, C-4 of ring), 22.3 (q, *gem*-methyls).

Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 600. Found: C, 77.23; H, 9.76; N, 5.91.

A dark control experiment was run in the following manner. A mixture of the pyrroline (192 mg, 1.3 mmol), isobutylene (ca. 10 mL, 0.11 mol), and perchloric acid (845 mg, 5.9 mmol) in 100 mL of CH_3OH was stirred at −10 °C for 1.75 h with Ar bubbling through the solution. Only 2-phenyl-1-pyrroline was obtained after basic workup as shown by ^{1}H NMR and GLC analyses.

Photolysis of 2-Phenylpyrrolinium Perchlorate with Cyclohexene. Preparation of 2-(2-Cyclohexenyl)-2-phenylpyrrolidine (6) and 2-(2-Methoxycyclohexyl)-2-phenylpyrrolidine (5). An argon-purged solution containing 2-phenyl-1-pyrroline (400 mg, 2.76 mmol), 70% (w/w) perchloric acid (530 mg, 3.69 mmol), and 15 mL of cyclohexene (12.2 g, 0.148 mol) in 200 mL of freshly distilled methanol was irradiated for 1 h through a Corex filter. Solid K_2CO_3 was then added, and the mixture was stirred for 3 min before the K_2CO_3 was filtered and the photolysate was concentrated in vacuo. The crude mixture was dissolved in chloro-

(47) Reduction potentials for the related aromatic systems, benzonitrile and *p*-dicyanobenzene, are −2.35 and −1.64 V.[37]

form, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), concentrated in vacuo, giving an oil which was purified initially by molecular distillation (50–70 °C, 0.025 torr) to remove the polymeric materials. Preparative TLC (silica gel, ether) gave four major products. The bands at R_f 0.47 (106 mg, 17%) and 0.39 (89.5 mg, 14%) were the diastereomeric 2-(2-cyclohexenyl)-2-phenylpyrrolidines (**6**). The bands at R_f 0.26 (98 mg, 9%) and 0.10 (100 mg, 9%) consisted of the diastereomeric 2-(2-methoxycyclohexyl)-2-phenylpyrrolidines (**5**).

For **6b**: R_f 0.47; IR ($CHCl_3$) 3030, 2900, 2840, 1600, 1490, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–3.3 (m, 14 H, all nonaromatic and nonolefinic protons), 5.88 (s, 2 H, olefinic protons), 7.1–7.6 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 227 (1, M^+), 226 (2), 147 (11), 146 (100), 144 (6), 134 (6), 117 (5), 104 (6), 77 (6), 41 (5); UV (EtOH) λ_{max} 251 nm (ϵ 611), 257 (568), 267 (383); ^{13}C NMR ($CDCl_3$) δ 146.6 (s, C-1 aromatic), 131.0 (d, C-2 on cyclohexenyl ring), 127.8 (d, meta aromatic), 127.3 (d, C-3 on cyclohexenyl ring), 126.6 (d, ortho aromatic), 125.8 (d, para aromatic), 71.3 (s, C-2 of pyrrolidine ring), 46.3 (t, C-5 of pyrrolidine ring), 45.3 (d, C-1 of cyclohexenyl ring), 37.3 (t, C-3 of pyrrolidine ring), 26.2 (t, C-6 of cyclohexenyl ring), 25.8 (t, C-4 of cyclohexenyl ring), 25.3 (t, C-5 of cyclohexenyl ring), 22.3 (t, C-4 of pyrrolidine ring); high-resolution mass spectrum (70 eV) calcd for $C_{16}H_{21}N$ *m/e* 227.166 701 ($C_{16}H_{21}N$ requires 227.167 395).

For **6a**: R_f 0.39; IR ($CHCl_3$) 3030, 2910, 2840, 1635, 1590, 1485, 1440, 1085 cm^{-1}; ^1H NMR (CCl_4) δ 1.0–3.2 (m, 14 H, all nonolefinic or nonaromatic protons), 5.61 (s, 2 H, olefinic protons), 7.1–7.5 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 227 (0.4, M^+), 226 (1), 147 (12), 146 (100), 117 (5), 115 (5), 104 (4), 91 (3), 77 (4), 41 (3); UV (EtOH) λ_{max} 251 nm (ϵ 590), 257 (495), 263 (360); ^{13}C NMR ($CDCl_3$) δ 146.0 (s, C-1 aromatic), 129.2 (d, C-2 of cyclohexenyl ring), 128.5 (d, C-3 of cyclohexenyl ring, 127.7 (d, meta aromatic), 126.7 (d, ortho aromatic), 126.0 (d, para aromatic), 71.7 (s, C-2 of pyrrolidine ring), 46.4 (d, C-1 of cyclohexenyl ring), 45.8 (t, C-5 of pyrrolidine ring), 35.6 (t, C-3 of pyrrolidine ring), 25.4, 25.1 (t, C-4, C-5, C-6 of cyclohexenyl ring), 22.1 (t, C-4 of pyrrolidine ring); high-resolution mass spectrum (70 eV), *m/e* 146.096 07 ($C_{10}H_{12}N$ requires 146.09697; calcd for $C_{10}H_{12}N$ 146.096 970).

Anal. Calcd for $C_{16}H_{21}N$: C, 82.89; H, 9.35; N, 6.04. Found: C, 82.83; H, 9.41; N, 5.96.

For **5**: (R_f 0.26); IR ($CHCl_3$) 2910, 2835, 1655, 1450, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–3.1 (m, 17 H, all ring protons), 3.30 (s, 3 H, OCH_3), 7.2–7.6 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 259 (0.58, M^+), 175 (4), 147 (13), 146 (100), 104 (4), 91 (4), 58 (9), 43 (27); UV (EtOH) λ_{max} 251 nm (ϵ 390), 257 (349), 263 (289); ^{13}C NMR ($CDCl_3$) δ 143.2 (s, C-1 aromatic), 127.6 (d, meta and ortho aromatic), 126.1 (d, para aromatic), 81.3 (d, C-2 of cyclohexyl ring), 71.5 (s, C-2 of pyrrolidine ring), 54.7 (q, OCH_3), 52.8 (d, C-1 of cyclohexyl ring), 13.3 (t, C-5 of pyrrolidine ring), 37.3 (t, C-3 of pyrrolidine ring), 30.5 (t, C-3 of cyclohexyl ring), 27.7 (t, C-5 of cyclohexyl ring), 26.0, 24.7 (t, C-4 C-5 of cyclohexyl ring, C-4 of pyrrolidine ring).

Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.90; H, 9.60; N, 5.51.

For **5** (R_f 0.10): ^1H NMR ($CDCl_3$) δ 0.8–3.2 (m, 16 H, CH_2 and CH ring protons), 3.19 (s, 3 H, OCH_3), 3.81 (br s, 1 H, NH), 7.1–7.5 (m, 5 H aromatic H); ^{13}C NMR ($CDCl_3$) δ 142.8 (s, C-1 aromatic), 127.5 (d, meta aromatic), 127.3 (d, ortho aromatic), 126.1 (d, para aromatic), 81.8 (d, C-3 of cyclohexyl ring), 70.9 (s, C-2 of pyrrolidine ring), 54.8 (q, OCH_3), 53.4 (d, C-1 of cyclohexyl ring), 43.8 (t, C-5 of pyrrolidine ring), 37.0 (t, C-3 of pyrrolidine ring), 30.3 (C-3 of cyclohexyl ring), 28.6 (t, C-6 of cyclohexyl ring), 26.3 (t, C-5 of cyclohexyl ring), 24.6 (t, C-4 of cyclohexyl ring), 22.1 (t, C-4 of pyrrolidine ring).

