The Chemistry of Allene Cation Radicals Probed by the Use of Theoretical and Electron-Transfer Photochemical Methods[1]

Keith Haddaway, Kenichi Somekawa,[2] Paul Fleming, John A. Tossell, and Patrick S. Mariano*

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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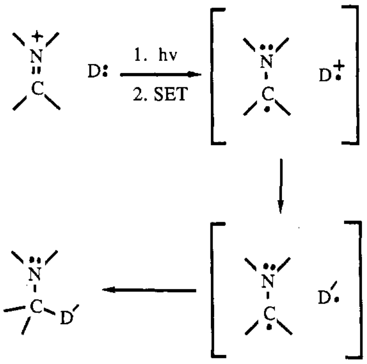
Theoretical and photochemical methods have been used to probe the structures, electronic distributions, and solution-phase chemical properties of allene cation radicals. Results of SCF-level (UHF) calculations show that the linear-45°-twisted structure of the parent allene cation radical represents the minimum energy geometry and that this species has high positive charge density at the central carbon and large odd electron density at the terminal carbons. In comparison, the linear-nontwisted structure serves as the low energy geometry for the 1,1-dimethylallene cation radical. Charge and odd electron density in this system are localized in the dimethyl-substituted C=C π-bond. The electron-transfer photochemistry of allenes with the electron acceptor, 2-phenyl-1-pyrrolinium perchlorate (**6**), is in accord with these representations of allene cation radicals. Photoadditions of allene to **6** in methanol give the allenyl-, propargyl-, and (methoxyallyl)pyrrolidines **15**–**17**. Analogous adducts are formed in 1,1-dimethylallene, tetramethylallene, and 1,2-cyclononadiene photoadditions to **6**. Mechanisms for these photoadditions involving generation of intermediate allene cation radicals by electron transfer to the singlet excited state of **6** are presented. Product formation occurs by deprotonation or methanol addition to the intermediate allene cation radicals followed by coupling of the resultant neutral radical pairs. Support for this proposal comes from studies of photoadditions of the allylsilane **34**, allenylsilane **41**, and propargylsilanes **42** and **43** to pyrrolinium salt **6**. These processes occur through documented pathways involving sequential electron-transfer–desilylation processes. Finally, photoadditions of allenes to **6** in acetonitrile follow 2 + 2 and 4 + 2 cycloaddition routes, the nature of which depends upon the allene used. The chemo- and regiochemical selectivities of these processes are discussed in terms of solvent polarity dependent partitioning of singlet exciplex intermediates to cycloadducts or radical ion pairs.

Interest in the area of photochemistry over the past decade has remained high as a result of a number of efforts focusing on excited-state processes which are promoted by electron transfer in donor–acceptor pairs.[3] The number of new and, in some cases, synthetically useful[3c] transformations following these pathways has broadened the applications of photochemical reactions in organic chemistry. Studies of this aspect of photochemistry have facilitated the exploration of physically interesting phenomena associated with excited-state complex formation and decay[4] and with distance, orientation, and energetic requirements for single electron transfer.[5] Time-resolved flash techniques for promotion of electron transfer have been ingeniously applied in investigations targeted at an understanding of the intimate details of ion pair structure and reaction dynamics.[6] Excited-state electron transfer serves as a photoelectrochemical technique for generating ion radical species from neutral precursors. As such, this method has been applied in studies of theoretically interesting radical cation intermediates whose production under controlled conditions would be otherwise difficult.[7]

Scheme I



Our attention during the past years has concentrated on the photochemistry of systems containing the iminium salt grouping. These investigations have uncovered interesting electron-transfer[8-11] and cycloaddition[8,11,12] processes of these systems. Mechanistic analysis of SET reactions occurring in donor–iminium salt systems (Scheme I) has demonstrated that the pathways followed are influenced by secondary transformations of initially formed cation radical intermediates $D^{\bullet+}$. In a complementary way, the adducts produced in these photochemical reactions (Scheme I) contain information about the solution-phase chemistry ($D^{\bullet+} \rightarrow D'^{\bullet}$) of the cation radical intermediates. As a result, these processes should aid in the evaluation of the charge and odd electron distributions in cation radicals systems.

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[2] Current address: Department of Applied Chemistry Kogoshima University, 1-21-40 Korimoto, Kagoshima, 890, Japan.

[3] For some recent reviews of single-electron-transfer photochemistry, see: (a) Fox, M. A. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Gollnick, K., Ed.; John Wiley and Sons: New York; 1986. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (c) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (d) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (e) Mariano, P. S.; Stavinoha, J. L. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 145. (f) Davidson, R. S. In *Molecular Association*; Foster, R., Ed.; Academic Press: New York, 1985; p 215.

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[9] Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130.

[10] Mariano, P. S. *Tetrahedron* **1983**, *39*, 3845.

[11] Mariano, P. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York; Vol. 8, in press.

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Table I. Structure vs. Energy Relationships for $[C_3H_4]^{\bullet+}$ Calculated by SCF (UHF) Methods

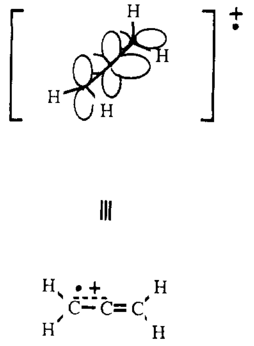
structure (symmetry)	energy relative to linear-44.7°-twist structure (kcal/mol) STO-3G	4-31G[c]
linear-0°-twist[a]	5.7	6.2
linear-30°-twist[a]	1.2	0.9
linear-44.7°-twist[b]	0.0	0.0
linear-60°-twist[a]	0.7	1.1
linear-90°-twist (D_{2h})[a]	2.0	4.3
bent-90°-twist (C_{2v})[a]	16.7	

[a] Bond lengths and angles are fully optimized. [b] The minimum energy geometry results from a complete structural optimization. [c] STO-3G geometries were used.

We have used this methodology in the context of a wider effort aimed at an investigation of allene–iminium salt photochemistry. Our initial goal was to explore the nature of reactions followed in these systems with the hope of gaining knowledge about the structure/reactivity patterns of allene cation radicals. The results reported below summarize various aspects of this effort. In addition, during the course of these studies we have uncovered an interesting solvent effect of the nature (SET vs. cycloaddition) of excited-state reactions of allene–iminium salt systems.

Theoretical Aspects. A preliminary valence-bond analysis of the parent allene cation radical $[C_3H_4]^{\bullet+}$ suggests that three limiting structures, each having unique electronic characteristics, are possible. The linear-0°-twisted structure **1** has the cation and radical centers localized in one of the two π-systems. Only π_{C-C}–σ_{C-H} hyperconjugative delocalization is available for stabilization. Its chemical behavior should closely resemble that of simple olefin derived cation radicals. The linear-90°-twisted (D_{2h}) species **2** would possess π-delocalization and high positive charge density at the central carbon.[13] Chemically, **2** would resemble a vinyl cation/allyl radical system. The allyl cation/vinyl radical representation **3** would best reflect the electron distribution in a bent-90°-twisted (C_{2v}) structure.[13]

Both prior to and simultaneous with our efforts, the structure of $[C_3H_4]^{\bullet+}$ was probed by use of spectroscopic (mass spectrometry,[14] electron spin resonance methods,[15] and photoelectron spectroscopy[16]), electrochemical[17] and molecular orbital techniques.[18] We have employed theoretical methods to gain a more clear picture of the relative energies and electronic properties of the limiting (**1**–**3**) and intermediate allene cation radical structures. The parent species $[C_3H_4]^{\bullet+}$ was investigated by use of SCF (UHF) level, ab initio methods with minimal (STO-3G) and a higher order (4-31G) basis sets[19] and the GAMESS program.[20] The fixed geometries represented by **1**–**3** as well as other linear structures with different twist angles were treated; bond angle and length optimization were allowed in order to obtain minimum energy species. In addition, a complete geometry optimization was conducted to find the minimum energy structure for $[C_3H_4]^{\bullet+}$. The results of these calculations in terms of the relationships between structure and energy, electron distribution, and bond lengths are summarized in Tables I and II. As can be seen, the linear and bent structures **1**–**3** have properties predicted on the basis of simple valence-bond reasoning. For example, lengthening of only the oxidized (C_1–C_2) π-bond in **1** is apparent in the optimized linear-0°-twisted species. Also, odd electron and positive charge densities exist at the carbons flanking the oxidized π-bond. The allyl radical/vinyl cation representation of **2** is supported by the equal and high odd electron density at the terminal carbons and high positive charge density at the central carbon in the linear-90°-twisted structure. Finally, the bent-90°-twisted cation radical has an electron distribution corresponding to a vinyl radical/allyl cation.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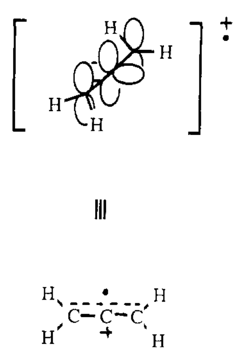
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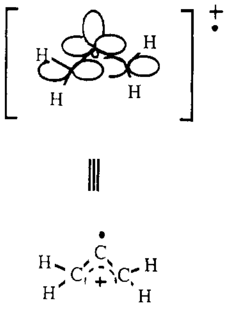
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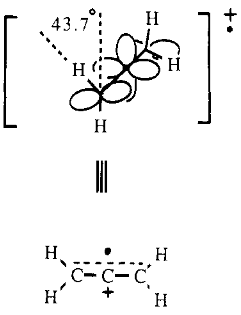

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The calculations suggest that twisting along the allene cation radical major axis leads to a reduction in energy (see Table I). Indeed, a complete geometry optimization of $[C_3H_4]^{\bullet+}$ revealed that the minimum energy structure corresponds to a linear system with 44.7° twisting (**4**). Importantly, this structure is similar to those found to be of lowest energy by other theoretical methods,[18b,d,e] by the analysis of fine structure associated with the PES spectrum of allene,[16] and by interpretation of the hyperfine splitting in the ESR spectrum of allene.[15] The comparable results are summarized in Table III. It should be noted, however, that Pasto[18c] has suggested that the bent-90°-twisted structure **3** is the most stable form of $[C_3H_4]^{\bullet+}$.

These calculations provide further insight into the electronic characteristics of minimum energy allene cation radicals. The positive charge density in **4** is weighted heavily on the central rather than terminal carbons and a large degree of charge delocalization into the C–H σ-

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(13) (a) Based upon sp and sp^2 hybridization of vinyl cations and radicals, respectively. (b) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808 and references therein.

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(18) (a) Frenking, G.; Schrarz, H. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 131. (b) Hasselbach, E. *Chem. Phys. Lett.* **1970**, *7*, 428. (c) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805. (d) We thank Professor Nathan L. Bauld and Kurt Lorenz for performing the MNDO (UHF) calculations.

(19) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1964**, *51*, 2657.

(20) Dupois, M.; Spangler, D.; Wendolowski, J. *Nat. Resor. Comput. Chem. Software Cat.* **1980**, *1*, Program No. QG01.

Table II. Charge and Odd Electron Densities and Bond Lengths for the Allene and 1,1-Dimethylallene Cation Radicals

	charge density		odd electron density[a]		
structure	terminal C	central C	terminal C	central C	bond lengths (Å)
		Allene			
linear-0°-twist	−0.10 (C_1) 0.33 (C_3)	+0.12	0.61 (C_1) 0.07 (C_3)	0.25	1.41 (C_1–C_2) 1.31 (C_2–C_3)
linear-30°-twist	−0.23	+0.13	0.34	0.27	1.35[b]
linear-44.7°-twist	−0.25	+0.17	0.38	0.20	1.35[b]
linear-60°-twist	−0.30	+0.22	0.43	0.11	1.35[b]
linear-90°-twist	−0.32	+0.28	0.50	0.00	1.36[b]
bent-90°-twist			0.06	0.69	
		1,1-Dimethylallene			
linear-0.1°-twist	+0.20 (C_1) −0.09 (C_3)	+0.16	0.28 (C_1) 0.05 (C_3)	0.36	1.41 (C_1–C_2) 1.32 (C_2–C_3)

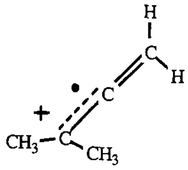
[a] Calculated from 4-31G basis set results at STO-3G geometries except for 1,1-dimethylallene which was calculated by using a STO-3G basis sets. [b] C_1–C_2 and C_2–C_3 bond lengths are equal.

Table III. Twist Angles Corresponding to the Minimum Energy, Linear Structures for $[C_3H_4]^{\cdot+}$

twist angle (deg)	method	ref
44.7	ab initio SCF(UHF) STO-3G and 4-31G	this work
52.0	MINDO/2	18a
45.0	MNDO-UHF	18d
52.0	doublet RHF(STO-3G)	18e
52.0	PES	16
50–60	ESR	15

bonds occurs (+0.34 at each H). To complement this, odd electron density is found to be high at the equivalent terminal carbons. In valence-bond terms, stabilization of 4 arises through partial maintenance of π-bonding in the oxidized π-bond, delocalization via a twisted allylic system, and hyperconjugative delocalization trough interaction of all four C–H π-bonds with the p orbitals at the central carbon.

In order to test the effects of alkyl substitution on structure, ab initio calculations (STO-3G) were conducted with complete geometry optimization on the 1,1-dimethylallene cation radical. The results show that a linear species with less than 1°-twisting, **5**, is the structure of minimum energy. This results is in agreement with the conclusions drawn by Cederbaum and his co-workers[16] on the basis of PES data. In addition, the localized cation radical nature of **5** is reflected in bond length, charge density, and odd electron density results summarized in Table II. Thus, oxidation of the substituted π-bond has occurred in this system and the cation radical generated is stabilized by alkyl substituents and as a result does not require twisting for further stabilization.



