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Exploratory and Mechanistic Studies of the Electron-Transfer-Initiated Photoaddition Reactions of Allylsilane–Iminium Salt Systems[1]

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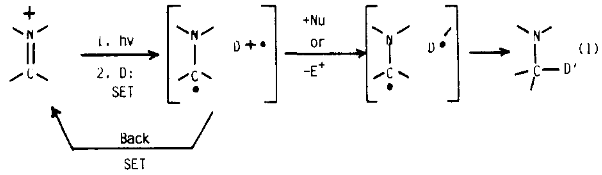
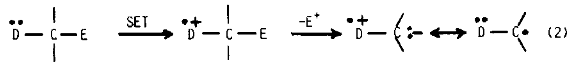
Exploratory studies have uncovered novel photoaddition reactions occurring upon irradiation of 1-methyl-2-phenyl-1-pyrrolinium perchlorate (**4**) in the presence of a variety of allylsilanes **5–10** and leading to production of 2-allylpyrrolidine photoadducts. Mechanistic studies demonstrate that the reactions occur from the singlet excited state of **4**. The effects of substituents on the allylsilane component on the reaction quantum efficiencies have been probed. Mechanisms for these processes involving electron transfer and cation radical desilylation are discussed.

In a series of recent publications[1,3-8] we have described our exploratory and mechanistic studies of the electron-transfer-initiated photoreactions of systems containing the iminium cation grouping. These efforts have demonstrated that the nature and efficiencies of excited-state processes followed by donor–iminium salt pairs are controlled by the type and rates of secondary reactions of the initially formed, donor derived, cation radical or diradical intermediates (eq 1). This is a general and important feature of photochemical processes operating via electron-transfer mechanisms and one that distinguishes them from the more classical excited-state reactions.[9] Thus, the unique characteristics of photochemical electron-transfer processes reflect the fact that neutral or charged radicals serve as key reactive intermediates and that the chemical behavior of these species is totally different from that of organic excited states.[10]



One of the more interesting reaction pathways available to certain cation radicals formed by excited-state electron transfer (SET) involves the nucleophile- or base-induced elimination of electrofugal groups located β to (e.g., allylic or benzylic) the charged radical sites (eq 2). Indeed, a number of excited-state transformations proceeding via sequential electron transfer–electrofugal group elimination pathways have been uncovered. Examples include decarboxylation of arylacetic acid[11] and α-amino acid[12] cation radicals, retro-Aldol fragmentation of amino ethanol radical cations,[13] deprotonation of alcohol,[5] ether,[5] amine,[14]



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[1] For a preliminary communication of a portion of the studies described herein see: Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617.

[2] (a) Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University, Oita, Japan. (b) Department of Chemistry, Busan National University, Busan, Korea.

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[7] Tiner-Harding, T.; Ullrich, J. W.; Chiu, F. T.; Chen, S. F.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 3360.

[8] Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130; *Tetrahedron*, in press.

[9] Lablache-Combier, A. *Bull. Soc. Chim. Fr.* **1972**, *12*, 4791. Davidson, R. S. "Molecular Association"; Ed. Foster, R., Ed.; Academic Press: New York, 1975; Vol 1, p 334.

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[11] Davidson, R. S.; Steiner, P. R. *J. Chem. Soc. C* **1968**, 1682. Brimage, D. R. G.; Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 526. Brimage, D. R. G.; Davidson, R. S. *Ibid.* **1973**, 496.

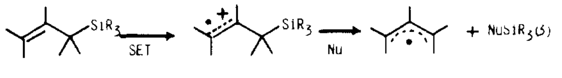
[12] Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1357.

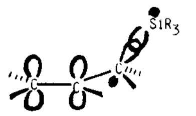
[13] Davidson, R. S.; Orton, S. P. *J. Chem. Soc., Chem. Commun.* **1974**, 209.

0022-3263/84/1949-0213$01.50/0

and toluene[15] radical ions, and demetalation of benzylstannane cation radicals.[16]

Our current investigations are focused on reactions of this type which are stimulated by excited-state electron transfer and guided by desilylation of allyl[1] and benzylsilane[15] cations radicals (eq 3). At the outset of this work we hypothesized that the presence of C–Si bonds β to alkene and arene π systems would facilitate electron transfer to excited acceptors through an effect on π oxidation potentials.[17] Our thoughts here were encouraged by the thorough studies of Bock[19] and Traylor[20] which amply demonstrate the effects of hyperconjugative π–σ_{C-Si} orbital interactions on π ionization potentials of allyl- and benzylsilanes, on the position of UV absorption maxima of ground-state charge-transfer (CT) complexes between allylsilanes and electron-deficient olefins, and on the persistence of allyl- and benzylsilane radical cations. We anticipated that the strong orbital interactions resulting from the close relative energies of σ_{C-Si} and singly occupied π_{HOMO} orbitals and the potential for good orbital overlap would be manifested in significant odd electron and positive charge delocalization into the σ_{C-Si} bonds of benzyl- or allylsilane cation radicals.[21] Accordingly, cation radicals of this type, e.g., 1, can be represented by contributing π_{HOMO} and σ_{HOMO} radical cation cannonical structures 2 and 3.[22] Thus, owing to contributions from delocalized structures 3, radical cations of this type should react like their β-silyl carbocation counterparts and form allylic and benzylic radicals though nucleophilic attack on silicon. This reaction pathway should compete effectively with nucleophilic attack on carbon and deprotonation of the cation radical species and, thus, could potentially provide a site-selective method for allylic or benzylic radical production. The studies described below and in the following papers[23] demonstrate the validity of the reasoning and show that electron-transfer-induced photoaddition and photocyclization reactions of allylsilane–iminium salt systems serve as useful methods for carbon–carbon bond formation.