A dark control experiment was run in the following manner. A mixture of the pyrrolidine (200 mg, 1.38 mmol), cyclohexene (10 mL, 8.1 g, 49.3 mmol), and perchloric acid (0.27 g, 1.88 mmol) in 100 mL of CH_3OH was heated at reflux for 1.5 h and worked up as in the photochemical reaction. Only the starting pyrroline was obtained as shown by ^1H NMR and GLC analyses.

Independent Synthesis of 2-(2-Cyclohexenyl)-2-phenylpyrrolidine (6a, R_f 0.39). A hexane solution of *n*-butyllithium (5 mL of 1.5 M) was added dropwise under Ar to a solution of cyclohexene (1.3 g, 15.8 mmol) containing 1 mL of dry tetramethylethylenediamine. The mixture was stirred at reflux for 4 h and at room temperature for 12 h. 2-Phenyl-1-pyrroline (1.0 g, 6.9 mmol) in THF (2 mL) was added dropwise to the cooled (−20 °C) solution. The mixture was stirred at −20 °C for 5 min, allowed to warm to room temperature, and stirred for 42.5 h before being quenched by the addition of water. The solution was extracted with ether. The ether portion was washed with brine, dried (Na_2SO_4), and concentrated in vacuo, giving 1.07 g of an oil. Molecular distillation (<50 °C, 0.025 torr) gave 0.66 g of the starting imine. The material collected from 50–65 °C (98 mg) was further purified by preparative TLC (silica gel, ether), giving 42 mg (7.9%) of the cyclohexenyl adducts **7a**, identical by TLC, GLC, ^1H NMR (100 MHz), and ^{13}C NMR comparisons with material obtained from the photochemical route.

Photolysis of 2-Phenyl-1-pyrrolinium Perchlorate with Butadiene. Preparation of 2-(4-Methoxybut-1-en-3-yl)-2-phenylpyrrolidine (11), 5-Phenyl-6-vinyl-1-azabicyclo[3.2.0]heptane (12), and 2-(4-Methoxy-*trans*-but-2-en-1-yl)-2-phenylpyrrolidine (10). An argon-purged solution contain 2-phenyl-1-pyrroline (400 mg, 2.76 mmol), 70% (w/w) perchloric acid (530 mg, 3.69 mmol), and 15 mL of butadiene (0.93 g, 0.17 mol) in 200 mL of methanol was irradiated for 1.5 h at −20 °C (ethylene glycol $-CO_2$ bath) before K_2CO_3 was added, and the mixture was stirred for 3 min. The K_2CO_3 was filtered and the photolysate concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo to give 0.69 g of an oil. This mixture was subjected to molecular distillation (35–85 °C, 0.025 torr) to remove polymeric material and then subjected to preparative TLC (silica gel, ether). Three major bands were obtained. The first (R_f 0.45, 131 mg) consisted of one diastereomer of **11** (83 mg, 13%) and the azabicyclo[3.2.0]heptane **12** (48 mg, 9%) (1.5:1) which were separated by GLC (5% SE-30, 155 °C, 5 ft × $^3/_8$ in.). The second band (R_f 0.31) was the other diastereomer of **11** (93 mg, 15%). The third band (R_f 0.18) was the trans-disubstituted olefin **10** (173 mg, 27%).

For **11** (R_f 0.45): IR ($CHCl_3$) 3055, 3040, 2990, 2945, 2910, 2860, 1665, 1455, 1105, 1000, 920 cm^{-1}; ^1H NMR (CCl_4) δ 1.4–2.2 (m, 5 H, NH and methylenes of ring at C-3 and C-4), 2.4–3.1 (m, 5 H, methylenes α to N and α to OCH_3, allylic H), 3.09 (s, 3 H, OCH_3), 4.92–5.88 (m, 3 H, vinyl protons), 7.05–7.45 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 147 (11), 146 (100), 144 (4), 117 (4), 104 (5), 91 (3), 77 (4); UV (EtOH) λ_{max} 257 nm (ϵ 669), 263 (467), 267 (367), 271 (249); ^{13}C NMR ($CDCl_3$) δ 145.6 (s, C-1 aromatic), 137.1 (d, methine olefinic C), 127.8 (d, meta aromatic), 126.8 (d, ortho aromatic), 126.2 (d, para aromatic), 118.0 (t, terminal olefinic C), 74.0 (t, CH_2 α to OCH_3), 69.1 (s, C-2 of pyrrolidine ring), 58.7 (q, OCH_3), 53.7 (d, methine α to vinyl group), 45.2 (t, C-5 of ring), 37.7 (t, C-3 of ring), 24.7 (t, C-4 of ring).

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.76; H, 9.09; N, 6.03.

For **12**: IR ($CHCl_3$) 3040, 3025, 2970, 2930, 2900, 2840, 1630, 1485, 1445, 1000, 985, 925 cm^{-1}; IR (CS_2) 765, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.1 (m, 2 H, C-3 CH_2), 2.1–2.5 (m, 2 H, C-4 methylene), 2.75–2.90 (m, 2 H, C-7 methylene), 3.1–3.5 (m, 3 H, C-2 methylene and allylic H at C-6), 4.7–5.7 (m, 3 H, vinyl protons), 7.0–7.2 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 199 (13, M^+), 198 (19), 146 (14), 145 (12), 144 (12), 117 (100), 104 (13), 103 (9), 77 (9); UV (MeOH) λ_{max} 253 nm (ϵ 356), 258 (315), 264 (332), 268 (180); ^{13}C NMR ($CDCl_3$) δ 145.6 (s, C-1 aromatic), 139.7 (d, methine olefinic C), 128.3 (d, para aromatic), 127.8 (d, meta aromatic), 125.8 (d, ortho aromatic), 115.0 (t, terminal vinyl C), 79.0 (s, C-5), 56.2 (t, C-2), 54.8 (t, C-7), 46.8 (d, C-6), 41.4 (t, C-4), 25.9 (t, C-2); high-resolution mass spectrum (70 eV), *m/e* 199.135 30 ($C_{14}H_{17}N$ requires 199.136 095).