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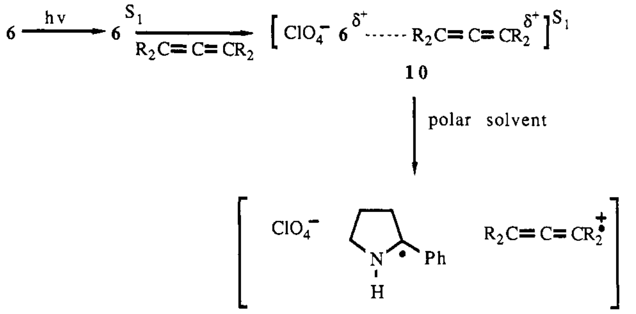
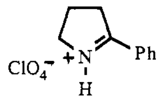
Mechanistic Considerations. With this theoretical view of allene cation radical structures and electronic distributions in mind, we next turned our attention to thoughts about generating and exploring the chemical properties of these reactive intermediates. Oxidation of allenes by one-electron transfer has been probed earlier by electrochemical techniques. Becker[17] has shown that the ground-state oxidation potentials ($E_{1/2}(+)$) of allenes in acetonitrile vary in the expected manner upon alkyl group substitution in the range of 1.8 to 2.1 V. The criteria for efficient electron transfer in excited-state systems suggest that allene cation radicals should be generated at near diffusion controlled rates[5] when the ground-state systems interact with acceptors having excited-state reduction potentials ($E_{1/2}^*(-)$) greater than ca. 2.1 V. Thus, electron transfer from allenes to singlet excited states of the 2-phenyl-1-pyrrolinium salt **6** ($E_{1/2}{}^{S_1}(-)$ = 2.9 V)[9] should be efficient. Indeed, the rate constants for fluorescence quenching of **6** by the allenes **7**–**9** (Table IV) are indicative of this feature. Specifically, these data show that these allenes are capable of participating in singlet exciplex $\mathbf{10}^{S_1}$ formation with $\mathbf{6}^{S_1}$ in which charge transfer occurs from the allene π-donor to the iminium salt acceptor (Scheme II). In solvents of high polarity (i.e., those capable of supporting charge separation) the exciplex $\mathbf{10}^{S_1}$ should dissociate into ion radical pairs or free species containing the allene cation radicals.[4]

Table IV. Fluorescence Quenching of Pyrrolinium Perchlorate 6 by Various Allene and Acetylene Donors

quencher	$10^9 k_q$ (25 °C, MeCN), $M^{-1} s^{-1}$
$Me_2C{=}C{=}CH_2$	5.6
$Me_2C{=}C{=}CMe_2$	3.8
$Me_2C{=}C{=}CHTMS$	8.1
$HC{\equiv}CCMe_2TMS$	4.7
$HC{\equiv}CCH_2TMS$	5.1

Scheme II





6

$R^1_2C{=}C{=}CR^2_2$

7 (R^1= H, R^2 = Me)

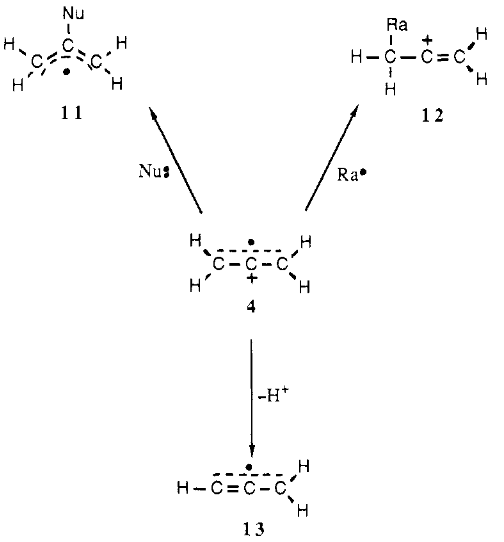
8 (R^1= R^2 = Me)

$Me_2C{=}C{=}CHTMS$

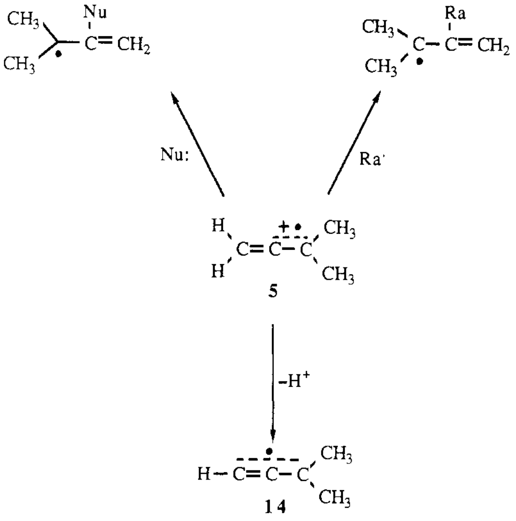
9

The theoretical pictures developed for the allene cation radicals aid in predicting the chemical reactivity profiles expected for these species. For the linear-45°-twisted species **4**, nucleophile capture should occur at the central carbon if charge density and developing radical stability are controlling factors (Scheme III). Note that the twisting in **4** allows for continuous orbital overlap in the reorganization required for developing allylic delocalization

Scheme III



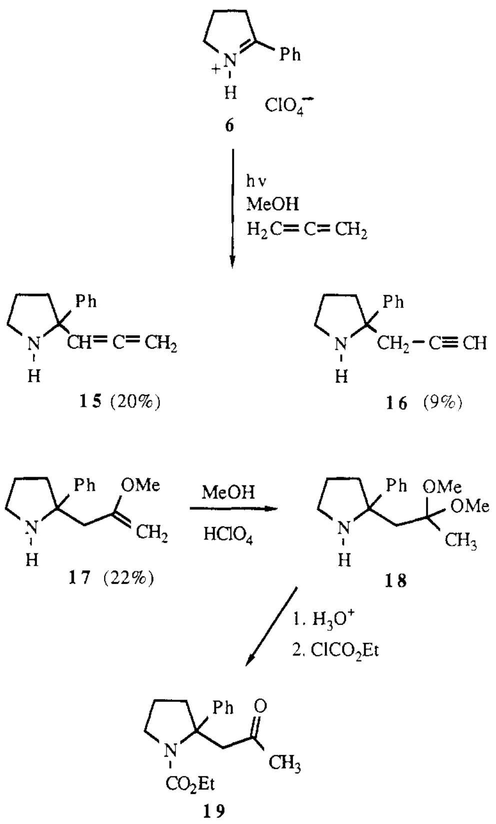
Scheme IV



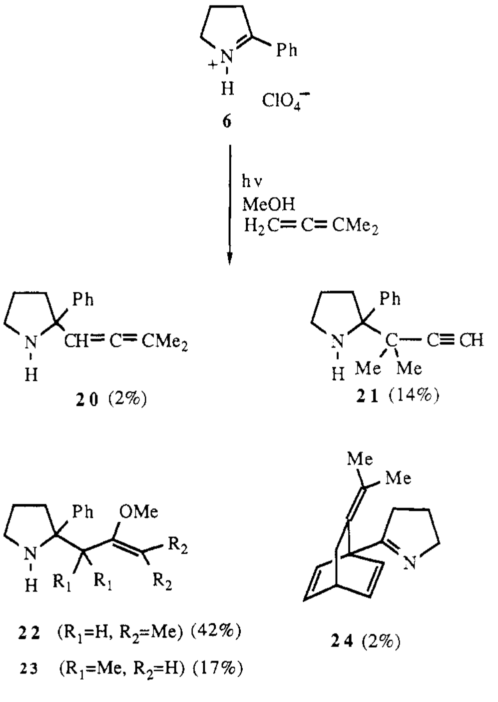
in **11**. Radical coupling to **4**, on the other hand, should be controlled by odd electron densities and, thus, prefer to occur at the terminal carbons producing vinyl cation **12**. Alternatively, loss of electrofugal groups (H$^+$) from **4** could occur to give the propargyl radical **13**. A predisposition for these processes should exist owing to the good orbital overlap in association with stabilizing effects of the σ_{C-H} or σ_{C-Si} bonds. The close correspondence between the 1,1-dimethylallene linear-0°-twisted cation radical with that derived from isobutylene suggests that radical and nucleophile addition should show preference for the central carbon as result of steric effects. Here twisting during or following addition is required for development of the allylic cation or radical framework. Finally, the σ_{C-H} orbitals at C-3 are perfectly oriented to allow for deprotonation to generate the propargyl radical **14** (Scheme IV).

Allene Photoadditions to 2-Phenyl-1-pyrrolinium Perchlorate in Methanol. Studies linking theoretical predictions of allene cation radical structure and electronic properties with chemical reactivity began with exploration of photoaddition reaction of allenes with 2-phenyl-1-pyrrolinium perchlorate (**6**). This salt, prepared by in situ protonation (1.3 equiv; 1.3 × 10^{-2} M $HClO_4$) of the corresponding pyrroline, was selected on the basis of its well-studied excited-state and electron-transfer properties.[8,9] Photoreactions are initiated by irradiation (Corex, λ >250 nm) of **6** (1 × 10^{-2} M) in methanol solutions (1 × 10^{-1} M)[21] of allene, 1,1-dimethylallene, tetramethylallene, and 1,2-cyclononadiene. The results of these processes are summarized in Schemes V–VIII.

Scheme V



Scheme VI



Irradiation of **6** in methanol solutions of allene followed by silica gel chromatography led to isolation of the allenyl (**15**), propargyl (**16**), and methoxyallyl (**17**) pyrrolidines in respective yields of 20%, 9%, and 22% (Scheme V).

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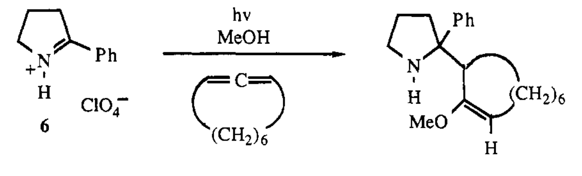
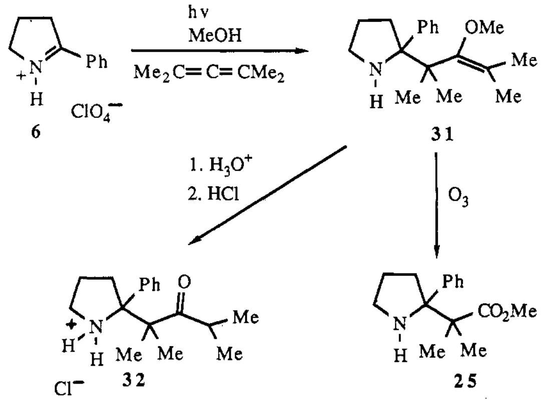
(21) Concentrations of the allenes are sufficient (based upon fluorescence quenching rate data) to insure that all singlets of **6** are captured.

Scheme VII



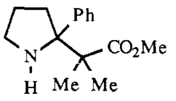
29 +30 (54%)

Scheme VIII



Structural assignments to these products were based upon spectroscopic data (Experimental Section). Also, the product ratios under these conditions were unaffected by irradiation time and were constant under dark control conditions. However, when irradiations are conducted on **6** in the presence of higher $HClO_4$ concentrations (2.3×10^{-2} M), pyrrolidines **16** and **17** are not detected in the crude photolysate. In this case, the allene adduct **15** is isolated in a 22% yield along with the dimethyl ketal **18** (21%). These differences are attributable to isomerization of **16** to **15** and methanol addition to **17** under the more strongly acidic condition. Additional evidence supporting the structures of **18** comes from isolation of keto carbamate **19** by sequential treatment of the crude photolysate (higher acid concentration) with aqueous acid and ethyl chloroformate.

Similarly, irradiation of **6** in methanol solution of 1,1-dimethylallene followed by alumina chromatography provides the adducts **20–24** (Scheme VI) which were identified by use of spectroscopic and chemical information. The alleneyl (**20**) and propargyl (**21**) pyrrolidines (2% and 14%, respectively) are produced along with the methoxyallyl pyrrolidine regioisomers **22** and **23** (42% and 17%, respectively). A minor adduct having the bicyclo[2.2.2]octadiene structure **24** is also formed (2%) under these conditions (see below). Importantly, the acetylene **21** to allene **20** ratio is independent of reaction time and is unaffected under the reaction conditions used. Ozonolysis of the allylpyrrolidines yields the corresponding amino esters **25** and **26**, the latter of which is characterized as the N-ethoxycarbonyl derivative **27**. Also, hydrolysis of enol ether **23** and hydration of acetylene **21** lead to production of the same aminoketone **28**.



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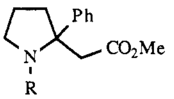
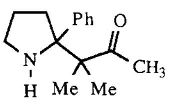


26 (R=H)

27 ($R{=}CO_2Et$)



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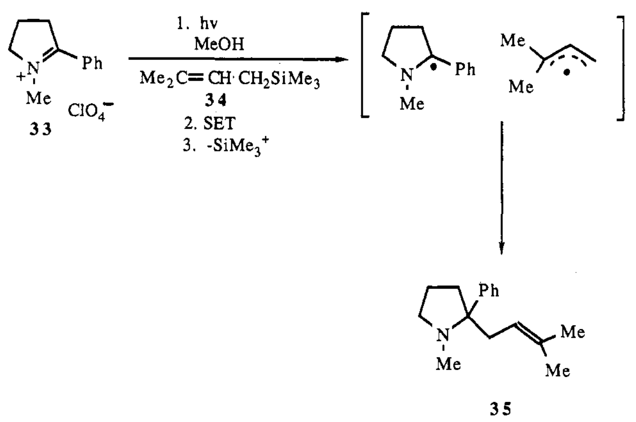
Scheme IX



1,2-Cyclononadiene photoaddition to pyrrolinium salt **6** in methanol gives rise to vinyl ether adducts, obtained as a separable (alumina) mixture of diastereomers **29** (26%) and **30** (28%) (Scheme VII). While spectroscopic analyses confidently support the structural assignments of these substances, they do not provide sufficient information to distinguish the erythro and threo isomers.

Finally, irradiation (MeOH) of **6** in the presence of tetramethylallene leads to clean production of one product, the (methoxyallyl)pyrrolidine **31** (58%) (Scheme VIII). This compound is transformed by aqueous acid hydrolysis to an amino ketone, which is characterized as its more stable hydrochloride **32**, and to the amino ester **25** upon ozonolysis. The latter product **25** has properties identical with those of material arising by ozonolysis of the enol ether **22** (see above).

In order to gain information about the mechanism for (methoxyallyl)pyrrolidine (**22** and **23**) formation in photoreactions of the pyrrolinium salt **6** with 1,1-dimethylallene, we have explored the photoaddition of the prenylsilane **34** to **6**. Our purpose here was to determine if the adducts **22** and **23** could have arisen by radical coupling pathways. Earlier,[22] we had shown that photoadditions of allylsilanes (e.g. **34**) to the *N*-methylpyrrolinium perchlorate **33** proceeds by electron-transfer mechanisms in which desilylation of the intermediate cation radical pairs occurs to produce allyl–pyrrolidinyl radical pairs. In the case of reaction **33** + **34**, radical coupling takes place exclusively at the unsubstituted allylic center to form the prenylpyrrolidine **35** (Scheme IX). An answer to the question of whether or not this high degree of regioselectivity is displayed by allyl radical coupling to the less sterically crowded N–H pyrrolidinyl radical would be helpful in our mechanistic evaluation.

Irradiation of **6** in a methanol solution of the prenylsilane **34** followed by silica gel chromatography provided the allylpyrrolidines **36** and **37** in respective yields of 33% and 15%. These products are identified on the basis of characteristic spectroscopic properties (e.g., Me protons in **36** occur at 1.48 and 1.64 ppm while those in **37** appear at 0.91 and 1.00 ppm). Thus, it appears that coupling in the prenyl NH–pyrrolidinyl radical pair is less regioselective owing to the diminished steric crowding at nitrogen.

Allenyl- and Propargylsilane Photoadditions to the Pyrrolinium Salt 6. Additional mechanistic information about the allene–iminium salt photoaddition reactions has come from exploratory studies with the allenyl- and propargylsilanes **41–43**. As noted above, previous efforts[22,23]

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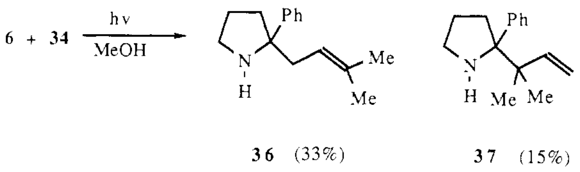
[22] Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.

[23] Lan, A. J. Y.; Quillen, S. L.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6439. Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. *Ibid.* **1984**, *106*, 6855. Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228.



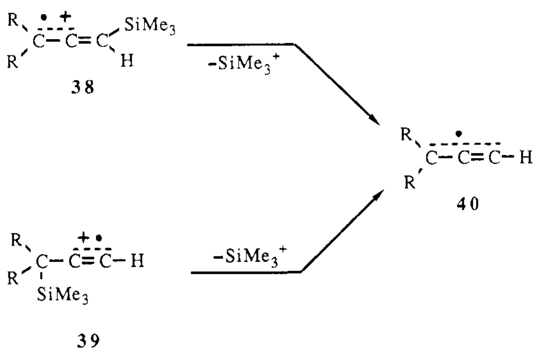
have demonstrated that cation radicals generated from silicon-substituted electron donors undergo facile desilylation to produce stabilized radical intermediates. On the basis of these observations, we envisaged that allenyl- and propargylsilane cation radicals **38** and **39** (Scheme X) would follow similar reaction pathways to generate the propargyl radicals **40**. Routes of this type would then serve as the basis for methods to independently form radicals like **40** which are potential intermediates in mechanisms for production of the allene and acetylene adducts shown in Schemes V and VI.