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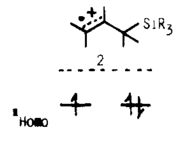

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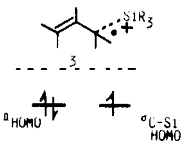

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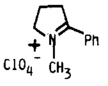
Results

Exploratory Photochemistry. Exploratory photochemical studies were conducted with 1-methyl-2-phenyl-1-pyrrolinium perchlorate (4)[5] and a series of known (5–8[24]) or easily prepared (9 and 10; see Experimental Section) allylsilanes in order to determine if the reasoning presented above is correct. Irradiation of a solution of 4 (0.01 M) and allylsilane 5 (0.88 M) in methanol through a Corex glass filter, which permits light absorption by 4 exclusively (λ_{max} = 258 nm), leads to production of two photoproducts isolated after base treatment of the photolysate, silica gel chromatography, and preparative GLC. The structure of the major product (42%) is assigned as 2-phenyl-2-allylpyrrolidine (11) on the basis of characteristic spectroscopic properties and comparisons with those of structurally related substances.[3,5] For example, the ^1H NMR spectrum of 11 contains key resonances for protons in the 1-methyl-2-phenylpyrrolidine moiety and the allyl side chain (vinyl proton resonances at δ 4.92–5.78, J_{trans} = 16.8 Hz, J_{cis} = 9.9 Hz, J_{gem} = 1.2 Hz, $J_{allylic}$ = 1.2 Hz). Further structural information is gained from the ^{13}C NMR spectrum of 11 which displays resonances at 116.8 and 135.5 ppm for the vinyl carbons of the allyl grouping and at 67.4 ppm for the quaternary C-2 pyrrolidine ring carbon. The minor photoproduct formed (21%) in this reaction is tentatively identified as a mixture of the spirocyclic amines 12 on the basis of spectroscopic data which compare favorably with those recorded for similar compounds prepared earlier in our laboratory.[3,25] Finally, irradiation of 4 in an acetonitrile solution containing 5 also gives 11 and 12 in yields nearly identical with the methanol photoreaction.



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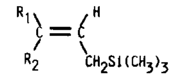
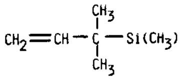


5 ($R_1 = R_2 = H$)
6 ($R_1 = R_2 = CH_3$)
7 (R_1 = TMS, R_2 = H)

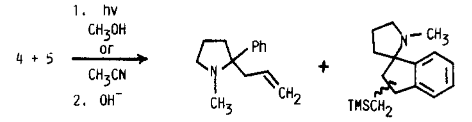


$CH_2{=}CH{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Si(CH_3)_3$

8

$(CH_3)_2C{=}CH{-}CH_2{-}SiR_3$

9 ($R_3 = Et_3$)
10 (R_3 = Me_2, t-Bu)



11 12

In a similar fashion, the photoadduct 13 (42%) is obtained by irradiation of 4 (0.02 M) in an acetonitrile so-

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[14] Cohen, S. G.; Parola, A. H.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141. Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152.

[15] Unpublished results of S. Quillen, A. Lan, R. Heuckeroth, and L. Klingler.

[16] Eaton, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 1735; **1980**, *102*, 3281.

[17] The rates of singlet electron transfer are known to be dependent upon the thermodynamics of electron transfer (ΔG_{et}) which are influenced by donor and acceptor electrochemical potentials and excited-state energies.[18]

[18] Rhem, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

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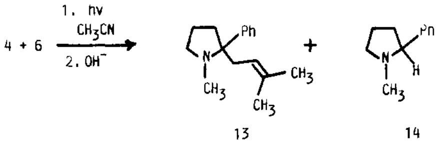
[24] (a) Methods for preparation of allylsilanes 6–8 are described in ref 24b–d, respectively, and spectroscopic data for 8 are provided in the Experimental Section. (b) Pillot, J. P.; Dunogues, J.; Calas, R. *Tetrahedron Lett.* **1976**, 1871. (c) Dunoguez, J.; Calas, R.; Ardoin, N.; Biran, C. *J. Organomet. Chem.* **1971**, *32*, C-31. Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, 2383. (d) hosomi, A.; Sakurai, H. *Ibid.* **1978**, 2589.

[25] Mariano, P. S.; Leone, A. A. *Tetrahedron Lett.* **1980**, *21*, 4581.

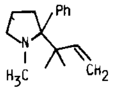
Table I. Product Yields for Photoreaction of the Pyrrolinium Salt 4 with Allylsilanes 5–10 in Acetonitrile

	product yield, %			
allylsilane	photoadduct	pyrrolidine 14	1,5-hexadienes 16 and 17	other
5	42 (11)	0		21% (12)
6	42 (13)	24	5	
7	85 (18)	0		
8	30 (13)	16	5	
9	42 (13)	24	5	
10	37 (13)	28	5	

lution containing 2-methyl-4-(trimethylsilyl)-2-butene (6, 0.21 M) followed by base treatment and either molecular distillation or preparative GLC. This process also generates the pyrrolidine 14[26] which is isolated in pure form (24%) by GLC. The structure of the major photoproduct was unraveled by use of the types of spectroscopic data alluded to above. The presence of the 3,3-dimethylprop-2-en-1-yl side chain in 13 rather than the regioisomeric 1,1-dimethyl-substituted appendage found in 15 is easily established by use of ^{1}H NMR [δ 1.64 (methyls), 5.02 (br t, J = 6.8 Hz, vinyl)] and ^{13}C NMR (132.3 and 121.2 ppm, vinyl carbons) methods. It is important to note that careful analysis of the crude photolysate by use of spectroscopic and chromatographic methods failed to reveal the presence of even minor quantities of the regioisomeric photoadduct 15. However, trace quantities (ca. 5%) of the 1,5-hexadienes 16 and 17[27] could be detected by GLC analysis of the crude photolysate prior to removal of volatile components. Finally, irradiation of the pyrrolinium salt 4 in acetonitrile solutions containing 3-methyl-3-(trimethylsilyl)-1-butene (8) leads to exclusive production of the (3,3-dimethylprop-2-en-1-yl)pyrrolidine 13 (30%) along with the unsubstituted pyrrolidine 14 (16%). Here again, none of the isomeric adduct 15 could be detected in the product mixture.