For **11** (R_f 0.31): IR ($CHCl_3$) 3035, 3020, 2990, 2950, 2910, 2860, 1660, 1455, 1440, 1100, 1000, 925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.2 (m, 5 H, methylenes at C-3 and C-4 of ring and NH), 2.4–3.5 (m, 5 H, methylenes α to OCH_3 and N, allylic H), 3.20 (s, 3 H, OCH_3), 5.0–5.8 (m, 3 H, vinyl protons), 7.1–7.5 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 147 (9), 146 (100), 144 (5), 128 (4), 117 (9), 115 (5), 104 (10), 103 (4), 91 (6), 77 (11), 53 (5), 50 (6), 45 (10), 41 (8), 39 (9), 27 (6); UV (EtOH) λ_{max} 252 nm (ϵ 396), 258 (383), 264 (321), 271 (192); ^{13}C NMR ($CDCl_3$) δ 143.9 (s, C-1 aromatic), 137.2 (d, methine vinylic C), 127.7 (d, meta aromatic), 127.2 (d, ortho aromatic), 126.4 (d, para aromatic), 118.0 (t, terminal vinylic C), 73.6 (t, CH_2 α to OCH_3), 69.8 (s, C-2 of ring), 58.8 (q, OCH_3), 52.9 (d, methine C, α to vinyl group), 44.8 (t, C-5 of ring), 36.1 (t, C-3 of ring), 24.2 (t, C-4 of ring).

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 78.07; H, 8.96; N, 6.04.

For **10**: IR ($CHCl_3$) 3040, 3020, 2900, 2840, 1670, 1495, 1445, 1110, 980, 915 cm^{-1}; IR (CS_2) 755, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.2 (m, 4 H, methylenes at C-3 and C-4 of ring), 2.5 (m, 2 H, allylic methylene), 2.68 (br s, 1 H, NH), 2.8–3.30 (m, 2 H, CH_2 α to N), 3.16 (s, 3 H, OCH_3), 3.75 (d, J = 4.5 Hz, 2 H, CH_2 α to OCH_3), 5.0–5.7 (m, 2 H, olefinic protons), 7.1–7.5 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 200 (3), 147 (10), 146 (100), 117 (3), 104 (6), 91 (4), 77 (8), 45 (4), 41 (5), 39 (4); UV (EtOH) λ_{max} 252 nm (ϵ 239), 257 (228), 264 (178); ^{13}C NMR (acetone-d_6) δ 148.4 (s, C-1 aromatic), 130.6, 130.1 (d, olefinic), 128.5 (d, meta aromatic), 127.0 (d, ortho aromatic), 126.5 (d, para aromatic), 73.1 (t, CH_2 α to OCH_3), 68.4 (s, C-2 of ring), 57.3 (q, OCH_3), 46.1, 45.8 (t, C-5 of ring, allylic CH_2 α

to C-2 of ring), 39.1 (t, C-3 of ring), 25.8 (t, C-4 of ring).

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.91; H, 9.21; N, 6.20.

A dark control experiment was run in the following manner. A mixture of the pyrroline **1** (100 mg, 0.69 mmol), butadiene (ca. 5 mL, 3.1 g, 57 mmol), and perchloric acid (0.13 g, 0.91 mmol) was stirred under Ar at −20 °C for 2 h and worked-up as in the photochemical reaction. Only the starting pyrroline was obtained as shown by ^{1}H NMR and GLC analyses.

Photolysis of 5-Phenyl-6-vinyl-1-azabicyclo[3.2.0]heptane (12). An argon-purged solution containing 5-phenyl-6-vinyl-1-azabicyclo[3.2.0]-heptane (21.1 mg, 0.11 mmol) and 70% (w/w) perchloric acid (200 mg, 1.39 mmol) in 200 mL of methanol was irradiated (Corex) for 1.5 h. Solid K_2CO_3 was then added, the mixture was stirred for a few minutes before the K_2CO_3 was removed by filtration, and the photolysate was concentrated in vacuo. ^{1}H NMR analysis of the crude mixture indicated that the azetidine had reacted (only aromatic and aliphatic protons were evident), and GLC analysis (OV-101, 165 °C) confirmed that the new product was not the allyl ether **11** (retention time of the new product was 1.4 min longer than that of **11**).

Attempted Methanolysis of 5-Phenyl-6-vinyl-1-azabicyclo[3.2.0]heptane (11). A solution containing 5-phenyl-6-vinyl-1-azabicyclo[3.2.0]heptane (21.1 mg, 0.11 mmol) and 70% (w/w) perchloric acid (200 mg, 1.39 mmol) in 12 mL of methanol was heated at reflux for 12 h. Solid K_2CO_3 was then added, the mixture was stirred for 3 min before the K_2CO_3 was removed by filtration, and the photolysate was concentrated in vacuo. ^{1}H NMR analysis of the crude material indicated that no reaction of the azetidine **11** had occurred.

Photolysis of 2-Phenylpyrrolinium Perchlorate with Methyl β,β-Dimethylacrylate. Preparation of *endo*- and *exo*-3-Methoxy-4,4-dimethyl-5-phenyl-1-azabicyclo[4.3.0]non-3-en-2-ones (14en and 14ex) and 4-Methyl-6-phenyl-1-azabicyclo[4.3.0]non-3-en-2-one (15). An argon-purged solution containing 2-phenyl-1-pyrroline (400 mg, 2.76 mmol), 70% (w/w) perchloric acid (530 mg, 3.69 mmol), and methyl β,β-dimethylacrylate (15 mL) in 200 mL of methanol was irradiated for 1.5 h through a Corex filter. Solid K_2CO_3 was then added, the mixture was stirred for 3 min before the K_2CO_3 was filtered, and the photolysate was concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo. This material was subjected to molecular distillation (60–80 °C, 0.06 torr) to yield 0.208 g of an oil. TLC (silica gel, ether) was used to obtain 93 mg (13%) of the *endo*- and *exo*-3-methoxy-4,4-dimethyl-5-phenyl-1-azabicyclo[3.3.0]octan-2-ones (**14**, ca. 1:1) as an oil, separated by careful TLC (R_f 0.44 and 0.36; silica gel, ether), and 27.5 mg (4%) of 4-methyl-6-phenyl-1-azabicyclo[4.3.0]non-3-en-2-one (**15**, R_f 0.11).

For **14en**: R_f 0.44; IR ($CHCl_3$) 3030, 2990, 2910, 2855, 2910, 1695, 1445, 1420, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 3 H, *exo*-CH_3), 1.05 (s, 3 H, *endo*-CH_3), 1.4–2.4 (m, 4 H, C-3 and C-4 methylenes), 2.9–3.2 (dddd, J = 12, 7, 4.5, 1.5 Hz, 1 H, H at C-8), 3.57 (s, 3 H, OCH_3), 3.50–3.85 (m, 1 H, H at C-8), 3.65 (s, 1 H, methine H α to OCH_3), 7.1–7.5 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 259 (10, M^+), 229 (11), 228 (13), 227 (15), 147 (16), 146 (100), 145 (22), 117 (38), 91 (13), 86 (60), 77 (13), 71 (26), 41 (19); UV (EtOH) λ_{max} 252 nm (ε 530), 258 (486), 264 (380); ^{13}C NMR ($CDCl_3$) δ 172.7 (s, C=O), 141.5 (s, C-1 aromatic), 128.2 (d, meta aromatic), 127.2 (d, para aromatic), 126.3 (d, ortho aromatic), 86.8 (d, C-3), 75.6 (s, C-5), 60.1 (q, OCH_3), 47.3 (s, C-4), 40.9 (t, C-8), 33.4 (t, C-6), 24.6 (t, C-7), 23.9, 19.1 (q, *gem*-dimethyls); high-resolution mass spectrum (70 eV), *m/e* 259.156 91 ($C_{16}H_{21}NO_2$ requires *m/e* 259.157 215).