The allenylsilane **41** and propargylsilanes **42** and **43** were prepared by modifications of standard procedures (see Experimental Section). Irradiation of methanol solutions of the pyrrolinium salt **6** in the presence of these silanes under conditions identical with those used in the allene photoadditions described above gave after chromatography the pyrrolidines shown in Scheme XI. The product ratios in each case were independent of irradiation time and were unchanged under dark conditions identical with those present in the photolysate. In addition, photoaddition to **6** of allenylsilane **41** also occurs in acetonitrile to produce **20** and **21**. This result is interesting in light of observations eminating from other studies of allene–iminium salt photoadditions in acetonitrile discussed below.

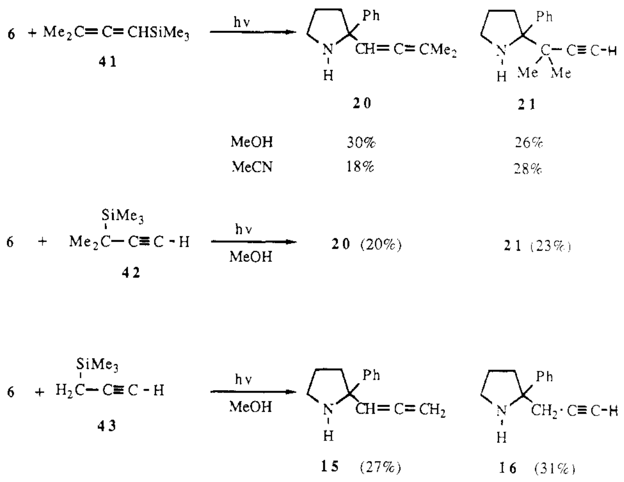
Allene Photocycloadditions to 2-Phenyl-1-pyrrolinium Perchlorate in Acetonitrile. Photoaddition reactions of allene to the 2-phenylpyrrolinium salt **6** follow remarkably different courses when the solvent is changed from methanol to acetonitrile. As the following results demonstrate, cycloaddition processes are the dominant reaction types for photoreactions of these systems in acetonitrile.

Irradiation of **6** in acetonitrile solutions containing allene provides after silica gel chromatography the four adducts shown in Scheme XII. In addition to the allene and acetylene adducts (**15** and **16** in respective yields of 15% and 5%), two other products identified as the 1,8-disubstituted cyclooctatetraene **44** (5%) and the bicyclo[4.2.0]octadiene **45** (15%) arise from this process. The presence of the 1-pyrroline ring in both **44** and **45** is indicated by characteristic ^{1}H NMR resonances for the H-3 and H-5 ring protons and the ^{13}C NMR resonance at ca. 173 ppm associated with the imine carbons. In these substances, the pyrroline ring H-3 and H-5 hydrogens appear as diastereotopic pairs, as evidenced by their nonequivalent ^{1}H NMR chemical shifts. This is expected, since chiral centers exist in the carbocyclic arrays in **44** and **45**. Significantly, the slow tub-tub conformational inversion and double-bond reorganization of the cyclooctatetraene (COT) ring in **44** imparts chirality to this group.[24] The ^{13}C NMR spectrum of **44** contains methine and quaternary resonances indicative of the COT ring. Assignment of the 1,8-methyl–pyrroline substitution pattern in **44** is based upon mass spectrometric and ^{1}H NMR results. First, the vicinal arrangement is deduced from the appearance of a peak at *m/e* 107.0745 (C_7H_9N) which arises from loss of three acetylenes from the molecular ion and which corresponds to the pyrrolinylacetylene cation radical **46**. Second, the 1,8- rather than

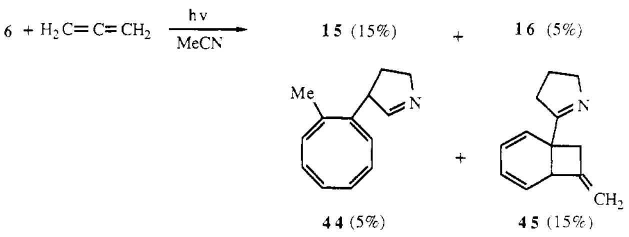
Scheme X

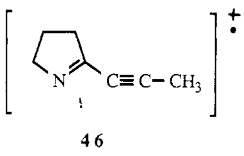


Scheme XI



Scheme XII





46

the 1,2-substitution pattern is seen by inspection of the vinyl hydrogen region of the ^{1}H NMR spectrum. Specifically, the COT-ring H-2 resonance, occurring downfield owing to mesomeric effects, appears as a simple doublet with a vicinal coupling (to H-3) constant of 3.7 Hz. This is expected for the nonzero dihedral angle relationship between H-2 and H-3 and is in accord with coupling data for the other COT ring protons (e.g., $J_{3,4}$ = 11.5 Hz, $J_{4,5}$ = 3.8 Hz).

The structure of the major adduct **45** is in complete accord with spectroscopic data. For example, the ^{13}C NMR chemical shifts for key carbons of the methylenecyclobutane ring in **45** compare favorably to those of the parent hydrocarbon (=CH_2 111 vs. 104 ppm and *C*= 149 vs. 146 ppm).

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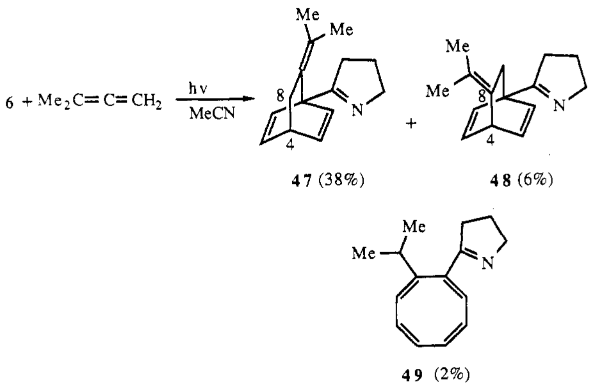
[24] Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576.

Scheme XIII



47 (38%) 48 (6%) 49 (2%)

Photocycloaddition reactions occur also when the pyrrolinium salt **6** is irradiated in acetonitrile solutions of 1,1-dimethylallene. In this case, the major adducts are the regioisomeric bicyclo[2.2.2]octadienes **47** (38%) and **48** (6%) with the 1,8-disubstituted cyclooctatetraene **49** (2%) serving as a minor product (Scheme XIII).

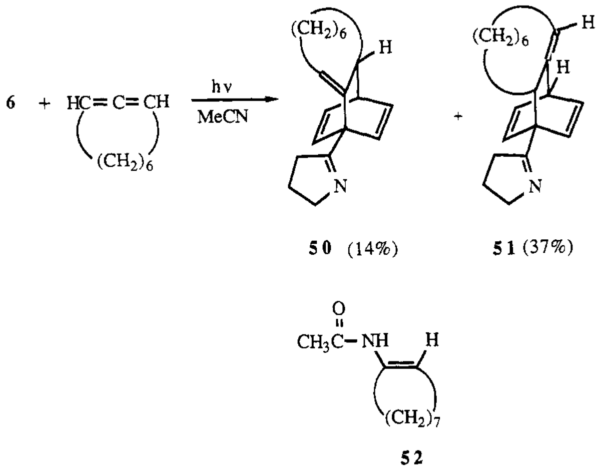
The symmetry in both of the 4 + 2 cycloadducts, **47** and **48**, is evident in their ^{13}C NMR spectra which contain only four olefinic carbons. The pyrroline ring C-2 carbon appears at ca. 180 ppm in both adducts. Distinction between these regioisomers which differ in the positioning of the isopropylidene function can be made on the basis of results from proton–proton decoupling experiments. For example, irradiation of the bridgehead proton at 3.66 ppm in the major adduct **47** results in collapse of the vinyl hydrogen resonance at 6.69 ppm (H-1 and H-6) to a doublet and in simplification of the multiplet at 2.01 ppm (H-8). Furthermore, irradiation at 2.01 ppm cause the triplet at 1.57 ppm, corresponding to the isopropylidene methyl which is syn to C-3, to collapse to a singlet. This pattern confirms the vicinal relationship between the bridgehead proton at C-4 (3.66 ppm) and the methylene hydrogens at C-8.

In contrast, the bridgehead proton (H-4) in **48** resonates at 4.41 ppm and is not coupled to the proton at H-8. The large downfield positioning of this resonance is due to the deshielding effect on H-4 of the isopropylidene π-systems.

The cyclooctatetraene **49** has spectroscopic parameters which closely match those of its methyl analogue **44**. Here again, the assignment of **49** as a 1,8-COT derivative is based upon mass spectrometric fragmentation patterns and ^1H NMR coupling data.

Irradiation of an acetonitrile solution of **6** containing 1,2-cyclononadiene leads to formation of three products consisting of a partially separable (silica gel) mixture of the bicyclo[2.2.2]octadiene derivatives **50** and **51** (2:5, 51%) and the acetamidocyclononene **52** (Scheme XIV). The solvent addition product **52** was found to arise from a nonphotochemical Ritter reaction occurring with equal efficiency in a dark control process. Repeated recrystallization (hexane) of the **50** + **51** mixture led to isolation of nearly pure (>95%) sample of the major adduct **51** (mp 93–96 °C) and material recovered from mother liquors which is highly enriched in **50**. This simplified structural and regiochemical assignments by spectroscopic methods. The similarity of both the ^1H and ^{13}C NMR spectra of **50** vs. **47** and of **51** vs. **48** suggest their structural correspondence. The chemical shifts for the H-4 bridgehead protons (3.97 ppm in **51** and 3.58 ppm in **50**) in the adducts are indicative of their regiochemistry. Major differences between the spectroscopic data for **50** and **51** as compared to **47** and **48** arise from the fact that the former substances lack symmetry in the bicyclo[2.2.2]octadiene framework.

Scheme XIV



50 (14%) 51 (37%) 52

Discussion

Several observations made in the studies outlined above warrant detailed discussion. These relate to the intriguing solvent effects noted for allene photoadditions to the pyrrolinium perchlorate **6**, the diverse types of cycloadditions seen in photoreactions occurring in acetonitrile, and the mechanisms for adduct formation in processes occurring in methanol. Importantly, all of the photoaddition reactions observed in these systems appear to be pyrrolinium salt **6** singlet-state processes based upon the fluorescence quenching results. Accordingly, the magnitudes for fluorescence quenching by the allenes (ca. 5–8 $\times 10^9$ M^{-1} s^{-1}) are sufficiently large to guarantee that the allenes (1×10^{-1} M) intercept the singlet state of **6** nearly exclusively.

Solvent Effects. In general, the results of this study indicate that photoreactions of allenes with the pyrrolinium salt occurring in methanol follow pathways which involve the intermediacy of allene cation radicals. These species are then transformed to neutral radicals by either deprotonation or methanol addition, providing neutral radical precursors of the observed adducts (see below). In acetonitrile, the nature of the processes differ in that cycloaddition of the allene to the arene grouping in **6** is the exclusive or predominant pathway followed. Importantly, the allenyl- and propargylsilanes do not cycloadd to **6** even in acetonitrile. Rather, electron transfer occurs followed by desilylation of the cation radical intermediates to produce adducts similar to those formed from the non-TMS counterparts.

Similar solvent effects have been observed in previous studies in this area. For example, the dihydroisoquinolinium perchlorate **53** is known[25] to undergo both electron-transfer-induced photocyclization to generate the spirocyclic amine **54** and intramolecular cycloaddition to form through rearrangement the tetracyclic amine **55**. The former pathway predominates when photolysis of **53** is conducted in methanol while the latter is preferred in acetonitrile irradiations. Other data which we feel relate to this issue are seen in the divergent behavior of pyrrolinium salt–olefin additions.[8] Accordingly, while isobutylene ($E_{1/2}(+)$ = ca. 2.3 V) and related electron-rich olefins photoadd to **6** in methanol to produce the adduct **56**, acrylonitrile ($E_{1/2}(+)$ = ca. 9.1 V) and other electron-poor olefins undergo 2 + 2 cycloaddition to **6** to form **57** even in methanol.

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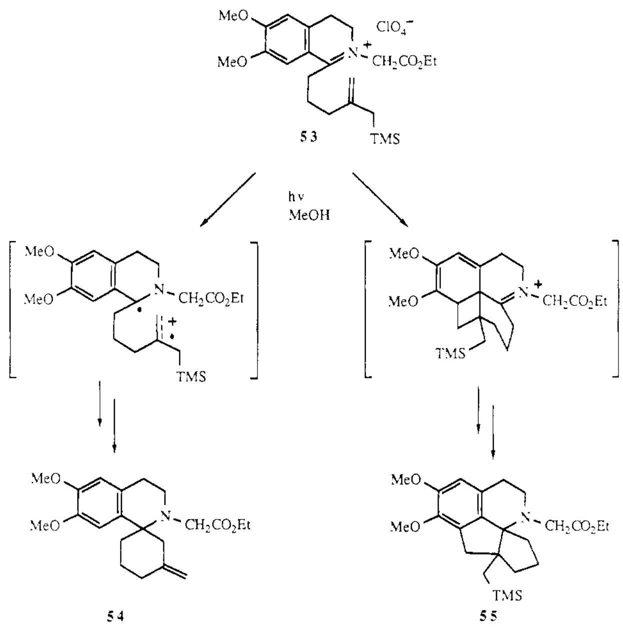
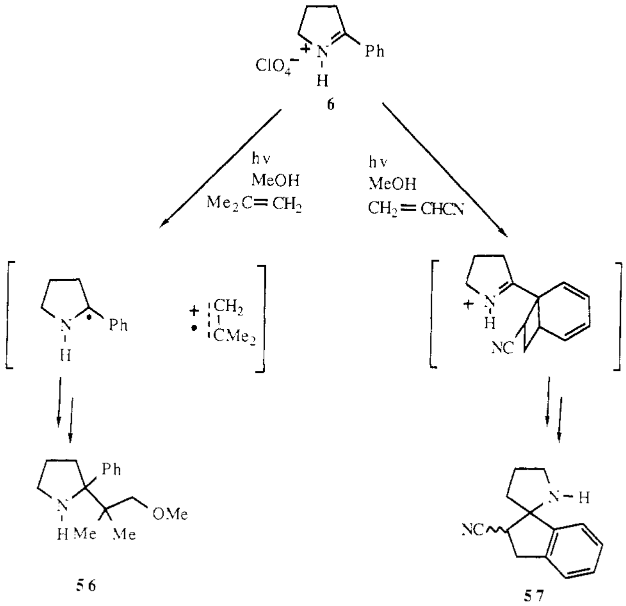
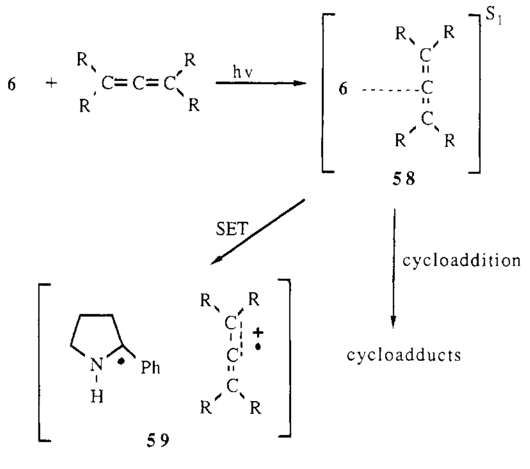
(25) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1985**, *50*, 5667.