13 14



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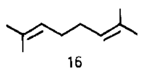

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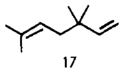
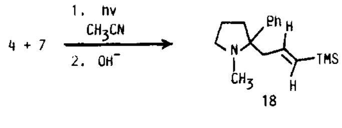


17

An analogous photoaddition process capable of providing similar mechanistic information is found in reaction of 4 with the bis(trimethylsilyl)propene 7. Accordingly, the adduct 18 is produced exclusively in an 85% yield when 4 (0.02 M) is irradiated in solutions of 7 (0.21 M) in acetonitrile followed by base treatment and molecular distillation. The ^{1}H NMR spectrum of 18 which contains two vinyl hydrogen resonances at δ 5.74 (dt, J = 18.5, 1.0 Hz) and 5.96 (dt, J = 18.5, 6.2 Hz) reveals the presence of the *trans*-1-(trimethylsilyl)prop-1-en-3-yl moiety in this substance.



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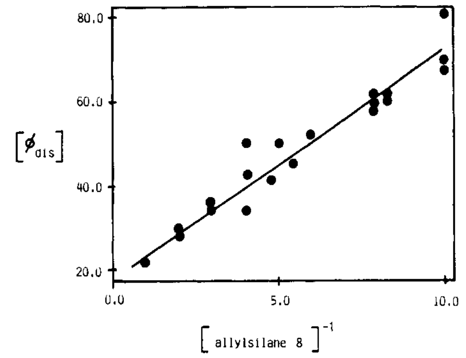

Figure 1. Double recipricol plot of the quantum yield for disappearance of 4 vs. the concentration of allylsilane 5 ($\phi_{4,\mathrm{dis}}^{-1}$ vs. $[5]^{-1}$).

Table II. Fluorescence Quenching Rate Constants for the Pyrrolinium Perchlorate 4–Allylsilane 5–10 Systems

allylsilane quencher	$10^{-9}k_q$, M^{-1} s^{-1} (in CH_3CN at 25 °C)	allylsilane quencher	$10^{-9}k_q$, M^{-1} s^{-1} (in CH_3CN at 25 °C)
5	4.1 ± 0.1	9	6.1 ± 0.3
6	6.2 ± 0.2	10	6.3 ± 0.3
8	3.5 ± 0.1		

As can be seen by inspection of the data provided in Table I, the allylsilanes 9 and 10, having more sterically congested substitution at silicon, also undergo photoaddition reactions with 4 to provide mixtures of the photoadduct 13, pyrrolidine 14, and trace amounts of the hexadienes 16 and 17.

Mechanistic Studies. Additional information about the mechanism for the allylsilane–iminium salt photoaddition reactions described above has come from studies of both fluorescence quenching and concentration dependencies of photoreaction quantum yields. Calculations based upon excited-state energies and donor–acceptor electrochemical potentials[18] suggest that electron transfer from the allylsilanes 5–10 to the singlet excited state of 4 should in all cases be exergonic. This is reflected in the observation that these silicon-substituted alkenes serve as efficient quenchers of the fluorescence of pyrrolinium perchlorate 4 even though exchange energy transfer in these cases would be strongly endergonic. In each instance, except for allylsilane 7 where overlaping absorption bands prevented accurate measurements, Stern–Volmer plots of $\phi_{\mathrm{fo}}/\phi_{\mathrm{fq}}$ vs. [allylsilane] were linear. The quenching rate constants (k_q) in acetonitrile, derived from the slopes ($k_q\tau$) of these plots were found to be close to the diffusion controlled limit (ca. 1×10^{10} M^{-1} s^{-1}; see Table II). Importantly, the emission and absorption spectroscopic properties of mixtures of 4 and the allylsilanes 5–10 do not indicate excited or ground-state complex formation.

Information about the nature of the excited state of 4 participating in the photoaddition reactions has come from studies of the allylsilane 5 concentration dependencies of the quantum yields for 4 disappearance (ϕ_{dis}) and photoadduct 11 formation (ϕ_r). Steady-state kinetic analysis of sequences for fluorescence quenching and photoaddition, in which electron transfer to the pyrrolinium salt excited state from the allylsilane serves as the primary event following excitation, offers a useful method for identifying the excited state undergoing the photoaddition process.

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[26] Blake, K. W.; Gillies, I.; Denney, R. C. *J. Chem. Soc., Perkin Trans. 1* 1981, 700.

[27] Thomas, A. F.; Pawlak, W. *Helv. Chim. Acta* 1971, *54*, 1822.

Table III. Limiting Quantum Yields for Pyrrolinium Salt 4 Disappearance (α_{dis}) and Photoproduct Formation (α_r)

			α_r	
allylsilane	solvent	α_{dis}	photoadduct	pyrrolidine 14
5	CH_3CN	0.04 ± 0.01	0.02	0.00
6	CH_3CN	0.38	0.17	0.12
8	CH_3CN	0.35	0.09	0.04
9	CH_3CN	0.37	0.14	0.11
10	CH_3CN	0.44	0.17	0.15
6	5% CH_3CN-95% *t*-BuOH		0.08	0.02
8	5% CH_3CN-95% *t*-BuOH		0.01	0.01
9	5% CH_3CN-95% *t*-BuOH		0.09	0.03
10	5% CH_3CN-95% *t*-BuOH		0.01	0.02

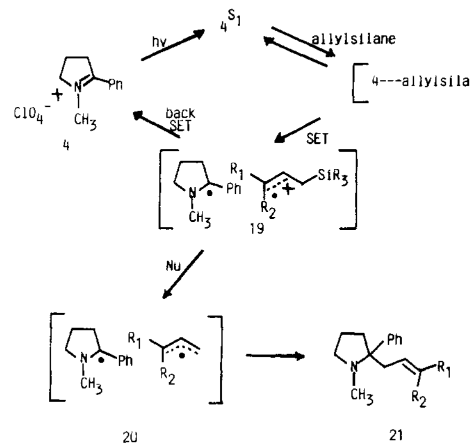
Accordingly, if photoadduct **11** formation proceeds via 4^{S_1}, a double reciprocol plot of $\phi_{4,dis}^{-1}$ or ϕ_{11r}^{-1} vs. $[5]^{-1}$ will be linear and will have an intercept to slope ratio equal to the slope (k_qT) obtained from a Stern–Volmer plot of fluorescence quenching data. The ratio of the intercept to slope from a plot of $\phi_{4,dis}$ vs. $[5]^{-1}$ (see Figure 1) is found to be 3.4 ± 0.6 M^{-1} while the quenching constant derived from fluorescence quenching of **4** by **5** is 4.1 ± 0.1 M^{-1}. The close agreement between these values strongly suggests that fluorescence quenching and photoaddition are kinetically coupled and, therefore, that both are initiated by electron transfer to the singlet excited state of **4**.