For **14ex**: R_f 0.36; IR ($CHCl_3$) 3030, 2990, 2910, 2855, 2810, 1695, 1445, 1345, 1135 cm^{-1}; IR (CS_2), 770, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 3 H, *exo*-CH_3), 1.24 (s, 3 H, *endo*-CH_3), 1.4–2.3 (m, 4 H, CH_2 at C-3 and C-4 of pyrrolidine ring), 2.9–3.3 (m, 1 H, H at C-8), 3.50 (s, 1 H, H α to OCH_3), 3.56 (s, 3 H, OCH_3), 3.55–3.90 (m, 1 H, H at C-8), 7.10–7.40 (m, 5 H, aromatic H); mass spectrum (70 eV), (relative intensity) 259 (6, M^+), 228 (10), 227 (11), 147 (11), 146 (88), 145 (17), 117 (42), 115 (13), 104 (10), 103 (10), 91 (34), 86 (100), 83 (11), 77 (28), 71 (59), 55 (21), 53 (12), 51 (29), 43 (45), 41 (47), 39 (30), 27 (29), 15 (51); UV (MeOH) λ_{max} 252 nm (ε 314), 258 (328), 264 (292), 267 (249); ^{13}C NMR ($CDCl_3$) 175.2 (s, C=O), 141.1 (s, C-1 aromatic), 127.9 (d, meta aromatic), 127.0 (d, para aromatic), 126.3 (d, ortho aromatic), 89.3 (d, C-3), 77.6 (s, C-5 C), 59.4 (q, OCH_3), 42.0 (s, C-4, t, C-8), 33.2 (t, C-6), 25.1 (t, C-7), 24.3, 21.0 (q, methyls); high-resolution mass spectrum (70 eV), *m/e* 259.156 909 ($C_{16}H_{21}NO_2$ requires *m/e* 259.157 215).

For **15** IR ($CHCl_3$) 3035, 2985, 2980, 2870, 1660, 1610, 1445, 1110, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.3–2.5 (m, 4 H, C-7, C-8 methylenes), 1.66 (d, J = 0.5 Hz, 3 H, CH_3), 2.75 (d, J = 0.5 Hz, 2 H, C-5 CH_2, allylic), 3.7 (m, 2 H, CH_2 at C-2), 5.72 (m, 1 H, vinyl H), 7.1–7.4 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 227 (21, M^+), 150 (100), 146 (98), 117 (35), 91 (21), 82 (61), 77 (39), 54 (23), 53 (27), 51 (27), 41 (37), 39 (54), 27 (21); UV (EtOH) λ_{max} 250 nm (ε 2508), 215 (9556); ^{13}C NMR ($CDCl_3$) δ 164.5 (s, C=O), 147.5 (s, C-1 aromatic), 143.8 (s, quarternary olefinic C), 128.2 (d, meta aromatic), 127.0 (d, para aromatic), 125.4 (d, ortho aromatic), 121.0 (d, olefinic C), 67.3 (s, C-6), 44.3, 43.9, 42.9 (t, C-5, C-7, C-9), 22.9 (q, CH_3), 20.8 (t, C-8); high-resolution mass spectrum (70 eV), *m/e* 227.130 290 ($C_{15}H_{17}NO$ requires *m/e* 227.131 005).

A dark control experiment was run in the following manner. A mixture of the pyrroline **1** (200 mg, 1.38 mmol), methyl β,β-dimethylacrylate (7 mL), and perchloric acid (0.27 g, 1.88 mmol) in 100 mL of CH_3OH was heated at reflux for 19 h and was worked up as in the photochemical reaction. Only the starting pyrroline was obtained as shown by ^{1}H NMR and GLC analyses.

Interconversion of *exo*- and *endo*-14. Each of the diastereomers of **14** was refluxed in 3 mL of 1 M NaOMe in MeOH for 22 h. The endo isomer was recovered unreacted from this mixture. The exo isomer was converted to ca. a 50:50 mixture of the two isomers. An equimolar mixture of the two diastereomers (180.4 mg) was refluxed in 60 mL of 1 M NaOMe/MeOH for 43.5 h. Water was added to the solution after cooling. The solution was extracted with $CHCl_3$. The $CHCl_3$ extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo, giving 171.9 of a mixture containing mainly the endo isomer (5.9:1).

Preparation of 3-Methoxy-4,4-dimethyl-5-phenyl-1-azabicyclo[3.3.0]-octane (16a). An ether solution (1 mL) of a 7:3 endo–exo mixture of the bicyclic lactams **14** (80 mg, 0.31 mmol) was added dropwise with stirring to a mixture of lithium aluminum hydride (60 mg, 1.6 mmol) in anhydrous ether (5 mL) under Ar. The mixture was heated at reflux for 1.3 h before being cooled to 0 °C. Sodium hydroxide (30% w/w) was then added to quench the reaction. The ether layer was separated, washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo, giving 70 mg (93%) of the pyrrolizidines **16a** as a 7:3 mixture of the endo and exo epimers. The reduction product was identical with material obtained from the photolysis of 1-(3-methyl-2-butenyl)-2-phenyl-1-pyrrolinium perchlorate (**16b**) in methanol by GLC, TLC, ^{1}H NMR, and ^{13}C NMR analysis.

Benzophenone-Sensitized Photolysis. An argon-purged solution containing 2-phenyl-1-pyrroline (0.363 g, 2.5 mmol), 70% (w/w) perchloric acid (0.48 g, 3.3 mmol), approximately 15 mL of isobutylene (0.165 mol), and benzophenone (6.00 g, 33.0 mmol) in 200 mL of methanol was irradiated at −20 °C for 2.0 h through a uranium-glass filter. Solid K_2CO_3 was then added, the mixture was stirred for 2 min before the K_2CO_3 was filtered, and the photolysate was concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography (silica gel, 5% ether–hexane to methanol, 105 × 2.5 cm) was used to separate the various components. The following products were obtained: oxetane **20** from cycloaddition of isobutylene to benzophenone (1.64 g, 5% ether–hexane), benzophenone (3.91 g, 5% ether–hexane), 2-phenyl-1-pyrroline (170 mg, chloroform).

A control irradiation was run without any imine present under the same conditions as above. The results from column chromatography were as follows: oxetane **20** (2.21 g), benzophenone (2.94 g), benzopinacol (0.70 g).