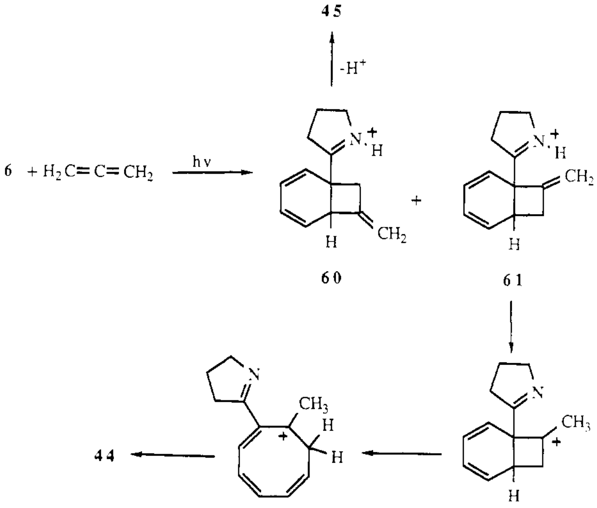




Scheme XV



Scheme XVI



These effects appear to originate from the influence of solvent polarity and donor oxidation potential on the reaction pathways available to excited-state complexes which serve as intermediates in these processes. It is clear from inspection of parameters which measure the microscopic polarity of solvents that methanol ($Z = 83.6$, $E_T = 55.5$) is better able to stabilize charge separation than the less polar acetonitrile ($Z = 71.3$, $E_T = 46.0$). In addition, the presence of an allylic C–Si σ-bond in the allenylsilane results in hyperconjugative stabilization (thermodynamic) of allene cation radicals. This phenomenon, seen in the effect of trialkylsilyl substitution on ionization and oxidation potentials,[26] results from an enhanced σ_{C-Si} π-MO interaction. Thus, the solvent and silyl substituent effects noted in the current studies appear to be due to their influence on the relative rates of electron transfer vs. cycloaddition from exciplex intermediates **58** produced by interaction of the allene π-donors with the singlet pyrrolinium salt **6** (Scheme XV). Electron transfer to form ion radical pairs **59** would be facilitated by more polar solvents which stabilize charge separation developed between the perchlorate anion and the less (compared to the iminium salt) delocalized π-cation radical. In addition, the stability of the cation radicals as judged by their oxidation potentials should also contribute to the efficiency of this pathway for exciplex collapse.

When electron transfer is inefficient, competing cycloaddition reactions related to those occurring from other exciplex intermediates[27] become important. Pathways involving partitioning of exciplexes by electron transfer vs. cycloaddition also serve to rationalize observations with the dihydroisoquinolinium salt **53** and in olefin additions to **6**.

Alternate explanations of these effects are possible. For example, both types of adducts could arise by sequences involving the contact ion pairs **59** as common intermediates. In this case, partitioning of **59** to the cycloadducts might be favorable when other reactions such as nucleophile addition, deprotonation, or desilylation of the cation radical component are unavailable. However, this rationalization suffers from the fact that it is difficult to explain the nature of the allene–pyrrolinium salt cycloadducts if they derive from collapse of cation radical pair intermediates. This point is discussed below in more detail.

Allene–Pyrrolinium Salt Cycloadditions. Allenes cycloadd to the aromatic ring of the pyrrolinium salt **6**, yielding a variety of unusually structured adducts. These include 2 + 2 cycloaddition, giving either bicyclo[4.2.0]-

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[26] Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 4429 and references therein. Bock, H.; Seidl, H. *J. Organomet. Chem.* **1968**, *13*, 87. Pitt, C. G.; Bock, H. *J. Chem. Soc., Chem. Commun.* **1972**, *11*, 146.

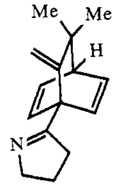
[27] Neuntefel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. Arnold, D. R.; Maroulis, A. J. *Ibid.* **1976**, *98*, 5931.

octadienes or cyclooctatetraenes, or 2 + 4 cycloaddition, generating bicyclo[2.2.2]octadienes. The parent allene participates in regioselective photocycloaddition across the ipso-ortho position of the phenyl group in **6**. This provides the protonated 7- and 8-methylidene bicyclic dienes **60** and **61**. The latter substance is not isolated as its free base but rather is transformed under the reaction conditions to the disubstituted cyclooctatetraene derivative **44**. The major differences in the stabilities of **60** and **61** might well be due to the facility for intramolecular acid catalysis of ring opening in the later substance (Scheme XVI).

2 + 2 cycloaddition to 2-phenyl-1-pyrrolinium perchlorate and related arenes is not an unfamiliar excited-state process. Thus, olefins are known to photoadd to benzonitrile, giving ipso-ortho 2 + 2 cycloadducts.[28] On the other hand, allenes do not produce 2 + 2 adducts with benzene.[29] Finally, electron-poor olefins add exclusively ipso-ortho in their 2 + 2 photocycloadditions to the pyrrolinium salt **6** (see conversion to **57** above). Interestingly, in these cases, the primary bicyclic diene photoproducts are neither stable nor do they rearrange to cyclooctatetraenes. Instead, spirocyclic amines related to **57** arise by ring expansion routes. The striking similarities and differences in these processes are remarkable.

Photocycloaddition of 1,1-dimethylallene to **6** follows a different course than that of the parent allene. Here, the major adducts **47** and **48** correspond to 4 + 2 cycloaddition across the ipso-para positions of the aromatic nucleus. A minor 2 + 2 cycloadduct derived product **49** is also formed. In addition, 1,2-cyclononadiene photoadds to **6** by a 4 + 2 route, giving adducts **50** and **51** exclusively. Although differing from the mode employed in addition of the unsubstituted allene, the 4 + 2 cycloaddition process represents the more typical behavior of allene–arene systems. Thus, Bryce-Smith[29] and Johnson[29] observed that irradiation of benzene in the presence of allene leads to formation of 1,4-adducts accompanied by products resulting from 1,3-addition.

One unusual aspect of the photoadditions of substituted allenes to **6** involves the regiochemistry of the process. In the case of 1,1-dimethylallene, the major adduct **47** has the isopropylidene group at C-7 of the bicyclo[2.2.2] framework. However, the 8-alkylidene product **51** predominates in 1,2-cyclononadiene cycloadditions. Importantly, no bicyclo[2.2.2]octadienes resulting from cycloaddition across the methyl-substituted π-moiety of 1,1-dimethyallene (e.g. **62** and **63**) are produced.



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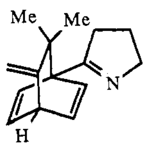
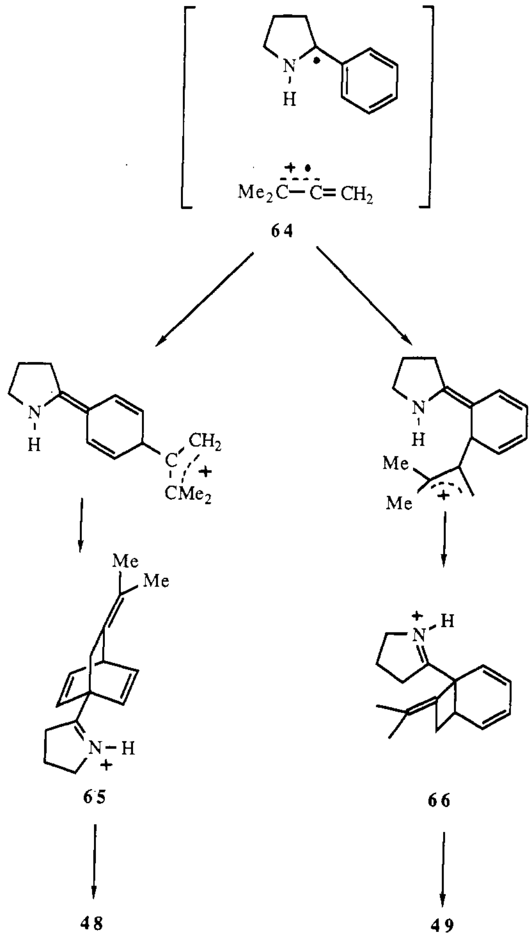


63

It is difficult to rationalize the regioselectivities observed in these cycloadditions utilizing mechanisms involving bonding in contact ion pairs. For example, while formation of the 2 + 4 adduct **48** and 2 + 2 adduct **66** (precursor of cyclooctatetraene **49**) is explainable in this fashion (Scheme XVII), it would be difficult to envisage similar routes for production of 2 + 4 adduct **47**. Thus, radical coupling in contact ion pair **64** between the para-phenyl and central dimethyallene carbons would provide a cation (**65**) capable of closing to protonated **48**. Likewise, ortho coupling would generate a precursor of **66**. However, in order to use this route to explain how the adduct **47** arises, para coupling would need to occur at the unsubstituted terminal carbon of the 1,1-dimethyallene cation radical in **66**. This is highly improbable on the basis of the theoretical results presented above. The data indicate that little if any odd electron density is located at the unsubstituted carbon center in the 1,1-dimethylallene, non-twisted cation radical.

Scheme XVII



Concerted mechanisms for these processes find precedence in the work of Gilbert[30] and Wilzbach[31] on related cycloaddition processes. In addition, Hammond[32] proposed earlier that exciplexes with charge-transfer character serve as intermediates in arene cycloadditions. Thus it appears likely that the allene–pyrrolinium salt cycloadditions reflect the chemistry of singlet exciplexes in less polar media. In this regard, the high yet varying regioselectivities for these processes might merely result from preferred orientations of the addends in these complexes.

Mechanisms for Photoadditions in Methanol. Electron-transfer mechanisms operate in allene–pyrrolinium salt photoadditions in methanol. The issue of importance in this regard is the timing of radical coupling vs. either methanol addition or deprotonation steps. In one possible route shown for allene additions in Scheme XVIII, radical coupling in the cation radical pair **67** would produce vinyl cation intermediates capable of partitioning to allene, acetylene, and methoxyallyl products by de-

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[28] Cantrell, T. S. *J. Org. Chem.* **1977**, 4238.

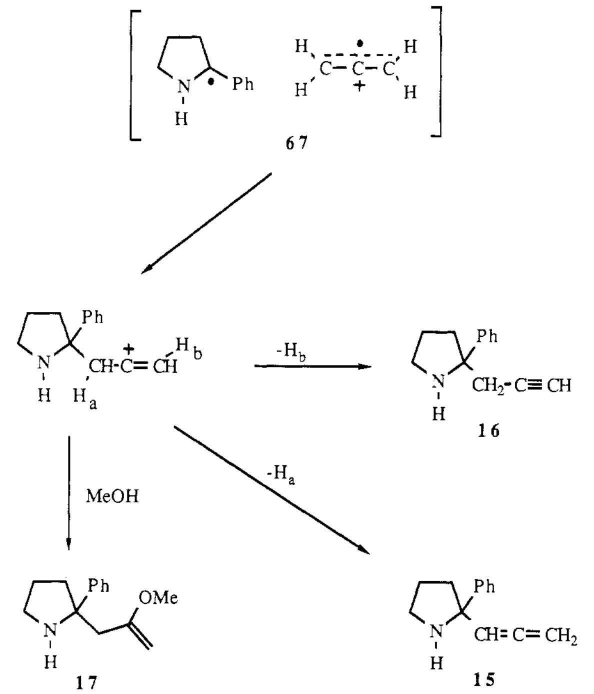
[29] (a) Bryce-Smith, D.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc. Chem. Commun.* **1972**, 664. (b) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.

[30] Berridge, J. C.; Forrester, J.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2425.

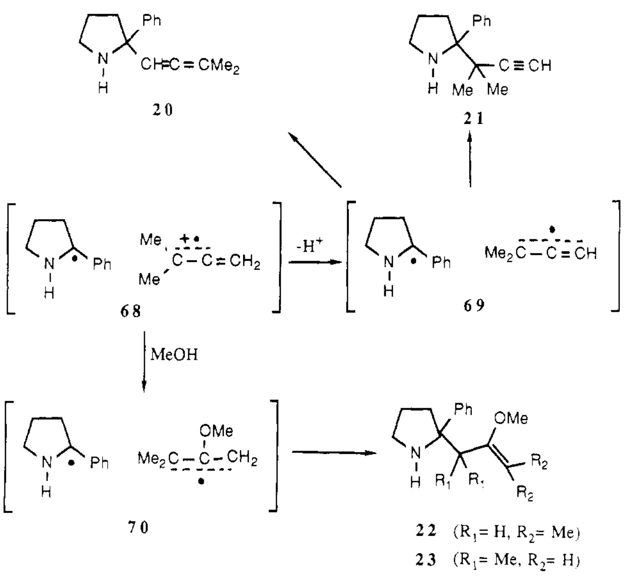
[31] Wilzbach, K. E.; Kaplan, L. *J. Am. Chem. Soc.* **1971**, *93*, 2073.

[32] McCall, M. T.; Hammond, G. S.; Yonemitsu, O.; Witkop, B. S. *J. Am. Chem. Soc.* **1970**, *92*, 6991 and references therein.

Scheme XVIII



Scheme XIX



Scheme XX

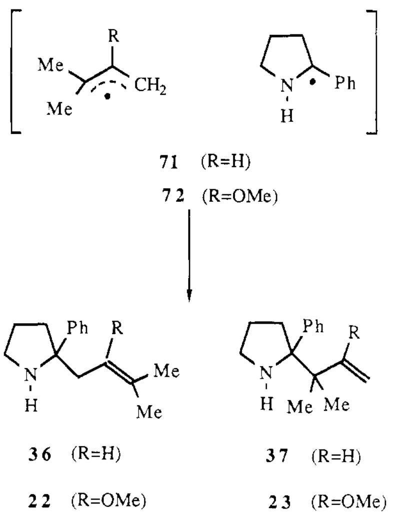


Table V. Allene/Acetylene Product Ratios from Photoadditions of Allene and Acetylenes to Pyrrolinium Salt 6

entry	substrate	solvent	product: allene	product: acetylene	allene/acetylene product ratio
a	$H_2C{=}C{=}CH_2$	MeOH	15	16	2.2:1
b	$H_2C{=}C{=}CH_2$	MeCN	15	16	3.0:1
c	$TMSCH{=}C{=}CH_2$	MeOH	15	16	0.8:1
d	$Me_2C{=}C{=}CH_2$	MeOH	20	21	0.2:1
e	$Me_2C{=}C{=}CH$-TMS	MeOH	20	21	1.2:1
f	$Me_2C{=}C{=}CH$-TMS	MeCN	20	21	0.6:1
g	$TMSMe_2CC{\equiv}CH$	MeOH	20	21	1.1:1

protonation or methanol addition. While examples of related processes involving radical coupling of radical cations have been reported,[33,34] this is not the most common mode of reaction of these intermediates.[8] In addition, this pathway cannot be used to explain production of the allenyl and (3′,3′-dimethyl-2′-methoxyallyl)pyrrolidines **20** and **22** from addition of 1,1-dimethylallene to **6**. These would require radical coupling at the unsubstituted carbon terminus in the intermediate cation radical, an unlikely event since odd electron density at this center is low.