Substitutent and Solvent Effects on Photoreaction Efficiencies. Additional information about the nature of the allylsilane–iminium salt photoreactions has come from quantitative studies of the photoaddition reactions of pyrrolinium salt **4** and allylsilanes **5**, **6**, and **8–10**. The quantum yields for pyrrolinium salt disappearance and for photoadduct (**11**, **13** or **18**) and pyrrolidine **14** formation were measured for reactions conducted with acetonitrile and 5% CH_3CN–95% *t*-BuOH solutions of **4**. In each case, the quantum yields for addition ought to be dependent upon allylsilane concentrations and k_qT values in the manner expected (vide supra) for singlet-state processes. For cancelation of these effects and, thus, derivation of values which can be used for comparison, the quantum efficiencies determined at various allylsilane concentrations have been converted to limiting quantum yields (α), i.e., ϕ at [allylsilane] → ∞. This has been done in the case of the **4** + **5** reaction by extrapolation of the linear plots of ϕ_{dis}^{-1} or ϕ_r^{-1} vs. $[5]^{-1}$ to $[5]^{-1} = 0$. However, this method fails when the more highly substituted allylsilanes are used since their longer wavelength absorption prevents quantum efficiency measurements at high allylsilane concentrations. However, in these cases limiting quantum yields can be derived from quantum efficiencies (ϕ) measured at low allylsilane concentration by use of the relationship $\alpha = \phi(1 + (1/k_qT)(1/[\text{allylsilane}]))$. In this way we have determined the limiting quantum yields given in Table III for pyrrolidine and addition product formation and for pyrrolinium salt disappearance in acetonitrile and 5% CH_3CN–95% *t*-BuOH solutions.[28]

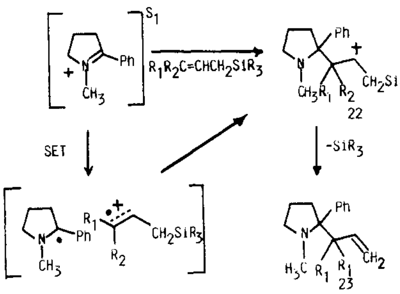
Discussion

Mechanistic Considerations. The allylsilane–pyrrolinium salt photoaddition reactions described above represent a novel class of carbon–carbon bond-forming excited-state reactions which we have shown possess interesting synthetic potential.[23] Several observations made in the course of our studies related to the nature and regiochemistry of the reaction, the origin of side products, and the lack of a pronounced silicon substitutent effect on reaction efficiency deserve detailed discussion.

Scheme I



Scheme II



Several features of the photoaddition reactions occurring in these systems appear to be consistent with the mechanism for adduct formation, shown in Scheme I, which involves the intermediacy of charged and neutral radical pair intermediates **19** and **20**. Accordingly, electron transfer from the allylsilane donor to 4^{S_1}, perhaps through intervention of an excited-state complex, should be an efficient process in polar solvents such as methanol or acetonitrile especially when the allylsilane contains a highly alkyl-substituted π bond. The resulting cation radical pair **19** can return to 4^{S_0} and allylsilane by reverse electron transfer as part of a major route for fluorescence quenching. However, the availability of an efficient, nucleophile-induced desilylation pathway transforming **19** to the neutral radical pair **20** allows for effective competition between the photochemical and photophysical processes.

The regiochemical selectivities observed for addition of allylsilanes **6–10** to **4** are in accord with the mechanism for photoaddition outlined in Scheme I. Coupling of radical pair **20** is expected to heavily favor the least substituted allyl carbon terminus.[29] The selectivities displayed here should be much larger than those noted for unsymmetric allyl radical trapping by agents such as chlorine, owing to the large steric demands dictated by the developing quaternary pyrrolidine ring C-2 carbon. It is important to note that the regiochemical courses of these processes are inconsistent with alternative mechanisms for these photo-

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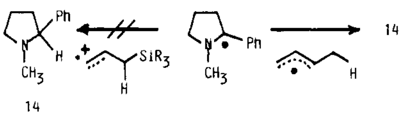
(28) The quenching constants for the allylsilane–pyrrolinium salt systems vary on changing the solvent system from CH_3CN to 5% CH_3CN–95% *t*-BuOH; e.g., 6.2 M^{-1} for **6** quenching of **4** in CH_3CN vs. 2.6 M^{-1} for **6** quenching of **4** in 5% CH_3CN–95% *t*-BuOH.

(29) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877. Oswald, A. A.; Briesbaum, K.; Thaler, W. A.; Hudson, B. E. *J. Am. Chem. Soc.* **1962**, *84*, 3897.

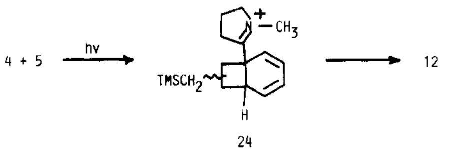
Scheme III



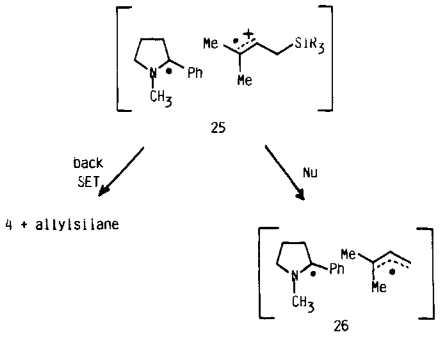
additions. For example, reactions initiated by addition of the electron-rich allylsilane to a high-energy electrophilic iminium cation or in which carbon–carbon bond formation in the radical ion pair precedes desilylation (Scheme II) would have produced adducts **23** with regioisomeric allyl side chains. Both of these routes would generate the β-silyl cation intermediate **22** and, as a result, lead to conjugate addition analogous to that seen in the reaction of allylsilanes with electrophiles,[30] owing to the σ–π stabilization of the cation by vincinally disposed C–Si bonds.