Photolysis of 2-Phenyl-1-pyrroline. Preparation of 2,2′-Diphenyl-2,2′-bipyrrolidine (21). An argon-purged solution containing 2-phenyl-1-pyrroline (400 mg, 2.76 mmol), potassium carbonate (4.0 g, 28.9 mmol), and isobutylene (ca. 15 mL, 0.16 mol) in 200 mL of methanol was irradiated (Vycor) at −20 °C for 10.5 h. The K_2CO_3 was removed by filtration, and the photolysate was concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo. Molecular distillation gave 2-phenyl-1-pyrroline (<50 °C, 0.05 torr; 210 mg, 53%) and a mixture (120 mg) consisting mainly of 2,2′-diphenyl-2,2′-bipyrrolidine (ca. 70 mg) and 2-phenyl-2-(1-methoxyprop-2-yl)-pyrrolidine (ca. 35 mg) by ^{1}H NMR analysis (50–80 °C, 0.05 torr). Recrystallization from EtOH yielded an analytical sample of the dimer [mp 128.5–130 °C (lit.[19] mp 130–131 °C)] with an ^{1}H NMR spectrum equivalent to that previously reported.[19]

Photolysis of 2-Phenyl-1-pyrrolinium Perchlorate with Acrylonitrile. Preparation of *syn*- and *anti*-9-Cyano[6,7]benzo-1-azaspiro[4.4]non-6-enes (22s and 22a). An argon-purged solution containing 2-phenyl-1-pyrroline (425 mg, 2.93 mmol), 70% (w/w) perchloric acid (560 mg, 3.90 mmol), and 15 mL of acrylonitrile (12.1 g, 0.23 mol) in 200 mL of methanol was irradiated for 2.5 h though a Corex filter. K_2CO_3 was added, and the

mixture was stirred for 3 min. The K_2CO_3 was removed by filtration, and the photolysate was concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo. This material was purified by molecular distillation (45–80 °C, 0.05 torr), giving starting pyrroline (70 mg) and a mixture of the epimeric spirocyclic amines **22s** and **22a** (1.5:1 syn/anti by ^{13}C NMR analysis) of ca. 90% purity. The epimers were separated by TLC (silica gel, ether), giving the syn isomer (87 mg, 15%; R_f 0.53; mp 68–71 °C) and the anti isomer (42 mg, 7%; R_f 0.33).

For **22s**: IR (CS_2) 3025, 3000, 2945, 2820, 2215, 1405, 1325, 1095, 1075, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9–2.2 (m, 5 H, NH, methylenes at C-4 and C-5), 3.1–3.4 (m, 5 H, CH_2 α to N (C-3), benzylic CH_2 (C-8), and CH α to CN), 7.1–7.3 (m, 4 H, aromatic H); mass spectrum (70 eV), 198 (100, M^+), 197 (48), 170 (62), 145 (19), 144 (50), 143 (15), 130 (87), 128 (19), 120 (19), 117 (33), 115 (36), 77 (21), 63 (18), 51 (16), 41 (17), 39 (21); UV (EtOH) λ_{max} 256 nm (ϵ 988), 264 (946), 272 (800); ^{13}C NMR ($CDCl_3$) δ 146.5 (s, C-6), 139.0 (s, C-7), 128.4, 127.9, 124.8, 122.5 (d, aromatics), 120.6 (s, CN), 74.4 (s, C-1), 47.0 (t, C-3), 42.9 (d, C-9), 38.1 (t, C-8), 36.6 (t, C-5), 26.4 (t, C-4); high-resolution mass spectrum (70 eV), m/e 198.11583 ($C_{13}H_{14}N_2$ requires m/e 198.115690).

For **22a**: IR ($CHCl_3$) 3055, 3010, 2945, 2905, 2850, 2215, 1475, 1460, 1410 cm^{-1}; IR (CS_2) 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7–2.6 (m, 5 H, NH, methylenes at C-4 and C-5), 3.0–3.5 (CH_2 α to N (C-3), benzylic CH_2 (C-8), and CH α to CN), 7.1–7.3 (m, 4 H, aromatic HO; mass spectrum (70 eV), m/e (relative intensity) 198 (100, M^+), 197 (47), 170 (55), 157 (12), 156 (15), 146 (11), 145 (17), 144 (37), 143 (14), 141 (11), 140 (17), 130 (71), 128 (18), 117 (28), 115 (30), 104 (13), 103 (13), 77 (17), 53 (15), 51 (18), 41 (21), 39 (22); UV (EtOH) λ_{max} 258 nm (ϵ 663), 265 (770), 271 (591); ^{13}C NMR ($CDCl_3$) δ 147.8 (s, C-6), 138.3 (s, C-7), 128.2, 128.0, 124.7, 122.1 (d, aromatics), 120.8 (s, CN), 75.0 (s, C-1), 47.2 (t, C-3), 43.3 (d, C-9), 36.3 (t, C-8), 34.6 (t, C-5), 25.9 (t, C-4); high-resolution mass spectrum (70 eV), m/e 198.11593 ($C_{13}H_{14}N_2$ requires 198.115690).

A dark control experiment was run in the following manner. A mixture of 2-phenyl-1-pyrroline (100 mg, 0.69 mmol), acrylonitrile (4 mL, 3.2 g, 60.1 mmol), and 70% (w/w) perchloric acid (135 mg, 0.94 mmol) in 50 mL of methanol was heated at reflux for 13 h and was worked up as in the photochemical reaction. No reaction of the pyrroline was evident by ^1H NMR or GLC analysis.

Interconversion of 22a and 22s. Epimerization of the nitriles was conducted by refluxing each isomer **22a** and **22s** (10–20 mg) in ca. 5 mL of 1 M NaOMe in methanol for ca. 10 h. Two spots were visible by analytical TLC from each reaction mixture. The R_f values of these correspond to the R_f values of the two epimers.

Ammonium Perchlorate Salt of 22a. The ammonium perchlorate derivative used in the X-ray crystallographic study was prepared by the addition of $HClO_4$ to a solution of **22a** in ethanol. Suitable crystals were obtained by the following procedure. Crystals that had twice been grown from methanol–chloroform (slow concentration by passing Ar over solution) were dissolved in methanol. Ether was then added to effect crystal formation (mp 210–212 °C dec).

Photolysis of 2-Phenylpyrrolinium Perchlorate with Methyl Acrylate. Preparation of *syn*- and *anti*-9-Carbomethoxy[6,7]benzo-1-azaspiro[4.4]non-6-enes (23s and 23a). An argon-purged solution containing 2-phenyl-1-pyrroline (400 mg, 2.76 mmol), 70% (w/w) perchloric acid (530 mg, 3.90 mmol), and 15 mL of methyl acrylate (14.3 g, 0.17 mol) in 200 mL of methanol was irradiated for 2 h through a Corex filter before K_2CO_3 was added, and the mixture was stirred for 3 min. The K_2CO_3 was removed by filtration, and the photolysate was concentrated in vacuo. This material was subjected to molecular distillation, giving 0.14 g of 2-phenyl-1-pyrroline (0.05 torr, <50 °C) and 0.24 g (58%) of an oil (0.05 torr, 50–85 °C) containing ca. 85% (GLC) of a 1.5:1 mixture of the syn and anti spirocyclic amines, **23s** and **23a**, respectively. Further purification was accomplished by preparative TLC (silica gel, 50% ether-hexane) which gave 43 mg of 2-phenyl-1-pyrroline (total recovered ca. 0.19 g, 48%), the syn epimer **23s** (59 mg, 18%; R_f 0.20), and the anti epimer **23a** (61 mg, 18%; R_f 0.16). Each ester contained 5–10% olefinic impurities.