An alternate and more likely sequence, shown in Scheme XIX for 1,1-dimethylallene additions, involves radical coupling in neutral radical pairs formed by methanol addition and deprotonation of intermediate cation radicals. This pathway is consistent with the more typical behavior of cation radical pairs[8] and is in accord with the theoretical picture of allene cation radical electronic distributions. Thus, deprotonation of the radical cation in **68** (Scheme XIX) would generate the propargyl radical pair **69**, which serves as a precursor of both the allene and acetylene adducts **20** and **21**. Also, the methoxyallyl radical **70** can couple to the α-pyrrolidinyl radical at either terminus to produce the adducts **22** and **23**.

Support of mechanisms for allene–pyrrolinium salt photoadditions in which deprotonation and methanol addition precedes radical coupling has come from studies with allyl-, allenyl-, and propargylsilanes. In earlier studies, we have provided evidence that indicates that cation radical derived from α-silyl donors undergo rapid[35] desilylation to generate radical species.[22,23] We have used this methodology (i.e., sequential electron transfer–desilylation) to generate radical intermediates that are either identical with closely related to those proposed as intermediates in this mechanistic sequence. The photoaddition of prenylsilane **34** to **6** in an example of this (see above). The allyl radical **71** (Scheme XX) which serves as an intermediate in this process is structurally similar to the allyl radical in **70** formed by methanol addition to the 1,1-dimethylallenyl cation radical. Importantly, the allylpyrrolidines, **36**, **37**, **22**, and **23**, are formed in nearly equal ratios (2.2:1 vs. 2.5:1), suggesting that the ultimate steps in both pathways involve allyl–pyrrolidinyl radical coupling.

The allenyl- and propargylsilanes **41**–**43** have been used as precursors to propargyl radical pairs related to **69** (Scheme XIX). Indeed, irradiation of pyrrolinium salt **6**

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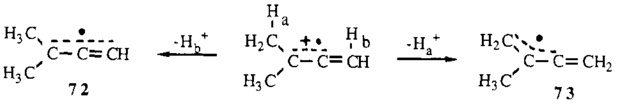
[33] Mazzocchi, P. H.; Fritz, G. *J. Am. Chem. Soc.* **1986**, *108*, 5362.
[34] Tu, C. L.; Mariano, P. S. *J. Am. Chem. Soc.*, in press.
[35] Unpublished results of S. Farid and S. L. Mattes indicate that benzylsilane cation radical undergoes desilylation (25 °C, MeCN) at a rate in excess of 5×10^9 s^{-1}.

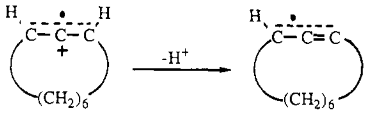
in the presence of these substrates leads to production of allene and acetylene adducts identical with those arising in photoadditions of allene and its 1,1-dimethyl analogue to **6**. A summary of these results is presented in Table V in the form of allene/acetylene product ratios as a function of substrate and irradiation solvent. The data clearly show that the allene/acetylene product ratios differ significantly. Variations in these ratios occur when both substrate and solvent are varied (e.g., entries a vs. b and e vs. f for solvent effects, and entries e vs. g for silyl precursor effects). The widely different coupling ratios might reflect differences in the mechanisms for these processes. However, it appears more plausible that these variations reflect the influence of solvent, method of radical production (deprotonation vs. desilylation), and substrate type (propargyl vs. allenyl silane) on the orientation of components in neutral radical pairs which serve as precursors of the pyrrolidine products.

The issue of allenyl cation radical deprotonation regiochemistry requires brief comment. For example, the results presented above suggest that the 1,1-dimethylallene cation radical undergoes selective proton loss from the allene rather than allylic position, generating the propargylic inium salt **6**. These phenomena appear related to kinetic acidity and ring strain effects. Thus, the higher kinetic acidity[36] of the allenyl protons (sp^2-center) over those of the methyl protons (sp^3-center) appears to strongly influence the relative rates of methanol addition and deprotonation of allenyl cation radicals. In addition, proton loss from the allenyl positions in the 1,2-cyclononadiene cation radical would be prohibited since it would produce the excessively strained cyclic propargyl radical **74**.



72

73



74

Conclusions. The results presented above have demonstrated that allenes participate in interesting electron-transfer-induced photoaddition reactions in methanol with the pyrrolinium perchlorate **6**. Mechanisms for these processes involving methanol addition and deprotonation of intermediate allene cation radicals appear consistent with the data accumulated. Allenyl- and propargylsilanes also undergo photoadditions to **6** by sequential electron-transfer–desilylation mechanisms. Finally, the nature of allene photoadditions to **6** changes when irradiations are conducted in acetonitrile. In this case, a variety of 2 + 2 and 4 + 2 cycloadditions occur with interesting regioselectivities. Clearly, while this study has uncovered a host of new chemistry, it has led to a number of interesting questions that should serve as the basis for continuing efforts in this area.

Experimental Section

MO Calculations. Ab initio MO calculations were conducted at the SCF level (UHF) by using the GAMyeSS program.[20] Geometries were first optimized by utilizing the STO-3G basis set and then with the higher level (4-31G) basis sets.[2] Energy minima were approached from two geometric directions. Charge densities were calculated by using the total electron populations (Mulliken) for each atom. Odd electron densities were calculated by summations of the appropriate atomic orbital densities (Mulliken) in the highest occupied α orbital. 1,1-Dimethylallene and the bent-90°-twisted (C_{2v}) allene were optimized only by use of STO-3G basis sets.

General Methods. NMR spectra were recorded on a Bruker WP-200 or AM-400 spectrometer. Spectra were obtained in deuteriochloroform as solvent and chemical shifts are reported in parts per million downfield from tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. UV spectra were obtained on a Perkin-Elmer Lambda 5 spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF 44B spectrometer equipped with a Perkin-Elmer DCSU-1 differential corrected spectral unit. Integrations were made with a LCD 308 digital integrator. Mass spectrometric data (low resolution) were recorded at 70 eV on a Hitachi RMU-6E mass spectrometer. High resolution mass spectra were taken at the Penn State Mass Spectrometric Facility. Melting points were taken on a Griffin Mel Temp capillary melting point apparatus and are reported uncorrected. Preparative TLC was performed on 20 × 20 cm plates coated with Merck-EM type 60 GF-254 silica gel or Baker Aluminum Oxide 9F. Flash column chromatography used either Woelm alumina 32-63 or Merck-EM Type 60 (230–400 mesh) silica gel. Gas chromatographic analyses and separations were conducted on a Varian 940 chromatograph with flame ionization detector or Varian Model 3700 chromatograph with thermal conductivity bridge. Unless otherwise mentioned, organic layers were dried by washing with brine followed by standing over anhydrous Na_2SO_4.

Preparative photolyses were conducted with an apparatus consisting of 450-W Hanovia medium pressure mercury vapor lamp surrounded by the indicated glas filter in a water-cooled quartz immersion well surrounded by the solution being irradiated under a N_2 atmosphere. Reaction progress was monitored by ultraviolet absorption spectrometry and irradiations were stopped at 70–100% completion. Yields reported are based upon starting material consumed. Crude photolysates were subjected to a general workup procedure involving the addition of K_2CO_3, filtration, and concentration of the filtrate in vacuo. Chloroform solutions of the residues were washed with aqueous staturated $NaHCO_3$, dried, and concentrated in vacuo. Residues obtained were subjected to the indicated chromatographic methods.

Fluorescence Measurements. For fluorescence measurements with 2-phenyl-1-pyrrolinium perchlorate (**6**), the wavelength of excitation was 275 nm and emission was monitored from 310 to 470 nm. Quenchers were added to acetonitrile solutions of the salt in varying concentrations ranging from 5×10^{-3} to 1×10^{-1} M. Stern–Volmer plots were linear and a least-squares analysis was used to obtain $k_q\tau$ values. For calculations of fluorescence quenching rate constants (k_q), the known lifetime of 2-phenyl-1-pyrrolinium perchlorate was used.[8]

Reagents. 2-Phenyl-1-pyrroline,[37] tetramethylallene,[38] 1,1-dimethylallene,[39] and 1,2-cyclononadiene[40] were prepared by the referenced methods. Allene was purchased from ICN Pharmaceuticals and used as the liquid by distillation into methanol or acetonitrile solutions at low temperature.

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with Allene in CH_3OH at High Acid Concentration. To a solution of 2-phenyl-1-pyrroline (236 mg, 1.63 mmol) and 70% perchloric acid (545 mg, 3.82 mmol) in methanol at −25 °C was added a solution of allene (ca. 2.0 mL, 33 mmol) in methanol at −78 °C. The total volume was adjusted to 180 mL. This solution was immersed in a dry ice–CCl_4 bath and irradiated by using Corex filtered light for 1 h. The crude photolysate was subjected to the general workup procedure followed by preparative TLC on alumina ($CHCl_3$–Et_2O) followed by alumina column chromatography

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(hexane–CHCl$_3$) to yield 2-allenyl-2-phenylpyrrolidine (**15**) (66 mg, 22%) and 2-(2′,2′-dimethoxy-1′-propyl)-2-phenylpyrrolidine (**18**) (85 mg, 1%).

Spectroscopic data for **15**: IR (CHCl$_3$) 3300, 2940, 1950, 850, 750 cm^{-1}; ^{1}H NMR 1.80–2.00 (m, 2 H, H-3), 2.20–2.40 (m, 2 H, H-2), 2.51 (br s, 1 H, NH), 3.05–3.25 (m, 2 H, H-5), 4.88 (dd, J = 6.5, 1.1 Hz, 2 H, H-3′), 5.33 (t, J = 6.5 Hz, 1 H, H-1′), 7.20–7.50 (m, 5 H, aromatic H); ^{13}C NMR 24.56 (C-4), 3.82 (C-3), 45.4 (C-5), 67.0 (C-2), 78.1 (C-3′), 99.2 (C-1′), 125.8, 126.5, 128.1, 148.8 (aromatic C), 205.9 (C-2′); mass spectrum, *m/e* (relative intensity). 185 (M$^+$, 20), 146 (M$^+$ – C$_3$H$_3$, 100); high resolution mass spectrum, *m/e* 185.1190 ($C_{13}H_{15}N$ requires 185.1176).

Spectrometric data for **18**: IR (CCl$_4$) 3310, 2960, 2840, 1600, 1500, 1115, 1053, 702 cm^{-1}; ^{1}H NMR 0.76 (s, 3 H, H-3′), 1.6–1.8 (m, 2 H, H-4), 2.0 (m, 1 H, NH), 2.25 (s, 2 H, H-1′), 2.26, 2.76 (m, 2 H, H-3), 3.00 (m, 2 H, H-5), 3.11, 3.13 (s, 6 H, *gem*-OCH$_3$), 7.26–7.49 (m, 5 H, aromatic H); ^{13}C NMR 22.3 (C-3′), 24.2 (C-4), 42.6 (C-3), 45.6 (C-5), 47.2 (C-1′), 47.8, 48.0 (*gem*-OCH$_3$), 66.6 (C-2), 101.7 (C-2′), 125.9, 126.3, 127.9, 147.6 (aromatic C); mass spectrum (relative intensity, *m/e* 249 (M$^+$, 100), 234 (15), 218 (22), 146 (M$^+$ – C$_5$H$_{11}$O$_2$, 100); high resolution mass spectrum, *m/e* 249.1730 ($C_{15}H_{23}NO_2$ requires 249.1730).

Preparation of the Ketone 19. The crude photolysate obtained by irradiation of 2-phenyl-1-pyrrolinium perchlorate (1.63 mmol) and allene (33 mmol) in methanol (180 mL) was subjected to the general workup procedure, giving a residue which was dissolved in a solution of THF (5 mL) and 10% aqueous HCl (6 mL). The resulting mixture was stirred at 25 °C for 2 h, poured into aqueous NaHCO$_3$, and extracted with CHCl$_3$. The CHCl$_3$ extracts were dried and concentrated in vacuo, giving a residue (244 mg) which was dissolved in a THF solution (15 mL) containing triethylamine (0.30 mL, 2.2 mmol). Ethyl chloroformate (0.19 mL, 2.0 mmol) in THF (3 mL) was added dropwise at 25 °C, and the resulting solution was stirred for 1 h, poured into ice water, and extracted with CHCl$_3$. The CHCl$_3$ extracts were washed with aqueous NaHCO$_3$, dried, and concentrated in vacou, giving a residue which was subjected to preparative TLC using silica gel (2:1 hexane/EtOAc) to yield 2-allenyl-1-(ethoxycarbonyl)-2-phenylpyrrolidine (88 mg, 21%) and 2-acetonyl-1-(ethoxycarbonyl)-2-phenylpyrrolidine (**19**) (58 mg, 13%).

Spectroscopic data for the allene: IR (CCl$_4$) 2860, 1960, 1710, 1415, 1378, 1128, 700 cm^{-1}; ^{1}H NMR (two conformers) 0.83, 1.00 (t, 3 H, CH$_3$), 1.25, 1.85 (m, 2 H, H-4), 2.05–2.55 (m, 2 H, H-3), 3.10, 3.70 (m, 2 H, H-5), 3.90, 4.14 (q, 2 H, OCH$_2$), 4.91, 4.93 (dd, J = 7.5, 2 Hz, 2 H, H-3′), 5.85, 6.15, (t, J = 7 Hz, 1 H, H-1′), 7.28 (m, 5 H, aromatic H); mass spectrum, *m/e* (relative intensity) 257 (M$^+$, 10), 218 (100); high resolution mass spectrum, *m/e* 257.1402 ($C_{16}H_{19}NO_2$ requires 257.1417).

Spectroscopic data for **19**: IR (CCl$_4$) 1960, 1705, 1415, 1380 cm^{-1}; ^{1}H NMR (two conformers) 1.23, 1.26 (t, 3 H, CH$_3$), 1.50–2.15 (m, 2 H, H-3), 2.15 (s, 3 H, COCH$_3$), 2.30–3.0 (m, 2 H, CH$_2$), 3.0–3.5 (m, 2 H, H-4), 3.60–4.00 (m, 2 H, H-5), 4.09 (q, 2 H, OCH$_2$), 7.16–7.35 (m, 5 H, aromatic H); mass spectrum, *m/e* (relative intensity) 275 (M$^+$, 16), 218 (100), 186 (40), 174 (35), 146 (50); high resolution mass spectrum, *m/e* 275.1522 ($C_{16}H_{21}NO_3$ requires 275.1522).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with Allene in CH$_3$OH at Low Acid Concentration. To a solution of 2-phenyl-1-pyrroline (254 mg, 1.69 mmol) and 70% perchloric acid (330 mg, 2.31 mmol) in methanol at –25 °C was added a solution of allene (ca. 2.5 mL, 44.8 mmol) in methanol at –78 °C. The total volume was adjusted to 180 mL. The solution was immersed in a dry ice–CCl$_4$ bath and irradiated by using Corex filtered light for 1.5 h. The crude photolysate was subjected to the general workup procedure followed by flash column chromatography on silica gel (2% MeOH/CHCl$_3$) to give recovered 2-phenyl-1-pyrroline (65 mg), the allenylpyrrolidine **15** (40 mg, 20%), the propargylpyrrolidine **16** (18 mg, 95%), and 2-(2′-methoxy-2′-propen-1-yl)-2-phenylpyrrolidine (**17**) (60 mg, 22%).