The minor photoproducts, pyrrolidine **14** and 1,5-hexadienes **16** and **17**, formed when **4** is irradiated in the presence of the allylsilanes **6** and **8–10** are also expected from reactions which occur through radical pair intermediates **19** and **20**. Accordingly, the pyrrolidine **14** could arise through disporportionation of either **19** or **20** by H-atom abstraction or through out-of-cage H-atom abstraction from the solvent. On the basis of the observation that **14** does not form in reaction of **4** with the nonalkyl-substituted allylsilanes **5** and **7** and that it is generated in photoreactions of the allylic *gem*-dimethyl-substituted silane **8**, it seems reasonable to suggest that the major pathway for pyrrolidine **14** formation involves disproportionation of the ultimate radical pair as delinated in Scheme III. Similarly, the dienes **16** and **17** are expected out-of-cage coupling products of the 3-methylbut-1-en-3-yl radical.

Substituent Effects. The limiting quantum efficiencies recorded in Table III for photoreaction of the allylsilanes serve as the focus for the final aspect of this photochemical reaction which will be discussed. First, large differences exist between the pyrrolinium salt disappearance and photoproduct formation, limiting quantum yields for the unsubstituted allylsilane **5** and the π-bond dimethyl-substituted systems **6**, **9**, and **10**. The low efficiency for reaction of allylsilane **5** with pyrrolinium salt **4** is consistent with the observation that a tricyclic adduct, **12**, forms as a secondary product in this case only. Thus, it appears that the lower oxidation potential and sterically more accessible π bond of **5** compared to those of the other allylsilanes combine to cause the electron-transfer photochemical pathways to be inefficient and to enhance the precedented[3] [2 + 2] cycloaddition reaction leading to **12** via the bicyclic-hexadiene **24**. An addition factor contributing to the inefficiency of photoaddition of **5** to **4** could be the low relative rate of desilylation vs. back electron transfer of the derived cation radical. Desilylation rates should reflect the stability of the forming allyl radical and, as such, should be greater in those systems which generate prenyl rather than simple allyl radicals.



Limiting quantum yields for photoadduct and pyrrolidine formation contain information about the partitioning of intermediates formed following excited-state electron transfer from allylsilanes to 4^{S_1}. For example, for a series of similarly substituted allylsilanes such as **6**, **9**, and **10**, the limiting product formation quantum yields would reflect the relative rate constants for nucleophile-induced desilylation (**25** → **26**), if partioning of the cation radical pair **25** to radical pair **26** by back electron transfer to 4^{S_0} and allylsilane serves as an important mechanistic branch point. In addition, this conclusion would be contingent upon the validity of the reasonable assumption that silicon substituents do not effect the rates of back electron transfer. With these points in mind, inspection of the data included in Table III for allylsilanes **6**, **9**, and **10** uncovers a rather intriguing result. The limiting quantum yields for pyrrolinium salt disappearance and photoadduct **13** and pyrrolidine **14** formation and the fluorescence quenching rate constants for **6** and **8–10** are nearly equal for all three systems. This suggests that the rates of nucleophile-induced desilylation of allylsilane-derived cation radicals are not dependent upon the nature of substituents which provide steric crowding at silicon.

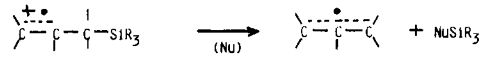


This is a remarkable finding in light of previous results from investigations of the acid- and base-catalyzed methanolysis reactions of variously substituted alkoxy- and phenoxysilanes.[31] In these cases, the second-order rate constants for the processes shown in eq 4 and 5 decrease

$$R_3SiOR' + CH_3O^- \longrightarrow R_3SiOCH_3 \qquad (4)$$

$$R_3SiOR' + CH_3\overset{+}{O}H_2 \longrightarrow R_3SiOCH_3 \qquad (5)$$

by approximately 3–5 orders of magnitude when the silicon substitutents are changed from trimethyl to the more bulky *tert*-butyldimethyl. Thus, if the rates of desilylation are important in controlling quantum efficiencies, our results would suggest that, unlike the case of the simple ground-state solvolytic displacement reactions, the rates of nucleophile-induced desilylation of cation radicals **27**



$$\overset{+\bullet}{C{=}C}-\underset{|}{C}-SiR_3 \xrightarrow[(Nu)]{} C\cdots\overset{\bullet}{C}\cdots C + NuSiR_3$$

are not governed by steric controls. It should be noted that the small changes in limiting quantum efficiencies observed when the solvent nucleophile is changed to *tert*-butyl alcohol might be a result of changes in the rates of desilylation caused by the greater steric demands of the more bulky nucleophile. However, the effects are small, suggesting perhaps that C–Si bond cleavage as part of cation radical desilylation is not the quantum efficiency limiting step.

Conclusions

The observations presented above demonstrate that allylsilane–iminium salt photoaddition reactions represent an interesting and potentially useful class of carbon–carbon

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[30] Colvin, E. W. "Silicon in Organic Synthesis"; Butterworth: London, 1981; p 97–124.

[31] Ackerman, E. *Acta Chem. Scand.* **1957**, *11*, 373. Sommer, L. H. "Stereochemistry Mechanism and Silicon"; McGraw-Hill: New York, 1965; p 132.

bond-forming reactions. Their regio- and sterochemical courses can be understood in terms of pathways involving nucleophile-induced desilylation of initially formed cation radical intermediates followed by coupling at the least substituted allyl radical termini. In this way, radical cation desilylation serves as an example of a general method for site-selective radical production through the excited-state manifold. Continuing studies in this area should provide further new insights into factors controlling electron-transfer-initiated processes and additional examples of useful transformations.