For **23s**: IR (CS_2) 3030, 2985, 2915, 2840, 1735, 1350, 1225, 1165, 770 cm^{-1}; ^1H NMR (CCl_4) δ 1.9–2.4 (m, 5 H, NH, methylenes at C-4 and C-5), 2.79–3.46 (m, 5 H, CH_2 α to CO_2Me), 3.61 (s, 3 H, OCH_3), 7.08–7.35 (m, 4 H, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 231 (35, M^+), 216 (26), 203 (20), 200 (19), 198 (15), 172 (100), 170 (48), 157 (25), 156 (18), 145 (22), 144 (68), 143 (37), 141 (20), 130 (57), 129 (30), 128 (51), 127 (19), 117 (52), 115 (93), 104 (17), 103 (19), 102 (15), 91 (18), 89 (18), 77 (28); UV (EtOH) λ_{max} 257 nm (ϵ 1526), 266 (1,594), 272 (1,503); ^{13}C NMR ($CDCl_3$) δ 173.6 (s, C=O), 148.7 (s, C-6), 140.7 (s, C-7), 127.7, 127.2, 124.6, 122.2 (d, aromatics), 74.5 (s, C-1), 55.5 (d, C-9), 51.4 (q, OCH_3), 47.0 (t, C-3), 38.7 (t, C-8), 33.3 (t, C-5), 26.6 (t, C-4); high-resolution mass spectrum (70 eV), m/e 231.124884 ($C_{14}H_{17}NO_2$ requires 231.125915).

For **23a**: IR ($CHCl_3$) 3040, 3005, 2935, 2850, 1735, 1445 cm^{-1}; IR (CS_2) 1380, 1200, 1115, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.2 (m, 4 H, methylenes at C-4 and C-5), 3.0 (br s, 1 H, NH), 3.06–3.38 (m, 5 H, CH_2 α to N (C-3), benzylic CH_2 (C-8) and CH α to CO_2Me), 3.72 (s, 3 H, OCH_3), 7.1–7.3 (m, 4 H, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 231 (53, M^+), 216 (16), 203 (22), 200 (22), 198 (10), 173 (16), 172 (100), 170 (25), 157 (16), 144 (42), 143 (17), 130 (29), 128 (16), 115 (32); UV (EtOH) λ_{max} 257 nm (ϵ 1090), 265 (1,033), 272 (937); ^{13}C NMR ($CDCl_3$) δ 173.8 (s, C=O), 149.4 (s, C-6), 139.7 (s, C-7), 127.6, 127.3, 124.5, 122.0 (d, aromatics), 75.3 (s, C-1), 56.9 (d, C-9), 51.7 (q, OCH_3), 47.3 (t, C-3), 35.3 (t, C-8), 33.1 (t, C-5), 26.0 (t, C-4); high-resolution mass spectrum (70 eV), m/e 231.124653 ($C_{14}H_{17}NO_2$ requires 231.125915).

A dark control experiment was run in the following manner. A mixture of 2-phenyl-1-pyrroline (200 mg, 1.38 mmol), 70% (w/w) perchloric acid (280 mg, 1.95 mmol), and 6 mL of methyl acrylate (57.2 g, 66.5 mmol) in 100 mL of methanol was heated under reflux for 13 h and was worked up as in the photochemical reaction. No reaction of the pyrroline was evident by NMR or GLC analyses.

Independent Synthesis of *syn*- and *anti*-9-Carbomethoxy[6,7]benzo-1-azaspiro[4.4]non-6-enes (23s and 23a). Syn Epimer 23s. *syn*-9-Cyano-[6,7]benzo-1-azaspiro[4.4]non-6-ene (**22s**; 60.0 mg, 0.30 mmol) was refluxed in a solution of 2 mL methanol and 1 mL concentrated H_2SO_4 for 3 h under Ar before the mixture was poured into ice–water. The solution was washed with chloroform, neutralized, and extracted with chloroform. The chloroform extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo, giving 39.1 mg (56%) of *syn*-9-(carbomethoxy)[6,7]benzo-1-azaspiro[4.4]non-6-ene (**23s**) which was shown to be identical with the photoproduct by ^1H NMR, ^{13}C NMR, and TLC (R_f 0.41, silica gel, ether) analyses.

Anti Epimer 23a. *anti*-9-Cyano[6,7]benzo-1-azaspiro[4.4]non-6-ene (**22a**; 97.3 mg, 0.49 mmol) was refluxed for 2 h in a solution of 4 mL of methanol and 2 mL of concentrated H_2SO_4 under Ar. The mixture was worked up exactly as above, giving 48.3 mg (43%) of *anti*-9-carbomethoxy[6,7]benzo-1-azaspiro[4.4]non-6-ene (**23a**) which was shown to be identical with the photoproduct by ^1H NMR, ^{13}C NMR, and TLC (R_f 0.28, silica gel, ether) analyses.

Photolysis of 2-Phenyl-1-pyrrolinium Perchlorate with Methyl Methacrylate. Preparation of *syn*- and *anti*-9-Carbomethoxy-9-methyl[6,7]-benzo-1-azaspiro[4.4]non-6-enes (24). An argon-purged solution containing 2-phenyl-1-pyrroline (400 mg, 2.76 mmol), 70% (w/w) perchlorate acid (530 mg, 3.90 mmol), and 18 mL of methyl methacrylate (16.8 g, 0.160 mol) in 200 mL of methanol was irradiated for 2.5 h through a Corex filter before K_2CO_3 was added, and the mixture was stirred for 2 min. The K_2CO_3 was filtered, and the photolysate was concentrated in vacuo. This material was subjected to molecular distillation, giving 147 mg (0.15 torr, >50 °C) of mainly recovered pyrroline and 288 mg (50%; 0.15 torr, 50–80 °C) of mainly the two diastereomeric spirocyclic amino esters **24** (>90% pure by GLC analysis). The epimers (3:4 ratio by ^{13}C NMR analysis) were further purified and separated by TLC (silica gel, ether), giving 47.2 mg (11%) with R_f 0.58 and 64.0 mg (15%) with R_f 0.48.

For **24** (R_f 0.58): IR ($CHCl_3$) 3050, 2930, 2850, 1725, 1460, 1440, 1310, 1290, 1210, 1130 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 245 (M^+, 48), 230 (28), 186 (100), 184 (15), 158 (32), 157 (15), 144 (18), 130 (21), 128 (17), 117 (21), 115 (18); ^1H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CH_3), 1.6–2.2 (m, 4 H, methylenes at C-3 and C-4), 2.3–3.4 (m, 5 H, benzylic CH_2, CH_2 α to N, NH), 3.73 (s, 3 H, CO_2CH_3), 7.1–7.2 (m, 4 H, aromatic H); UV (EtOH) 252 nm (ϵ 821), 259 (848), 266 (978), 273 (962); ^{13}C NMR ($CDCl_3$) δ 175.9 (s, C=O), 148.5 (s, quaternary aromatic α to spirocyclic junction), 140.4 (s, other quaternary aromatic), 127.5, 126.8, 125.2, 122.4 (d, aromatics), 77.5 (in acetone-d_6, s, C-2), 57.8 (s, C-9), 51.5 (q, OMe), 46.5 (t, C-3), 41.4 (t, C-8), 31.5 (t, C-4), 27.5 (5, C-4), 21.9 (q, CH_3); high-resolution mass spectrum, m/e 245.140882 ($C_{15}H_{19}NO_2$ requires 245.141565).