Spectroscopic data for **16**: IR (CHCl$_3$) 3300, 2950, 1380, 700 cm^{-1}; ^{1}H NMR 1.31–1.90 (m, 2 H, H-4), 1.95 (t, J = 2.5 Hz, 1 H, H-3′), 1.99–2.13 (m, 2 H, H-3), 2.24 (br s, 1 H, NH), 2.60, 2.67 (dd, J = 8.5, 2.5 Hz, 2 H, H-1′), 2.87, 3.20 (m, 2 H, H-5), 7.17–7.51 (m, 5 H, aromatic H); ^{13}C NMR 25.2 (C-4), 32.0 (C-1′), 37.3 (C-3), 45.7 (C-5), 66.9 (C-2), 70.5 (C-2′), 81.7 (C-3′), 125.9, 126.5, 128.0, 146.4 (aromatic C); mass spectrum, *m/e* (relative intensity) 185 (M$^+$, 2%), 146 (100); high resolution mass spectrum, *m/e* 185.1191 ($C_{13}H_{15}N$ requires 185.1178).

Spectroscopic data for **17**: IR (CHCl$_3$) 3300, 2950, 1650, 1610, 1450, 1280, 810, 700 cm^{-1}; ^{1}H NMR 1.65–1.90 (m, 2 H, H-4) 2.03–2.13 (m, 2 H, H-3), 2.12 (br s, 1 H, NH), 2.54, 2.55 (s, 2 H, H-1′), 2.84–3.30 (m, 2 H, H-5), 3.41 (s, 3 H, OCH$_3$), 3.65, 3.84 (d, J = 1.9 Hz, 2 H, =CH$_2$), 7.17–7.46 (m, 5 H, aromatic H); ^{13}C NMR 24.8 (C-4), 37.9 (C-3), 45.3 (C-5), 46.9 (C-1′), 54.6 (OCH$_3$), 67.8 (C-2), 84.7 (vinyl CH$_2$), 125.9, 126.0, 127.8, 147.1 (aromatic C) 161.0 (C-2′); mass spectrum, *m/e* (relative intensity) 217 (M$^+$, 1), 146 (100); high resolution mass spectrum, *m/e* 217.1458 ($C_{14}H_{19}NO$ requires 217.1467).

Methanolation of Enol Ether 17. Enol ether **17** (14 mg, 65 mmol) was dissolved in 10 mL of MeOH and 70% perchloric acid (21 mg, 152 mmol) was added. This solution was stirred for 1 h and subjected to the general workup procedure followed by preparative TLC on alumina (5% MeOH in CHCl$_3$) to give the ketal **18** (15 mg, 92%). Spectral properties of **18** were identical with those of this substance obtained in the irradiation of **6** with allene in methanol at high acid concentration.

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 1,1-Dimethyallene in CH$_3$OH. A solution of 2-phenyl-1-pyrroline (236 mg, 1.63 mmol), 1,1-dimethylallene (2.22 g, 32.6 mmol), and 70% perchloric acid (545 mg, 3.81 mmol) in 180 mL of methanol was irradiated by using Corex filtered light for 1.2 h. The crude photolysate was subjected to the general workup procedure followed by column chromatography on alumina (4:1 hexane/CHCl$_3$) to yield 2-(2′-methyl-3′-butyn-2′-yl)-2-phenylpyrrolidine (**21**) (49 mg, 14%), 2-(3′-methyl-1′,2′-butadien-1′-yl)-2-phenylpyrrolidine (**20**) (8 mg, 2%), 2-(3′-methoxy-2′-methyl-3′-buten-2′-yl)-2-phenylpyrrolidine (**23**) (68 mg, 17%), 2-(2′-methoxy-3′-methyl-2′-butenyl)-2-phenylpyrrolidine (**22**) (168 mg, 42%), and 7-isopropylidene-1-(pyrrolin-2′-yl)bicyclo[2.2.2]-octa-2,5-diene (**24**) (8 mg, 2%).

Spectroscopic data for **21**: IR (CCl$_4$) 3310, 2920, 2100, 1600 cm^{-1}; ^{1}H NMR 1.07, 1.21 (s, 6 H, *gem*-CH$_3$), 1.50–1.80 (m, 2 H, H-4), 2.01 (br s, 1 H, NH), 2.22 (s, 1 H, C≡CH), 2.19–2.39 (m, 2 H, H-3), 2.61–3.07 (m, 2 H, H-5), 7.28–7.61 (m, 5 H, aromatic H); ^{13}C NMR 25.8 (C-4), 26.2, 26.7 (*gem*-CH$_3$), 35.2 (C-3), 39.7 (C-2′), 45.8 (C-5), 70.0 (C-3′), 73.2 (C-2), 90.7 (C-4′), 126.5, 127.2, 29.9, 141.5 (aromatic C); mass spectrum, *m/e* (relative intensity) 213 (M$^+$, 60), 145 (M$^+$ – C$_5$H$_8$, 100); high resolution mass spectrum, *m/e* 213.1511 ($C_{15}H_{19}N$ requires 213.1519).

Spectroscopic data for **20**: IR (CHCl$_3$) 1600, 1440, 1360, 1490, 910, 700 cm^{-1}; ^{1}H NMR 1.72, 1.73 (d, J = 3 Hz, 6 H, *gem*-CH$_3$), 1.80–1.90 (m, 2 H-4), 2.01 (br s, 1 H, NH), 2.10–2.50 (m, 2 H, H-3), 3.09 (m, 2 H, H-5), 5.11 (septet, J = 3 Hz, 1 H, H-1′), 7.26–7.46 (m, 5 H, aromatic H); ^{13}C NMR 20.6, 20.7 (*gem*-CH$_3$), 24.7 (C-4), 38.3 (C-3), 45.4 (C-5), 67.7 (C-2), 98.0 (C-1′), 125.9, 126.2, 128.1, 147.6 (aromatic C), 198.9 (C-2′); mass spectrum, *m/e* (relative intensity) 213 (M$^+$, 2), 146 (100); high resolution mass spectrum, *m/e* 213.1507 ($C_{15}H_{19}N$ requires 213.1517).

Spectroscopic data for **23**: IR (CCl$_4$) 2920, 2730, 1608, 1100 cm^{-1}; ^{1}H NMR 1.03, 1.07 (s, 6 H, *gem*-CH$_3$), 1.30–1.60 (m, 2 H, H-4), 2.03 (br s, 1 H, NH), 2.30–2.40 (m, 2 H, H-3), 2.56–2.97 (m, 2 H, H-5), 3.53 (s, 3 H, OCH$_3$), 3.97 (s, 2 H-4′), 7.26–7.54 (m, 5 H, aromatic H); ^{13}C NMR 23.9, 24.5 (*gem*-CH$_3$), 25.3 (C-4), 34.1 (C-3), 45.0 (C-5), 45.4 (C-2), 54.5 (OCH$_3$), 73.6 (C-2′), 82.4 (C-4′), 125.9, 126.8, 128.9, 144.0 (aromatic C), 169.2 (C-3′); mass spectrum, *m/e* (relative intensity), 245 (M$^+$, 1), 146 (100); high resolution mass spectrum, *m/e* 245.1770 ($C_{16}H_{23}NO$ requires 245.1781).

Spectroscopic data for **22**: IR (CCl$_4$) 2920, 2860, 1660, 1600, 1443, 1100, cm^{-1}; ^{1}H NMR 1.30, 1.63 (s, 6 H, *gem*-CH$_3$), 1.73 (m, 2 H, H-4), 1.95 (br s, 1 H, NH), 2.10–2.28 (m, 2 H, H-3), 2.50–2.58, (d, J = 7 Hz, 2 H, H-1′), 2.84–3.08 (m, 2 H, H-5), 3.39 (s, 3 H, OCH$_3$), 7.26–7.58 (m, 5 H, aromatic H); ^{13}C NMR 16.9, 18.7 (*gem*-CH$_3$), 25.0 (C-4), 37.0 (C-3), 38.0 (C-1′), 45.1 (C-5), 56.7 (OCH$_3$), 77.2 (C-2), 118.8 (C-3′), 125.7, 126.1, 127.6, 147.6 (aromatic C), 147.9 (C-2′); mass spectrum, *m/e* (relative intensity) 245 (M$^+$, 1), 146 (100); high resolution mass spectrum, *m/e* 245.1781 ($C_{16}H_{23}NO$ requires 245.1781).

Spectroscopic data for **24**: IR (CCl$_4$) 3080, 2980, 1645, 1620 cm^{-1}; ^{1}H NMR 1.54 (s, 3 H, CH$_3$ syn to pyrroline), 1.57 (t, J = 1.54 Hz, 3 H, CH$_3$ anti to pyrroline), 2.01 (m, 4 H, H-3, H-4′), 2.85 (tt, J = 8.09, 1.81 Hz, 2 H, H-3′), 3.66 (m, 1 H, H-4), 3.99 (tt, J = 7.46, 1.81 Hz, 2 H, H-5′), 6.46 (dd, 2 H, H-3.5, J = 7.4, 6.1) 6.69

(dd, J = 7.4, 1.8 Hz, 2 H, H-2,6); ^{13}C NMR 20.5, 24.4 (CH_3), 22.5 (C-4′), 37.2 (C-8), 38.3 (C-4), 35.9 (C-3′), 55.8 (C-1), 60.7 (C-5′), 120.9 (C-1″), 131.1 (C-7), 134.5 (C-3,5), 134.8 (C-2,6), 179.6 (C-2′); mass spectrum, m/e (relative intensity), 213 (M^+, 25), 186 ($M^+ - C_2H_3$, 100), 146 ($M^+ - C_5H_7$, 55); high resolution mass spectrum, m/e 213.1506 ($C_{15}H_{19}N$ requires 213.1519).

Ozonolysis and Carbethoxylation of 22. A N_2-purged solution of the (methoxybutenyl)pyrrolidine **22** (123 mg, 0.50 mmol) in 15 mL of MeOH containing 70% perchloric acid (71.7 mg, 0.50 mmol) at −78 °C was purged with an ozone in oxygen stream until a blue solution was obtained. This solution was then purged with N_2, quenched with dimethyl sulfide (47 mg, 0.5 mmol), warmed to 25 °C, poured into saturated aqueous $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried over Na_2SO_4 and concentrated in vacuo, giving a residue which was dissolved in 10 mL of THF containing triethylamine (56 mg, 0.55 mmol). To this solution at −78 °C was added ethyl chloroformate (54 mg, 0.5 mmol). The resulting mixture was stirred for 1 h at −78 °C, warmed to 0 °C, poured into ice water, and extracted with $CHCl_3$. The $CHCl_3$ extracts were washed with saturated aqueous $NaHCO_3$, dried, and concentrated in vacuo. The residue was subjected to silica gel preparative TLC (1:1 hexane/$CHCl_3$) to give methyl 2-(1-(ethoxycarbonyl)-2-phenylpyrrolidin-2-yl)ethanoate (**27**) (127 mg, 87%): IR (CCl_4) 1745, 1703, 1420, 1380, 1173, 1130, 700 cm^{-1}; ^{1}H NMR 1.28 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.68 (m, 2 H, H-4), 2.04 (m, 2 H, H-3), 2.53, 2.75 (m, 2 H, H-5), 3.15, 3.38 (two d, J = 15 Hz, 2 H, H-1′), 3.68 (s, 3 H, OCH_3), 4.13 (g, J = 7 Hz, 2 H, OCH_2), 7.2–7.3 (m, 5 H, aromatic H); ^{13}C NMR (two conformers) 14.1, 14.7 (CH_2CH_3), 21.4, 22.7 (C-4), 29.6, 32.7 (C-3), 40.5, 40.8 (C-1′), 48.7, 49.2 (C-5), 51.3, 51.4 (OCH_3), 60.6, 61.5 (OCH_2), 66.4, 66.7 (C-2), 124.8, 125.1, 126.5, 127.5, 127.8, 128.2, 128.7, 130.1 (aromatic); mass spectrum (relative intensity), m/e 291 (M^+, 7), 218 (82), 146 ($M^+ - C_6H_{21}NO_4$, 100); high resolution mass spectrum, m/e 291.1476 ($C_{16}H_{21}NO_4$ requires 291.1471).

Ozonolysis of 23. A N_2-purged solution of the (methoxybutenyl)pyrrolidine **23** (20 mg, 0.08 mmol) in 2 mL of MeOH containing 70% perchloric acid (11 mg, 0.08 mmol) at −78 °C was purged with an ozone in oxygen stream until a blue solution was obtained, then purged with N_2, and treated with dimethyl sulfide (8 mg, 0.08 mmol). The solution was warmed to 25 °C, poured into saturated aqueous $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo to give 23 mg of a crude product containing methyl 2-methyl-2-(2′-phenylpyrrolidin-2′-yl)propanoate (**25**): IR (CCl_4) 2905, 1720, 1140, 910, 705 cm^{-1}; ^{1}H NMR 1.13, 1.15 (s, 6 H, *gem*-CH_3), 1.45–1.66 (m, 2 H, H-4′), 1.98 (dd, 1 H, NH), 2.54 (m, 2 H, H-3′), 2.64–2.98 (m, 2 H, H-5′), 3.63 (s, 3 H, OCH_3), 7.24–7.49 (m, 5 H, aromatic H); ^{13}C NMR 22.7, 22.8 (*gem*-CH_3), 25.1 (C-4′), 34.0 (C-3′), 45.1 (C-5′), 49.4 (C-2), 51.5 (OCH_3), 72.6 (C-2′), 126.5, 127.3, 128.4, 143.0 (aromatic C), 177.4 (C-1): mass spectrum, m/e (relative intensity) 247 (M^+, 1), 145 ($M^+ - C_5H_{10}O_2$, 100) ($C_{15}H_{21}NO_2$ requires 247.1573).

Hydrolysis of Enol Ether 23. Enol ether **23** (50 mg, 0.20 mmol) was dissolved in 2 mL of THF and 2.5 mL of 10% aqueous HCl. The solution was stirred at 25 °C for 5 h, saturated aqueous $NaHCO_3$ was added, and the solution was extracted with $CHCl_3$. The $CHCl_3$ layer was dried and subjected to preparative TLC on silica gel (4:1 $CHCl_3$/hexane) to give 2-(2′-methyl-3′-oxobut-2′-yl)-2-phenylpyrrolidine (**28**, 46 mg, 92%): IR (CCl_4) 3310, 2980, 1700, 1450, 920, 720 cm^{-1}; ^{1}H NMR 1.18 (s, 6 H, *gem*-CH_3), 1.4–1.6 (m, 2 H, H-3), 1.95 (s, 3 H, $COCH_3$), 2.02 (s, 1 H, NH), 2.1–2.4 (m, 2 H, H-3), 2.8–3.2 (m, 2 H, H-5), 7.29–7.43 (m, 5 H, aromatic H); mass spectrum, m/e (relative intensity) 231 (M^+, 1), 214 (28), 186 (42), 146 ($M^+ - C_5H_9O$, 100); high resolution mass spectrum, m/e 213.1611 ($C_{15}H_{21}NO$ requires 213.1623).

Hydration of 21. To a solution of **21** (26 mg, 0.12 mmol) in THF (0.4 mL), water (0.2 mL), and concentrated H_2SO_4 (0.1 mL) was added $HgSO_4$ (10 mg, 0.03 mmol). The mixture was stirred at room temperature for 1 h, poured into saturated aqueous $NaHCO_3$ at 0 °C, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving a residue which contained ketone **28** by comparison of analytical TLC and NMR spectroscopic data.