Experimental Section

General Method. 1-Methyl-2-phenyl-1-pyrrolinium perchlorate **4** was prepared by the reaction of 2-phenyl-1-pyrroline with methyl iodide followed by perchlorate anion exchange[5] and then was recrystallized from ethanol. 3-(Trimethylsilyl)propene (**5**) was obtained from Aldrich or Petrarch and purified by fractional distillation. 2-Methyl-4-(trimethylsilyl)-2-butene (**6**) was preparted as described[24b] and purified by distillation; further purification for the quenching experiment was done by preparative GLC. *trans*-1,3-Bis(trimethylsilyl)propene (**7**)[24c] was prepared by trimethylsilylation of (trimethylsilyl)allyllithium and then purified by distillation and preparative GLC. Acetonitrile and methanol were of spectral grade (Aldrich) and were used without further purification. 2,5,5-Trimethylhepta-2,6-diene (**17**) and 2,7-dimethylocta-2,6-diene (**16**) were prepared as described by Thomas and Pawlak.[27]

NMR spectra were recorded on a Varian EM-360, XL-100, or XL-200 spectrometer with tetramethylsilane as an internal standard. UV absorption spectra were measured by using a GCA McPherson EV-700-56 spectrophotometer. Analytical GLC (5% silicon OV-101, 10 ft × $^1/_8$ in.) was performed on a Varian-940 chromatograph with flame-ionization detector. Preparative GLC (20% SE-30, 6 ft × $^5/_{16}$ in.) was done on a Varian-2700 chromatograph. Fluorescence emission was recorded on a Perkin-Elmer MPF-44B spectrometer equipped with a Perkin-Elmer DCSU-1 differential corrected spectra unit. All preparative irradiations were carried out by using a 450-W Hanovia medium-pressure mercury lamp in a quartz immersion well through a Corex filter. The progress of the reactions was followed by UV. Molecular distillation was performed with a Kugelrohr apparatus in vacuo. Elemental analyses were performed by Dr. F. Kasler at the University of Maryland.

3,3-Dimethyl-3-(trimethylsilyl)-1-propene (8). This material was prepared according to the procedure described by Hosomi and Sakurai.[24d] Spectroscopic data for **8** are as follows: ^{1}H NMR ($CDCl_3$) δ -0.10 (s, 9 H, $Si(CH_3)_3$), 0.96 (s, 6 H, $C(CH_3)_2$), 4.59 (d of d, 1 H, J = 17, 2 Hz, CH_2=), 4.75 (d of d, 1 H, J = 10.5, 2 Hz, CH_2=), 5.80 (d of d, 1 H, J = 17, 10.5 Hz, CH=); ^{13}C NMR ($CDCl_3$) δ -4.52 (q, $Si(CH_3)_3$), 2.20 (q, $C(CH_3)_2$), 26.67 (s, allylic), 108.96 (t, CH_2=), 146.82 (d, CH=).

2-Methyl-4-(triethylsilyl)-2-butene (9). To a solution of 2-methyl-2-butenyl magnesium chloride (Mg, 1.4 g, 0.058 mol; 4-chloro-2-methyl-2-butene, 5.08 g, 0.048 mol) in THF (80 mL) was added 4.3 g (0.029 mol) of triethylsilyl chloride in 20 mL of ether. The resulting mixture was refluxed for 24 h. The mixture was poured into water and extracted with ether. The ethereal extracts were dried (Na_2SO_4) and concentrated by fractional distillation. The residue was purified by preparative GLC (20% SE-30, 10 ft × $^5/_{16}$ in. column, 150 °C, 60-mL/min flow rate) which gave 4.5 g (85% in yield) of pure 2-methyl-4-(triethylsilyl)-2-butene (**9**): ^{1}H NMR ($CDCl_3$) δ 0.55 (q, 6 H, J = 6.5 Hz, $Si(CH_2CH_3)_3$), 0.89 (t, 9 H, J = 6.5 Hz, $Si(CH_2CH_3)_3$), 1.40 (br d, 2 H, J = 8 Hz, =$CHCH_2Si$), 1.56 (s, 3 H, allylic CH_3), 1.67 (s, 3 H, allylic CH_3), 5.09 (br t, 1 H, J = 8 Hz, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 3.54 (t, $SiCH_2CH_3$), 7.31 (q, $SiCH_2CH_3$), 13.60 (t, =$CHCH_2Si$), 17.48 (q, CH_3C=), 25.67 (q, CH_3C=), 120.25 (d, CH=C), 128.32 (s, CH=C); mass spectrum, *m/e* (relative intensity) 184 (M^+, 9.7), 169 ($M^+ - \cdot CH_3$, 0.3), 155 ($M^+ - \cdot CH_2CH_3$, 2.3), 115 ($^+Si(CH_2CH_3)_3$, 53.5), 87 (75.4), 85 (73.2), 83 (100). Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12. Found: C, 71.43; H, 13.42.

2-Methyl-4-(*tert*-butyldimethylsilyl)-2-butene (10). To magnesium (6.68 g, 0.275 mmol) in 50 mL of THF was added 4-chloro-2-methyl-2-butene (22 g, 0.21 mol) in 300 mL of THF dropwise over a 6-h period with vigorous stirring at 0 °C. To this solution was added *tert*-butyldimethylsilyl chloride (22 g, 0.146 mol) in 100 mL of ether. The resulting mixture was refluxed for 36 h. The mixture was poured into ice–water and extracted with ether. The ethereal extracts were washed with water, dried, and concentrated by fraction distillation, giving 25 mL of clear yellow solution which contained mainly the desired product (**10**). Further purification by preparative GLC (20% SE-30, 10 ft × $^1/_{16}$ in column, 140 °C, 60-mL/min flow rate) provided pure 2-methyl-4-(*tert*-butyldimethylsilyl)-2-butene (**10**): 13.5 g (50% yield); ^{1}H NMR ($CDCl_3$) δ -0.08 (s, 6 H, $Si(CH_3)_2$), 0.88 (s, 9 H, $C(CH_3)_3$), 1.38 (br d, 2 H, J = 8.5 Hz, =$CHCH_2Si$), 1.55 (s, 3 H, allylic CH_3), 1.67 (s, 3 H, allylic CH_3), 5.10 (br t, 1 H, J = 8.5 Hz, vinyl CH); ^{13}C NMR ($CDCl_3$) δ -6.24 (q, $C(CH_3)_3$), 14.62 (t, C=$CHCH_2Si$), 6.78 (s, $C(CH_3)_3$), 17.55 (q, CH_3C=CH), 25.69 (q, CH_3C=CH), 26.62 (q, $C(CH_3)_3$), 120.53 (d, C=CH), 128.44 (s, C=CH); mass spectrum, *m/e* (relative intensity) 184 (M^+, 27.3), 169 ($M^+ - \cdot CH_3$, 7.2), 127 ($M^+ - \cdot C(CH_3)_3$, 92.1), 115 ($^+Si(CH_3)_2C(CH_3)_3$, 12.6), 99 (32.7), 85 (32.0), 83 (100), 73 (99.9). Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12. Found: C, 71.92; H, 13.40.