For **24** (R_f 0.48): IR ($CHCl_3$) 3050, 2940, 2860, 1725, 1630, 1460, 1440, 1380, 1280, 1210, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (s, 3 H, CH_3), 1.52–2 (m, 4 H, methylenes at C-3 and C-4), 2.3–3.7 (m, 5 H, NH, benzylic CH_2, CH_2 α to N), 3.71 (s, 3 H, CO_2CH_3), 7.10–7.25 (m, 4 H, aromatic H); mass spectrum (70 eV), m/e 245 (M^+, 64), 230 (30), 214 (12), 187 (19), 186 (100), 184 (20), 158 (36), 157 (16), 144 (18), 130 (23), 128 (12), 117 (12), 115 (12); UV (EtOH) λ_{max} 259 nm (ϵ 1005), 266 (1047), 272 (906); ^{13}C NMR ($CDCl_3$) δ 176.3 (s, C=O), 149.5 (s, quaternary aromatic α to spirocyclic junction), 139.0 (s, other quaternary aromatic C), 127.2, 126.9, 124.8, 122.3 (d, aromatics), 77.9 (in acetone-d_6, s, C-3), 57.9 (s, C-9), 51.8 (q, OCH_3), 47.4 (t, C-3), 41.0 (t, C-8), 36.3 (t, C-5), 25.5 (t, C-4), 20.5 (q, CH_3); high-resolution mass

spectrum, *m/e* 245.142 583 ($C_{15}H_{19}NO_2$ requires 245.141 565).

A dark control experiment was run in the following manner. A mixture of the pyrroline (100 mg, 0.69 mmol), methyl methacrylate (5 mL), and 70% (w/w) perchloric acid (135 mg, 0.94 mmol) in 50 mL of CH_3OH was heated at reflux for 20 h and was worked up as in the photochemical reaction. No reaction of the pyrroline was evident by GLC and ^1H NMR analyses.

Irradiations of 2-Phenyl-1-pyrrolinium Perchlorate and the Electron-Deficient Olefins in Acetonitrile. When photolyses were conducted with the iminium salt **2** and either methyl acrylate, acrylonitrile, or methyl methacrylate at −20 °C with the same concentrations of iminium salt and olefin, the spirocyclic amines were obtained in approximately the same reaction yields. With methyl methacrylate, the spirocyclic amines **24** (333 mg, 49%) were isolated after molecular distillation (ca. 95% pure by GLC analysis). When methyl acrylate was used, the spirocyclic amines **23** (326 mg, 58%, based on recovered pyrroline (54 mg)) were obtained (ca. 90% pure by GLC analysis). The amines **22** (ca. 200 mg) were obtained when acrylonitrile was used.

Isopropenylcyclopropane. Methylenetriphenylphosphorane was prepared by adding *n*-butyllithium in decalin (1.4 M, 125 mL, 0.18 mol) to triphenylmethylphosphonium bromide (80.4 g, 0.23 mol) in 150 mL of dry decalin under Ar over 1–2 h with stirring. Methyl cyclopropyl ketone (12.6 g, 14.8 mL, 0.15 mol) was added dropwise to the phosphorane solution over 30 min. The mixture was allowed to stir for an additional 30 min. Distillation (to 180 °C) gave 15.6 g of product consisting mainly of benzene and the olefin. Separation of the vinylcyclopropane was accomplished by GLC (20%, SE-30, 15 ft × $^5/_{16}$ in., 50 °C) from which isopropenylcyclopropane (6.2 g, 50%) was obtained in greater than 99% purity.

Photolysis of 2-Phenylpyrrolinium Perchlorate with Isopropenylcyclopropane. Preparation of 2-Phenyl-2-(1-methoxy-2-cyclopropylprop-2-yl)pyrrolidine (17). An argon-purged solution containing 2-phenyl-1-pyrroline (50 mg, 0.34 mmol), 70% (w/w) perchloric acid (ca. 60 mg, 0.42 mmol), and 2 mL of isopropenylcyclopropane in 25 mL of methanol was irradiated (Corex) for 4.25 h at 0 °C. Solid K_2CO_3 was then added, the mixture was stirred for 3 min before the K_2CO_3 was removed by filtration, and the photolysate was concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate and brine, dried (Na_2SO_4), and concentrated in vacuo to give an oil (ca. 95% pure by GLC analysis). An analytical sample of pure photoadduct **17** was obtained by TLC (silica gel, 60% ether–hexane). The spectral data are as follows: IR ($CHCl_3$) 3080, 2970, 2900, 1630, 1450, 1380, 1210, 1100, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, CH_2Cl_2 as internal standard) δ 0.08–0.40 (m, 4 H, cyclopropyl methylenes), 0.49, 0.53 (s, 3 H, diast methyls), 0.6–3.7 (m, 9 H, all other ring protons, NH), 3.28 (s, 3 H, OCH_3), 7.0–7.6 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 147 (12), 146 (100), 117 (4), 91 (5), 77 (5), 55 (4), 45 (5), 43 (4), 41 (9), 39 (4); UV (EtOH) λ_{max} 258 nm (ε 820), 263 (605), 268 (487); ^{13}C NMR ($CDCl_3$) δ 144.6, 144.2 (s, C-1 aromatic), 80.1 (t, CH_2 α to O), 75.0 (s, C-2 or pyrrolidine ring), 59.1 (q, OCH_3), 44.8, 44.4 (t, C-5 of pyrrolidine ring), 41.9 (s, quaternary α to cyclopropyl ring), 33.9, 33.7 (t, C-3 of pyrrolidine ring), 24.7, 24.6 (C-4 or pyrrolidine ring), 15.1, 14.6, 14.1, 13.8 (d and q, CH of cyclopropyl ring, CH_3); high-resolution mass spectrum (70 eV), *m/e* 146.096 499 ($C_{10}H_{12}N$ requires 146.096 970).

Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.52; H, 9.99; N, 5.34.

Quantum Yield Measurements. Quantum yields were measured by using a "linear optical bench" system equipped with a high-pressure, 500-W mercury lamp (Illumination Industries Model CA-200-8003), the output of which was focused with a quartz collimator and passed through a quartz-faced, water-cooled filter solution cell with three 1-cm compartments containing separately 1.0 M (262.86 g/L) nickel sulfate hexahydrate in 5% sulfuric acid, 0.8 M (224.88 g/L) cobalt sulfate heptahydrate in 5% sulfuric acid, and 0.0001 M (0.0315 g/L) bismuth chloride in 10% hydrochloric acid. The UV transmission of this filter system was 250–310 nm, with a maximum at 280 nm. The filtered light passed through a beam splitter which diverted light 90°. The light not diverted passed through two quartz-faced, water-cooled cells aligned in series. During actinometer calibration runs, both the front and back cells were filled with 0.006 M potassium ferrioxalate. During photolysis runs, the front cell contained iminium salt solutions. The back cell contained potassium ferrioxalate in order to monitor light not absorbed by the substrate. The diverted light was received by a silicon solar cell in order to monitor the light output. The signal received by the solar cell was amplified and fed through a Raytheon RC-4151 voltage/frequency converter. Integration of this signal was performed by counting the frequency transmitted by the converter.