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 2-Methyl-4-(trimethylsilyl)-2-butene in CH_3OH. A solution of 2-phenyl-1-pyrroline (205 mg, 1.42 mmol), 70% perchloric acid (266 mg, 1.86 mmol), and 2-methyl-4-(trimethylsilyl)-2-butene (2.27 g, 16.0 mmol) in 180 mL of MeOH was irradiated with Corex filtered light for 1.3 h. The crude photolysate was subjected to the general workup procedure followed by silica gel flash column chromatography (2% MeOH in $CHCl_3$) to yield 56 mg of 2-phenyl-1-pyrroline, 2-(2′-methyl-3′-buten-2′-yl)-2-phenylpyrrolidine (**37**) (34 mg, 15%), and 2-(3′-methyl-2′-buten-2′-yl)-2-phenylpyrrolidine (**36**) (73 mg, 33%).

Spectroscopic data for **37**: IR (CCl_4) 3080, 2980, 1635, 1600, 1500, 925, 915, 710 cm^{-1}; ^{1}H NMR 0.91, 1.00 (s, 6 H, *gem*-CH_3), 1.35–1.81 (m, 2 H, H-4), 1.8–2.1, 2.2–2.4 (m, 2 H, H-3), 2.5 (br s, 1 H, NH), 2.5–2.7, 2.9–3.1 (m, 2 H, H-5), 5.04 (dd, 1 H, J = 17.4, 1.5 Hz), 5.09 (dd, 1 H, J = 10.9, 1.5 Hz, $=CH_2$), 6.03 (dd, 1 H, J = 17.4, 10.9 Hz, H-3′), 7.2–7.7 (m, 5 H, aromatic); ^{13}C NMR 23.3 (C-4), 23.8, 24.3 (*gem*-CH_3), 32.5 (C-3), 42.2 (C-2′), 44.6 (C-5), 73.2 (C-2), 114.8 ($=CH_2$), 144.0 (C-3′), 127.0, 127.6, 128.4, 139.5 (aromatic C); mass spectrum, m/e (relative intensity) 215 (M^+, 1), 146 ($M^+ - C_5H_9$, 100); high resolution mass spectrum, m/e 215.1687 ($C_{15}H_{21}N$ requires 215.1674).

Spectroscopic data for **36**: IR (CCl_4) 3080, 2960, 1600, 1450, 710 cm^{-1}; ^{1}H NMR 1.48, 1.64 (s, 6 H, *gem*-CH_3), 1.7–2.0 (m, 2 H, H-4), 2.0–2.2 (m, 2 H, H-3), 2.44 (d, J = 7.5 Hz, 2 H, H-1′), 2.75 (br s, 1 H, NH), 2.90–3.25 (m, 2 H, H-5), 4.94 (m, 1 H, H-2′), 7.10–7.55 (m, 5 H, aromatic H); ^{13}C NMR 17.8, 25.7 (*gem*-CH_3), 21.8 (C-4), 34.3 (C-3), 37.9 (C-1′), 43.4 (C-5), 72.2 (C-2), 117.2 (C-2′), 136.5 (C-3′), 126.2, 127.7, 128.5, 139.8 (aromatic C); mass spectrum, m/e (relative intensity) 215 (M^+, 1), 146 ($M^+ - C_5H_9$, 100); high resolution mass spectrum, m/e 215.1672 ($C_{15}H_{21}N$ requires 215.1974).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 1,2-Cyclononadiene in CH_3OH. A solution of 2-phenyl-1-pyrroline (355 mg, 2.45 mmol), 1,2-cyclononadiene (5.64 g, 49 mmol), and 70% perchloric acid (818 mg, 5.73 mmol) in 180 mL of methanol was irradiated for 2.5 h by using Corex filtered light. The crude photolysate was subjected to the general workup procedure followed by alumina column chromatography (4:1 hexane/$CHCl_3$) to give 203 mg of the unknown substance produced in the dark control reaction, 2-methoxy-3-(2-phenylpyrrolidin-2-yl)cyclonone (**29**) (190 mg, 26%) and its diastereomer **30** (202 mg, 28%).

Spectroscopic data for **29**: IR (CCl_4) 2940, 2865, 1660, 1448, 1205, 705 cm^{-1}; ^{1}H NMR 1.13–2.6 (m, 14 H, H-4–9, H-4′), 2.00 (br s, 1 H, NH), 2.12 (m, 2 H, H-3), 2.70 (m, 2 H, H-3′), 2.99 (m, 2 H, H-5′), 3.27 (m, 2 H, H-1), 3.49 (s, 3 H, OCH_3), 4.66 (t, J = 7 Hz, 1 H, H-3), 7.20–7.73 (m, 5 H, aromatic H); ^{13}C NMR 24.8, 25.3, 25.8, 26.2, 26.6, 27.3, 28.4 (C-4–9, C-4′), 38.0 (C-3′), 45.6 (C-5′), 46.5 (C-3), 53.9 (OCH_3), 72.1 (C-2′), 100.0 (C-1), 125.9, 126.6, 127.8, 146.8 (aromatic C), 158.0 (C-2); mass spectrum, m/e (relative intensity) 299 (M^+, 1), 146 (100); high resolution mass spectrum, m/e 299.2236 ($C_{20}H_{29}NO$ requires 299.2251).

Spectroscopic data for **30**: IR ($CHCl_3$) 3060, 2928, 2860, 1660, 1448, 1220, 700 cm^{-1}; ^{1}H NMR 1.40–1.80 (m, 14 H, H-4–9, H-4′), 2.15 (m, 1 H, NH), 2.3 (m, 2 H, H-3′), 2.90–3.03 (m, 2 H, H-5′), 3.2 (m, 1 H, H-1), 3.25 (s, 3 H, OCH_3), 4.21 (t, 1 H, H-3), 7.20–7.45 (m, 5 H, aromatic H); ^{13}C NMR 24.3, 25.4, 25.6, 26.2, 26.4, 26.8, 28.2 (C-4–9, C-4′), 36.4 (C-3′), 46.0 (C-5′), 47.2 (C-3), 53.5 (OCH_3), 70.3 (C-2′), 98.4 (C-3), 125.5, 126.5, 127.2, 148.8 (aromatic C), 158.1 (C-2); mass spectrum, m/e (relative intensity) 299 (M^+, 1), 146 (100); high resolution mass spectrum, m/e 299.2230 ($C_{20}H_{29}NO$ requires 299.2251).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with Tetramethylallene in CH_3OH. A solution of 2-phenyl-1-pyrroline (236 mg, 1.63 mmol), tetramethylallene (3.14 g, 32.6 mmol), and 70% perchloric acid (545 mg, 3.81 mmol) in 180 mL of MeOH was irradiated for 1.2 h by using Corex filtered light. The crude photolysate was subjected to the general workup procedure followed by Florisil column chromatography (hexane/ethyl acetate) to give 20 mg of 2-phenylpyrroline and 2-(2′,4′-dimethyl-3′-methoxy-3′-penten-2′-yl)-2-phenylpyrrolidine (**31**) (258 mg, 58%): IR (CCl_4) 3300, 2930, 1650, 1100, 700 cm^{-1}; ^{1}H NMR 1.13, 1.20 (s, 6 H, *gem*-CH_3), 1.47, 1.71 (s, 6 H, *gem*-CH_3-4′), 1.30–1.60 (m, 2 H, H-4), 1.93 (m, 1 H, NH), 2.20–2.40 (m, 2 H, H-3), 2.53–2.96 (m, 2 H, H-5), 3.59 (s, 3 H, OCH_3), 7.30–7.60 (m, 5 H, aromatic H); ^{13}C NMR 19.8, 21.9 (*gem*-CH_3-2′), 25.0 (C-4), 26.0, 26.4 (*gem*-CH_3-4′), 33.7 (C-3), 44.8 (C-5), 48.2 (C-2′), 61.5 (OCH_3), 75.8 (C-2), 120.1 (C-4′), 125.8, 126.6, 129.2, 143.7 (aromatic C), 156.1 (C-3′); mass spectrum, *m/e* (relative intensity) 271 (M^+, 1), 146 (100); high resolution mass spectrum, *m/e* 273.2092 ($C_{18}H_{27}NO$ requires 273.2092).

Hydrolysis of 31. A solution of **31** (120 mg, 0.44 mmol), 15% aqueous HCl (3 mL), and THF (2 mL) was stirred for 24 h at 25 °C. Saturated aqueous $NaHCO_3$ was added and the solution extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving a residue that was subjected to Florisil column chromatography (hexane/ethyl acetate) to give 2-(2′,4′-dimethyl-3′-oxopent-2′-yl)-2-phenylpyrrolidine (**32a**) (64 mg, 56%), which is an unstable substance. This material was converted to its stable hydrochloride salt (**32**) by introduction of HCl gas to a solution of **32a** in diethyl ether.

Spectroscopic data for **32a**: ^{1}H NMR 0.80, 0.84 (d, $J = 7$ Hz, 6 H, *gem*-CH_3-4′), 1.03, 1.08 (s, 6 H, *gem*-CH_3-2′), 1.65–2.0 (m, 2 H, H-4, H-4′, NH), 2.4–2.8 (m, 4 H, H-3, H-5), 7.2–7.7 (m, 5 H, aromatic H).

Spectroscopic data for **32**: IR (CCl_4) 3000–2700, 1592, 1100 cm^{-1}; ^{1}H NMR 0.93, 0.97 (d, $J = 7$ Hz, 6 H, *gem*-CH_3-4′), 1.46 (s, 6 H, *gem*-CH_3-2′), 1.70–2.10 (m, 2 H, H-4), 2.25 (m 1 H, H-4′), 2.80–3.10 (m, 2 H, H-3), 3.65 (m, 2 H, H-5), 7.45–7.8 (m, 5 H, aromatic H), 9.8 (br s, 2 H, NH_2); ^{13}C NMR 19.1, 19.8 (*gem*-CH_3-4′), 20.5 (C-4), 22.3, 23.4 (*gem*-CH_3-2′), 31.9 (C-3), 36.1 (C-4′), 43.3 (C-5), 52.5 (C-2′), 78.3 (C-2), 128.4, 128.9, 135.0 (aromatic C), 220.5 (C-3′); mass spectrum, *m/e* (relative intensity) 260 ($M^+ - Cl$, 1); 146 (100); high resolution mass spectrum, *m/e* 260.2001 ($C_{17}H_{26}NO$ requires 260.2016).

Ozonolysis of 31. A solution of **31** (136 mg, 0.50 mmol) and 70% perchloric acid (71 mg, 0.5 mmol) in 15 mL of MeOH was subjected to ozonolysis in the same manner as described for **22**. Workup and purification gave the ester **25** with spectroscopic data identical with that reported above.

Ozonolysis and Carbethoxylation of 31. A solution of **31** (165 mg, 0.6 mmol) in 15 mL of MeOH was subjected to ozonolysis. The crude product mixture was dissolved in 10 mL of THF and a solution of ethyl chloroformate (115 mL, 1.2 mmol) in 2 mL of THF was added dropwise. The mixture was stirred for 1 h at 25 °C, poured into ice–water, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving a residue which was subjected to alumina column chromatography (hexane/$CHCl_3$) to give methyl 2-methyl-2-(1′-(ethoxycarbonyl)-2′-phenylpyrrolidin-2′-yl)propanoate (46 mg, 24%): IR (CCl_4) 2960, 1740–1720, 1448, 1140, 710 cm^{-1}; ^{1}H NMR 1.12, 1.14 (s, 6 H, *gem*-CH_3), 1.25 (t, 3 H, CH_3), 1.4–1.6 (m, 2 H, H-4′), 2.30–2.60 (m, 2 H, H-3′), 2.9–3.3 (m, 2 H, H-5′), 2.61 (s, 3 H, OCH_3), 4.1 (m, 2 H, OCH_2), 7.25–7.40 (m, 5 H, aromatic H); mass spectrum, *m/e* (relative intensity) 218 ($M^+ - C_5H_9O_2$, 1), 146 (100); high resolution mass spectrum, *m/e* 218.1189 ($C_{13}H_{16}NO_2$ requires 218.1182).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with Allene in CH_3CN. To a solution of 2-phenyl-1-pyrroline (282 mg, 1.94 mmol) and 70% perchloric acid (529 mg, 3.70 mmol) in acetonitrile was added a solution of allene (ca. 3 mL, 53.8 mmol) in CH_3CN to make a total volume of 180 mL. The solution was immersed in a dry ice/CCl_4 bath and irradiated with Corex filtered light for 0.75 h. The crude photolysate was subjected to the general workup procedure followed by flash column chromatography on alumina (0–15% $CHCl_3$ in hexane) to give recovered 2-phenyl-1-pyrroline (32 mg) the allenylpyrrolidine **15** (49 mg, 15%), the propargylpyrrolidine **16** (17 mg, 5%), 8-methyl-1-(pyrrolin-2′-yl)-1,3,5,7-cyclooctatetraene (**44**) (15 mg, 5%), and 7-methylene-1-(pyrrolin-2′-yl)bicyclo[4.2.0]octa-2,4-diene (51 mg, 15%) (**45**).

Spectroscopic data for **44**: IR (CCl_4) 3035, 2960, 1645, 1635, 1430 cm^{-1}; ^{1}H NMR 1.80–1.96 (m), 1.91 (t, $J = 1.5$ Hz, CH_3) (5 H, C-4′, CH_3), 2.5–2.6 (m, 2 H, H-3′), 3.9 (m, 2 H, H-5′), 5.72 (dd, $J = 11.5$, 3.8 Hz, 1 H, H-5), 5.75 (q, $J = 1.5$ Hz, 1 H, H-7), 5.87 (dd, $J = 11.5$, 3.8 Hz, 1 H, H-4), 5.95 (d, $J = 11.5$, 1 H, H-6), 6.02 (dd, $J = 11.5$, 3.7 Hz, 1 H, H-3), 6.25 (d, $J = 3.7$ Hz, 1 H, H-2); ^{13}C NMR 22.3 (C-4′), 23.4 (CH_3), 24.8 (C-3′), 61.7 (C-5′), 126.9, 129.3, 130.2, 132.0, 133.0, 134.8 (C-2–7), 140.8 (C-8), 143.0 (C-1), 172.7 (C-2′); mass spectrum, *m/e* (relative intensity) 185 (M^+, 42), 184 (100), 158 (40), 107 ($C_7H_9N^+$, 9); high resolution mass spectrum, *m/e* 185.1199 ($C_{13}H_{15}N$ requires 185.1206).

Spectroscopic data for **45**: IR (CCl_4) 2920, 2880, 1630, 1430, 895, 700 cm^{-1}; ^{1}H NMR 1.85 (m, 2 H, H-4′), 2.5 (m, 2 H, H-3′), 2.8 (br m, 2 H, H-8), 3.5 (br m, 1 H, H-6), 3.8 (t, 2 H, H-5′), 4.6 (br d, $J = 1.2$ Hz, 1 H), 4.9 (dd, $J = 1.2$, 2.7 Hz, 1 H) (=CH_2), 5.8 (m, 2 H, H-3, H-4), 6.1 (dd, $J = 1.0$, 2.7 Hz, 1 H, H-5), 6.4 (dd, $J = 0.9$, 2.7 Hz, 1 H, H-2); ^{13}C NMR 21.3 (C-1), 23.0 (C-4′), 31.8 (C-8), 34.4 (C-3′), 49.8 (C-6), 60.9 (C-5′), 110.8 (=CH_2), 126.6, 127.9, 136.8, 139.4 (C-2-5), 145.9 (C-1), 179.2 (C-2′); mass spectrum, *m/e* (relative intensity) 185 (M^+, 10), 184 (28), 160 (100), 158 (30), 97 (56), 85 (56), 83 (50), 71 (70); high resolution mass spectrum, *m/e* 185.1199 ($C_{13}H_{15}N$ requires 185.1204).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 1,1-Dimethylallene in CH_3CN. A N_2-purged solution containing 2-phenyl-1-pyrroline (120 mg, 0.83 mmol), 70% perchloric acid (291 mg, 2.0 mmol), and 1,1-dimethylallene (1.12 g, 16.4 mmol) in 100 mL of CH_3CN was irradiated with Corex filtered light for 0.75 h. The crude photolysote was subjected to the general workup procedure followed by silica gel flash column chromatography (5% ethyl acetate in hexane) to give 2-phenyl-1-pyrroline (65 mg), 7-isopropylidene-1-(2′-pyrrolinyl)bicyclo[2.2.2]octa-2,5-diene (**47**) (31 mg, 385), 8-isopropylidene-1-(2′-pyrrolinyl)bicyclo[2.2.2]-octa-2,5-diene (**48**) (5 mg, 6%), and 1-(2′-pyrrolinyl)-8-isopropyl-1,3,5,7-cyclooctatetraene (**49**) (2 mg, 2%). Spectroscopic data for **22** were identical with those of this substance obtained from irradiation of **10** with 1,1-dimethylallene in methanol.