Photolysis of 1-Methyl-2-phenylpyrrolinium Perchlorate with 3-(Trimethylsilyl)propene. Preparation of 1-Methyl-2-phenyl-2-(prop-1-en-3-yl)pyrrolidine (11). A nitrogen-purged solution (100 mL) containing 1-methyl-2-phenyl-1-pyrrolinium perchlorate (268 mg, 1.03 mmol) and 3-(trimethylsilyl)propene (10 g, 0.088 mol) in methanol was irradiated for 30 min in a preparative photolysis apparatus. The photolysate was then concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicaronbate, dried over sodium sulfate, and concentrated in vacuo. The crude mixture was dissolved in chloroform, washed with saturated sodium bicarbonate, dried over sodium sulfate, and concentrated in vacuo. GLC of the oily residue showed the formation of two products (10% OV-101, 6 ft × $^1/_8$ in. column, 190 °C, 35-mL/min flow rate; R_f 4.9, 14.8 min) in a ratio of ca. 2:1. Preparative GLC (10% OV-101, 2 ft × $^5/_{16}$ in. column, 170 °C, 33-mL/min flow rate) gave 87 mg (42%) of the photoadduct **11** (R_f 4.9 min) and 45 mg of the tricyclic amine **12** (R_f 14.8 min). Spectroscopic data for **11**: ^{1}H NMR ($CDCl_3$) δ 1.8–2.2 (m, 4 H, methylenes at C-3 and C-4 of ring), 2.11 (s, 3 H, NCH_3), 2.2–3.1 (m, 4 H, methylene α to N and allylic H), 4.92–5.78 (m, J_{trans} = 16.8 Hz, J_{cis} = 9.9 Hz, J_{gem} = 1.2 Hz, J_{vic} = 6.9 Hz $J_{allylic}$ = 1.2 Hz, 3 H, vinyl H), 7.1–7.4 (m, 5 H, aromatic H); mass spectrum (70 eV), (relative intensity) 201 (2.7 M^+), 174 (9), 160 (100), 158 (41), 124 (6), 118 (16), 105 (31), 91 (15), 77 (26); ^{13}C NMR ($CDCl_3$) δ 142.3 (C-1 aromatic), 135.5 (methine vinylic C), 127.5 (meta aromatic), 127.2 (ortho aromatic), 126.1 (para aromatic), 116.8 (terminal vinylic C), 67.4 (C-2 of ring), 53.6 (C-5 of ring), 40.1 (CH_2 α to vinyl group), 37.4 (NCH_3), 35.0 (C-3 of ring), 22.0 (C-4 of ring); high-resolution mass spectrum (70 eV), *m/e* 201.1489 ($C_{14}H_{19}N$ requires 201.151).

Characteristic spectroscopic data for **12**: ^{1}H NMR ($CDCl_3$) characteristic regions τ 2.75–3.25 (NCH_2), 2.20–1.85 (NCH_3), 0.5–1.0 (CH_2Si), 7.0–7.25 (aromatic); ^{13}C NMR ($CDCl_3$) characteristic regions 140–150 (arom quatern, 120–130 (arom mthine), 75–77 (spiro quatern), 50–60 (NCH_2), 35–45 ppm (NCH_3); mass spectrum (70 eV), *m/e* (relative intensity, identity) 273 (63, M), 258 (30, M – CH_3), 200 (100, M – Me_3Si), 186 (71, M – CH_2SiMe_3), 173 (32), 73 (45); high-resolution mass spectrum (70 eV), *m/e* 273.1903 ($C_{17}H_{27}NSI$ requires 273.1913).

Photolysis of 1-Methyl-2-phenyl-1-pyrrolinium Perchlorate with 2-Methyl-4-(trimethylsilyl)-2-butene. Preparation of 1-Methyl-2-(2-methylbut-2-en-4-yl)-2-phenylpyrrolidine (13). A nitrogen-purged solution (100 mL) containing 1-methyl-2-phenyl-1-pyrrolinium perchlorate (400 mg, 1.54 mmol) and 2-methyl-4-(trimethylsilyl)-2-butene (3 g, 0.021 mol) in acetonitrile was irradiated for 85 min in a preparative photolysis apparatus. The photolysate was worked up with base in the same manner as for irradiation with 3-(trimethylsilyl)propene. GLC analysis of the oily residue showed the formation of two products (**13** and **14**) which were separated by preparative GLC. The physical properties of the pyrrolidine **14** (53 mg, 21%) were identical with those reported for the known compound.[26] The photoadduct **13** (132 mg, 37%) showed the following spectroscopic properties: ^{1}H NMR ($CDCl_3$) δ 1.64 (br s, 6 H, *gem*-CH_3), 1.7–2.2 (m, 4 H, methylenes at C-3 and C-4 of ring), 2.10 (s, 3 H, NCH_3), 2.2–3.1 (m, 4 H, methylene α to N and allylic H), 5.02 (br t with additional splitting by *gem*-dimethyl, J_{vic} = 6.8 Hz, 1 H, olefinic H), 7.1–7.4 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 229 (0.2, M^+), 160 (100), 158 (4.1), 118 (4.3), 91 (4.8), 77 (4.9); ^{13}C NMR ($CDCl_3$) δ 142.8 (s, C-1 aromatic), 132.3 (s, disubstituted olefin), 127.5 (d, meta aromatic), 127.3 (d, ortho aromatic), 126.0 (d, para aromatic), 121.2 (d, monosubstituted olefin), 68.1 (s, C-2 of ring), 53.7 (t, C-5 of ring), 37.6 (t, allylic CH_2 α to C-2 of ring), 35.0 (q, NCH_3), 33.9 (t, C-3 of ring), 25.9, 18.1 (q, *gem*-methyls), 22.2 (t, C-4 of ring); high-resolution mass spectrum (70 eV), *m/e* 229.1852 ($C_{16}H_{23}N$ requires 229.1831).