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

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

All quantum yields were determined with the solutions at 22 °C. Olefin concentrations were held constant at 1 M. The 2-phenyl-1-pyrrolinium perchlorate concentration was 0.91 mM. The total volume of solution irradiated in each run was 132 mL. Other pertinent data are listed as follows: olefin (solvent); run number; light absorbed; product(s) (amount); quantum yield of formation; percent conversion; internal standard for GLC; column temperature.

Cyclohexene (CH_3OH); run 1, 0.83 millieinstein; ether product **5** (0.0998 mmol), Φ = 0.012; olefinic product **5** (0.0167 mmol), Φ = 0.020; 2.98% conversion; pyrene; 162 °C. Run 2; 1.18 millieinstein; ether product **5** (0.0138 mmol), Φ = 0.012; olefinic product 6 (0.0229 mmol), Φ = 0.019; 4.01% conversion; pyrene; 162 °C.

Methyl β,β-dimethylacrylate (CH_3OH);[48] run 1; 0.325 millieinstein; ether adduct **14** (2.86×10^{-3} mmol); Φ = 0.008; 0.42% conversion; triphenylmethane; 160 °C. Run 2; 0.35 millieinstein; ether adduct **14** (2.69×10^{-3} mmol); Φ = 0.008; 0.50% conversion; triphenylmethane; 160 °C.

The quantum yield of the olefinic product **15** was determined based on its yield in the preparative runs as compared to that of the pyrrolizidine **14**.

Acrylonitrile (CH_3OH); run 1; 0.604 millieinstein; spirocyclic amine **22** (4.48×10^{-3} mmol); Φ = 0.008; 0.49% conversion; triphenylmethane; 160 °C. Run 2; 0.0557 millieinstein; spirocyclic amine **22** (3.35×10^{-3} mmol); Φ = 0.006; 0.37% conversion; triphenylmethane; 160 °C.

Acrylonitrile (CH_3CN); 0.63 millieinstein; spirocyclic amine **22** (1.40×10^{-2} mmol); Φ = 0.022; 1.53% conversion; triphenylmethane; 160 °C. Run 2; 0.66 millieinstein; spirocyclic amine **22** (1.38×10^{-2} mmol); Φ = 0.021; 1.52% conversion; triphenylmethane; 160 °C.

Methyl methacrylate (CH_3OH); 1.00 millieinstein spirocyclic amine **24** (7.11×10^{-3} mmol); Φ = 0.007; 0.78% conversion; triphenylmethane; 160 °C. Run 2; 0.75 millieinstein; spirocyclic amine **24** (5.35×10^{-3} mmol); Φ = 0.007; 0.59% conversion; triphenylmethane; 160 °C.

Methyl methacrylate (CH_3CN); 0.67 millieinstein; spirocyclic amine **24** (1.87×10^{-2} mmol); Φ = 0.028; 2.06% conversion; triphenylmethane; 160 °C. Run 2; 0.62 millieinstein; spirocyclic amine **24** (1.83×10^{-2} mmol); Φ = 0.030; 2.01% conversion; triphenylmethane; 160 °C.

Fluorescence Quantum Yields and Fluorescence Quenching Experiments. Fluorescence measurements were taken by using either a Spex Fluorolog or an Aminco-Bowman ratio spectrofluorometer. The observed emission was shown to correspond to the fluorescence of the substrates by the identities of excitation and absorption curves and by the mirror image relationships between excitation and emission curves. The relative fluorescence quantum yields of 1-phenyl-1-pyrrolinium perchlorate and related systems were measured in degassed solutions at 25 °C according to the method of Parker and Reese[49] using naphthalene (Φ_f = 0.205 in ethanol[50]) as the standard.

The concentrations of the quenchers were normally in the 10^{-3}–10^{-1} M range, and in the cases where quenching was not very efficient, the range extended to 1 M. In most cases the fluorescence was measured at seven quencher concentrations. The iminium salt concentrations were in the (3–7) × 10^{-5} M range. The values of k_q and k_d were obtained from Stern–Volmer plots of the data. The confidence factor (r^2) from the least-squares analyses of the plots was 0.98 or better for all quenchers.

Singlet Lifetime Measurement. The singlet lifetime was measured by using a single photon counting, nanosecond spectrofluorometer based upon ORTEC components. An acetonitrile solution containing 2-phenyl-1-pyrrolinium perchlorate (7×10^{-5} M) was degassed prior to and maintained at 25 °C during the measurement. The value for τ (16 ns) was calculated by a Digital RXOI computer using the method of moments program. The instrument was calibrated by using the quinine bisulfate standardization method.[51]

(48) A correction was made for light absorbed by olefin.
(49) Parker, C. A.; Reese, W. T. *Analyst (London)* **1960**, *85*, 587.
(50) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251.
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Polarography. The reduction potential of 2-phenyl-1-pyrrolinium perchlorate **2**; (0.87 V) was obtained through differential pulsed polarography (Parr Model 174A) at a dropping mercury electrode. The experimental conditions were as follows: concentration of iminium salt, $\sim 2 \times 10^{-4}$ (CH_3CN); concentration of electrolyte (tetraethylammonium perchlorate), 0.1 M; reference electrode, saturated calomel electrode; range, 0 to -1.5 V; sensitivity, 5 μA; scan rate 2 mV/s.

Acknowledgment. Financial support by the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged. Partial financial support from the Robert A. Welch Foundation and NSF (Grant No. CHE 8009813) is acknowledged.

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

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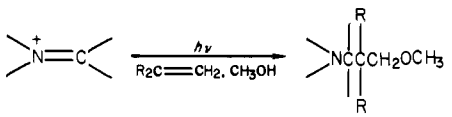
Received October 10, 1980

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

Introduction

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

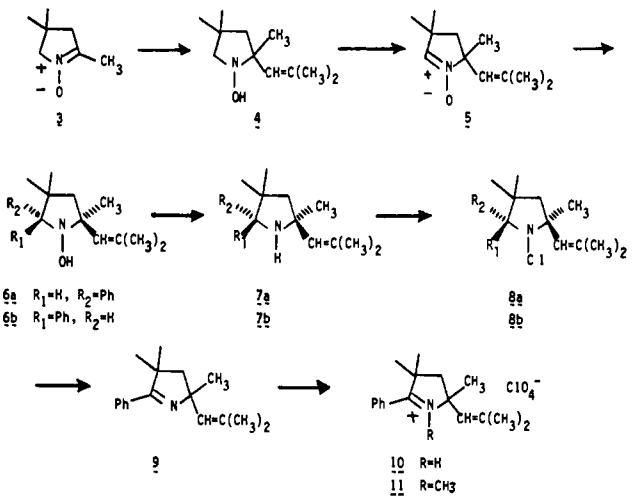


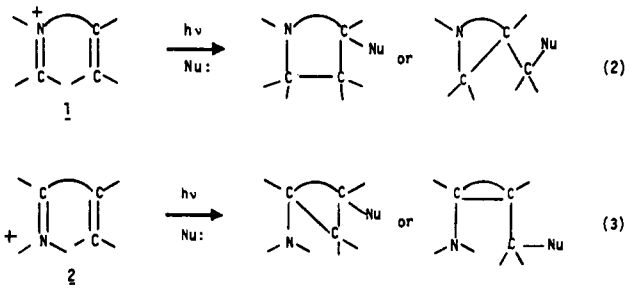
(1)

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

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

Scheme I





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