Spectroscopic data for **48**: IR (CCl_4) 2960, 2920, 2850, 1640, 1460, 1360 cm^{-1}; ^{1}H NMR 1.55 (s, 3 H, CH_3), 1.77 (t, $J = 1.5$ Hz, 3 H, CH_3), 1.99 (m, 2 H, H-4′), 2.75 (t, $J = 8.6$ Hz, 2 H, H-3′), 2.12 (m, 2 H, H-7), 3.96 (t, $J = 7.3$ Hz, 2 H, H-5′), 4.41 (tt, $J =$ 1.9, 5.6 Hz, 1 H, H-4), 6.41 (dd, $J = 1.9$, 7.3 Hz, 2 H, H-3, H-5), 6.47 (dd, $J = 5.6$, 7.3 Hz, 2 H, H-2, H-6); mass spectrum, *m/e* (relative intensity) 213 (M^+, 70), 198 (67) 169 (40), 146 (24), 71 (100); high resolution mass spectrum, *m/e* 213.1513 ($C_{15}H_{19}N$ requires 213.1517).

Spectroscopic data for **49**: IR (CCl_4) 2960, 2920, 2850, 1470, 1380 cm^{-1}; ^{1}H NMR 0.88 (d, $J = 7$ Hz, 3 H, CH_3), 1.08 (d, $J =$ 7 Hz, 3 H, CH_3), 1.78–1.87 (m, 2 H, H-4′), 2.41–2.55 (m, 2 H, H-3′), 2.72–2.78 (m, 1 H, isopropyl H), 3.87 (t, $J = 7.4$ Hz, 2 H, H-5′), 5.66–5.69 (m, 2 H), 5.70–5.81 (m, 1 H), 5.95–6.02 (m, 2 H, H-3–7), 6.28–6.29 (m, 1 H, H-2); ^{13}C NMR 20.5, 24.2 (*gem*-CH_3), 22.4 (H-4′), 32.7 (isopropyl C), 35.0 (C-3′), 61.7 (C-5′), 122.9, 129.0, 130.3, 131.5, 135.4 (C-2–7), 142.4 (C-8), 151.8 (C-1), 173.4 (C-2′); mass spectrum, *m/e* (relative intensity) 213 (M^+, 58), 212 (51), 198 (100), 186 (68), 170 (567), 146 (56), 135 (44); high resolution mass spectrum, *m/e* 213.1510 ($C_{15}H_{19}N$ requires 213.1517).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 1,2-Cyclononadiene in CH_3CN. A N_2-purged solution containing 2-phenyl-1-pyrroline (240 mg, 1.66 mmol), 70% perchloric acid (6770 mg, 4.7 mmol), and 1,2-cyclononadiene (3.77 g, 30.9 mmol) in 180 mL of CH_3CH was irradiated with Corex filtered light for 3.0 h. The crude photolysate was subjected to the general workup procedure followed by silica gel flash column chromatography (0–15% ethyl acetate in hexane) to give 2-phenyl-1-pyrroline (40 mg), a difficult to separate 5:2 (NMR) mixture of 1-(2′-pyrrolinyl)tricyclo[$9.2.2^{1,11}.0^{2,10}$]pendadeca-9,12,14-triene (**51**) and 1-(2′-pyrrolinyl)tricyclo[$9.2.2^{1,11}.0^{2,0}$]pentadeca-2,12,14-triene (**50**) (192 mg, 52%) and 1-acetamido-*cis*-cyclononene (**52**), mp 84–84 °C (275 mg). Crystallization of the mixture of **50** and **51** from hexane gave **51** in pure form, mp 93–96 °C.

Spectroscopic data for **51**: IR (CCl_4) 3050, 2920, 1450, 1325 cm^{-1}; ^{1}H NMR 0.89–1.91 (m, 10 H, H-3–7), 1.98 (m, 2 H, H-4′) 2.03–2.19 (m, 2 H, H-8), 2.32 (m, 1 H, H-2), 2.66 (m, 2 H, H-3′), 3.97 (m, 3 H, H-11, H-5′), 5.22 (ddd, $J = 11.0$, 6.4, 1.8 Hz, 1 H, H-9), 6.08 (dd, $J = 7.2$, 1.3 Hz, 1 H, H-13), 6.38 (dd, $J = 7.11$, 6.0 Hz, 1 H, H-15), 6.58 (dd, $J = 7.2$, 6.2 Hz, 1 H, H-12), 6.80 (dd, $J = 7.11$, 1.2 Hz, 1 H, H-14); ^{13}C NMR 20.8, 27.4, 28.2, 29.9, 30.0, 30.3 (C-3–8), 22.9 (C-4′), 35.2 (C-3′), 48.4 (C-2), 50.9 (C-11), 61.0 (C-5′), 119.5 (C-9), 131.5, 134.3, 137.2 (C-12–15), 144.7 (C-10), 178.7 (C-2); mass spectrum, *m/e* (relative intensity) 276 (M^+, 8), 1 70 (16), 146 (100); high resolution mass spectrum, *m/e* 267.1985 ($C_{19}H_{25}N$ requires 267.1989).

Partial spectroscopic data for **50** obtained from enriched mixtures containing the regioisomer **51**: ^{1}H NMR 0.9–2.4 (m, 15 H, H-4′, H-14–20), 2.6–2.8 (m, 2 H, H-3′), 3.50–3.65 (m, 1 H, H-9), 3.85–4.20 (m, 2 H, H-5′), 4.70–4.90 (m, 1 H, H-3), 6.30 (dd, $J =$ 7.3, 1.7 Hz, 1 H, H-13 or H-14), 6.40 (dd, $J = 1.6$, 7.4 Hz, 1 H, H-14 or H-13), 6.49 (dd, $J = 5.9$, 7.4 Hz, 1 H, H-12 or H-15), 7.00 (m, 1 H, H-15 or H-12); ^{13}C NMR 21.0, 23.2, 27.6, 28.0, 20.0, 30.0, 30.4, 34.6 (C-4′, C-4–9), 36.0 (C-3′), 45.3 (C-10), 48.3 (C-11), 58.2 (C-1), 671.0 (C-5′), 119.2 (C-3), 132.5, 132.9, 135.4, 137.1 (C-12–15), 146.1 (C-2), 177.8 (C-2′).

Spectroscopic data for **52**: 3450, 3010, 2850, 1650, 1371 cm^{-1}; ^{1}H NMR 1.25–1.75 (m, 10 H, H-4–8), 1.94 (s, 3 H, $COCH_3$, 2.20 (m, 2 H, H-9), 4.83 (m, 1 H, H-3), 5.14 (t, J = 7 Hz, 1 H, H-2), 5.43 (br s, 1 H, NH), 5.63 (q, J = 7 Hz, 1 H, H-1); mass spectrum, *m/e* (relative intensity) 181 (M^+, 11), 122 ($M^+ - C_2H_5NO$, 53), 82 ($C_5H_8N^+$, 100); high resolution mass spectrum, *m/e* 181.1462 ($C_{11}H_{19}NO$ requires 181.1468).

Dark Reaction of 2-Phenyl-1-pyrrolinium Perchlorate with 1,2-Cyclononadiene in CH_3CN. A solution of 2-phenyl-1-pyrroline (120 mg, 0.82 mmol), 70% perchloric acid (156 mg, 1.09 mmol), and 1,2-cyclononadiene (1.88 g, 16.4 mmol) in 100 mL of CH_3CN was stirred under N_2 for 10 h at 25 °C. After the general workup procedure, 2-phenyl-1-pyrroline was recovered quantitatively along with the cyclononene **52** (238 mg).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 1,1-Dimethylallene in MeCN at Low Temperature. A solution of 2-phenyl-1-pyrroline (236 mg, 1.63 mmol), 1,1-dimethylallene 2.22 g, 32.6 mmol), and 70% perchloric acid (547 mg, 3.81 mmol) in 180 mL of acetonitrile was immersed in a dry ice/CCl_4 bath and irradiated for 1.25 h by using Corex filtered light. The crude photolysate was subjected to the general workup procedure followed by silica gel flash chromatography (5% EtOAc in hexane to give cycloadducts **47** (125 mg, 36%), **48** (17 mg, 5%), and **49** (8 mg, 2%). Spectral properties for these compounds were identical with those obtained from the room-temperature irradiation described above.

Irradiation of 2-Phenyl-1-pyrroline with 1,1-Dimethylallene in MeCN. A solution of 2-phenyl-1-pyrroline (156 mg, 1.08 mmol) and 1,1-dimethylallene (1.66 g, 24.5 mmol) in 115 mL of acetonitrile was irradiated for 16 h by using Vycor filtered light. The crude photolysate was subjected to the general workup procedure followed by preparative TLC on silica gel (3:1 hexane/EtOAc) to give only recovered 2-phenyl-1-pyrroline (150 mg).

Synthesis of Allenyl- and Propargylsilanes/Propargyltrimethylsilane. Propargyltrimethylsilane was prepared by the method of Cadiot[41] modified by adding tri-*n*-butylamine and cyclohexanol 1 h after addition of propargyl bromide in order to suppress formation of hexamethyldisiloxane. Aqueous workup followed by fractional distillation gave propargyltrimethylsilane in 45% yield. Spectroscopic properties of this substance were identical with those previously reported.[41,42]

3-Methyl-1-(trimethylsilyl)-1,2-butadiene[43,44] was prepared as previously described. 3-Methyl-3-(trimethylsilyl)-1-butyne was generated from 3-methyl-1,3-bis(trimethylsilyl)-1-butyne by the method previously described.

1-(Trimethylsilyl)-3-methyl-1-butyne. A solution of 3-methyl-1-butyne (25 g, 368 mmol) in 500 mL of anhydrous THF was cooled to −78 °C. BuLi (10.5 M, 37.5 mL, 394 mmol) was added dropwise over a period of 20 min. Stirring was continued for 30 min and TMSCL (42.8 g, 394 mmol) was added. The solution was stirred at −78 °C for 30 min, warmed to 25 °C, diluted with 5% aqueous $NaHCO_3$, and extracted with pentane. The pentane extracts were washed with water, dried, and concentrated in vacuo to give 3-methyl-1-(trimethylsilyl)-1-butyne (55.1 g, 100%). Spectral properties of this substance were identical with those previously reported.[45]

3-Methyl-1,3-bis(trimethylsilyl)-1-butyne. To a solution of *n*-BuLi (10.5 M, 37.5 mL, 394 mmol) and TMEDA (45.7 g, 394 mmol) in 400 mL of anhydrous ether at 0 °C was added a solution of 1-(trimethylsilyl)-3-methyl-1-butyne (55.1 g, 368 mmol) in 50 mL of anhydrous ether. The solution was warmed to 25 °C and stirred for 3 h. The temperature was then lowered to −78 °C and TMSCl (42.8 g, 394 mmol) added. The mixture was stirred 30 min, warmed to 25 °C, stirred 18 h, poured into saturated aqueous $NaHCO_3$, and extracted with pentane. The pentane extracts were washed with 5% aqueous $CuSO_4$ and brine, dried, and concentrated in vacuo, giving a 12:1 mixture of 3-methyl-1,3-bis(trimethylsilyl)-1-butyne and 3-methyl-1,1-bis(trimethylsilyl)-1,2-butadiene (32.8 g, 42%). Spectral properties of these substances were identical with those previously reported.[45,46]

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with Propargyltrimethylsilane in CH_3OH. A solution of 2-phenyl-1-pyrroline (105 mg, 0.72 mmol), 70% perchloric acid (233 mg, 1.63 mmol), and propargyltrimethylsilane (1.52 g, 13.6 mmol) in 100 mL of CH_3OH was irradiated for 0.75 h by using Corex filtered light. The crude photolysate was subjected to the general workup procedure followed by silica gel flash chromatography (5–10% MeOH in $CHCl_3$), giving recovered 2-phenyl-1-pyrroline (41 mg), the allenylpyrrolidine **15** (22 mg, 27%) and the propargylpyrrolidine **16** (26 mg, 31%).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 1-(Trimethylsilyl)-3-methyl-1,2-butadiene in CH_3OH. A N_2-purged solution of 2-phenyl-1-pyrroline (114 mg, 0.79 mmol), 70% perchloric acid (165 mg, 1.15 mmol), and 1-(trimethylsilyl)-3-methyl-1,2-butadiene (1.12 g, 8.0 mmol) in 100 mL of CH_3OH was irradiated with Corex filtered light for 1.75 h. The crude photolysate was subjected to the general workup procedure followed by alumina flash column chromatography (1–10% $CHCl_3$ in hexane) to yield recovered 2-phenyl-1-pyrroline (16 mg), the propargylpyrrolidine **21** (44 mg, 30%), and the allenylpyrrolidine **20** (38 mg, 26%).

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 3-Methyl-3-(trimethylsilyl)-1-butyne in CH_3OH. Solutions of 2-phenyl-1-pyrroline (14 mg, 0.09 mmol), 70% perchloric acid (18 mg, 0.13 mmol), and 3-methyl-3-(trimethylsilyl)-1-butyne (132 mg, 0.95 mmol) in 10 mL of MeOH were irradiated with Corex filtered light for 7 h. The crude photolysates (3) were combined and subjected to the general workup procedure followed by alumina preparative TLC (2:1 $CHCl_3$/hexane) to yield 2-phenyl-1-pyrroline (15 mg), the propargylpyrrolidine **21** (9 mg, 23%), the allenylpyrrolidine **20** (10 mg, 26%), and 5-phenylaza-3-oxabicyclo[3.3.0]octane (3 mg, 7%). Spectral properties were identical with those previously reported.[8]

Irradiation of 2-Phenyl-1-pyrrolinium Perchlorate with 1-(Trimethylsilyl)-3-methyl-1,2-butadiene in CH_3CN. A solution of 2-phenyl-1-pyrroline (11 mg, 0.77 mmol), 70% perchloric acid (151 mg, 1.06 mmol), and 1-(trimethylsilyl)-3-methyl-1,2-butadiene (1.11 g, 7.89 mmol) in 90 mL of CH_3CN was irradiated with Corex filtered light for 1.2 h. The crudy photolysate was subjected to the general workup procedure followed by alumina flash column chromatography (5–15% $CHCl_3$ in hexane) to give recovered 2-phenyl-1-pyrroline (10 mg), the propargylpyrrolidine **21** (26 mg, 18%), and the allenylpyrrolidine **20** (41 mg, 28%).

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