Photolysis of 1-Methyl-2-phenylpyrrolinium Perchlorate with *trans*-1,3-Bis(trimethylsilyl)propene. Preparation of 1-Methyl-2-phenyl-2-[*trans*-1-(trimethylsilyl)prop-1-en-3-yl]pyrrolidine (18). A nitrogen-purged solution (100 mL) containing 1-methyl-2-phenyl-1-pyrrolinium perchlorate (400 mg, 1.54 mmol) and *trans*-1,3-bis(trimethylsilyl)propene (5 g, 0.027 mol) in acetonitrile was irradiated for 100 min in a preparative photolysis apparatus. The photolysate, after the same basic workup as for irradiation with 3-trimethylsilyl)propene, was subjected to molecular distillation, giving 359 mg (85%) of the photoadduct 18 as an oil, which was further purified by preparative GLC: ^1H NMR ($CDCl_3$) δ 0.004 (s, 9 H, $Si(CH_3)_3$), 1.81–1.95 (m, 2 H, methylene at C-4 of ring), 2.07–2.15 (s, 3 H, NCH_3), 2.49 and 2.95 (m, J_{gem} = 14.5 Hz, J_{vic} = 6.2 Hz, $J_{allylic}$ = 1.0 Hz, 2 H, allylic CH_2), 2.7–2.9 (m, 2 H, methylene at C-5 of ring), 5.74 and 5.96 (m, J_{trans} = 18.5 Hz, 2 H, olefinic H), 7.1–7.4 (m, 5 H, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 273 (1.1, M^+), 196 (5.5), 161 (100), 158 (18.9), 118 (20.5), 91 (17.2), 77 (15.9), 73 (42.0); ^{13}C NMR ($CDCl_3$) δ 145.0 (d, olefin β to silyl group), 144.9 (s, C-1 aromatic), 134.3 (d, olefin α to silyl group), 128.8 (d, meta aromatic), 128.4 (d, ortho aromatic), 127.3 (d, para aromatic), 68.9 (s, C-2 of ring), 55.1 (t, C-5 of ring), 44.3 (t, allylic CH_2 α to C-2 of ring), 39.1 (t, C-3 of ring), 36.3 (q, NCH_3), 23.4 (t, C-4 of ring), 1.26 (q, $Si(CH_3)_3$); high-resolution mass spectrum (70 eV), *m/e* 273.1882 ($C_{17}H_{27}NSi$ requires 273.1913).

Fluorescence Quenching Experiments. Fluorescence measurements for 1-methyl-2-phenyl-1-pyrrolinium perchlorate (4, 1×10^{-3} M) were made at 25 °C. Excitation of 4 was at 280 nm. Concentrations of the quenchers were in the 5×10^{-2}–4×10^{-1} M ranges. The quenchers do not absorb light in the excitation region of the pyrrolinium salts. The fluorescence efficiencies were measured at six or more quencher concentrations. Slopes and intercepts of Stein–Volmer plots were obtained by least-squares analysis of the data. Quenching rate constants were then calculated on the basis of the known[5] lifetime of 4^{S_1} of 1 ns.

Relative Quantum Yields for Disappearance of 1-Methyl-2-phenyl-1-pyrrolinium Perchlorate (4) at Different Concentrations of 3-(Trimethylsilyl)propene. Aliquots (2 mL) of solutions containing 4 (5×10^{-3} M) and 3-(trimethylsilyl)propene at different concentrations were put into quartz tubes (4-mm i.d.). The photolysis tubes were immersed in a water bath at the center of which was a 450-W Hanovia medium-pressure mercury lamp surrounded by cooling water and a Corex filter. Each photolysis tube was held at the same distance from the lamp. The versatility and accuracy of this simple device was checked first by using the same samples in all tubes: the conversions of 4 in four samples ([3-(trimethylsilyl)propene] = 0.5 M) were 43.7%, 43.2%, 42.5%, and 41.3%, when they were irradiated for 10 min. The temperature of the water bath was kept constant (25 ± 1 °C) during irradiation. Relative quantum yields for disappearance of 4 were obtained from the decrease of absorbance of photolysis solutions at the λ_{max} of 254 nm.

Quantum Yield Measurements. Quantum yields were measured with a "linear optical bench" system equipped with a 500-W high-pressure mercury lamp (Illumination Industries, Type 500-2-1288), with photocell actinometry as previously described,[6] and with a filter solution cell with three 1-cm compartments containing, separatey, 1.0 M nickel sulfate in 5% sulfuric acid, 0.8 M cobalt sulfate in 5% sulfuric acid, and 0.0001 M bismuth chloride in 10% hydrochloric acid. The UV transmission of this filter was 250–310 nm with a maximum at 280 nm.

The quantum yield for the formation of the photoadduct 11 was measured by use of a solution of 4 (5.00×10^{-3} M) and 3-(trimethylsilyl)propene (0.200 M) in 135 mL of acetonitrile. Product analyses were performed by GLC on the reaction mixtures, worked up as in the preparative run, by using 2-methoxynaphthalene as an internal standard: ϕ = 0.010, 0.011, and 0.0091 at 0.47%, 0.65%, and 0.71% conversion to the product, respectively.

The quantum yields for disappearance of 4 at different concentrations of 3-(trimethylsilyl)propene were obtained from the ratio [1.98 ± 0.14 at 0.2 M 3-(trimethylsilyl)propene] of the disappearance yield to the photoadduct 11 formation yield, the averaged quantum yield (0.0099) for the product formation at 0.2 M 3-(trimethylsilyl)propene, and the relative quantum yields for 4 disappearance. The product formation yields were 7.33%, 12.7%, 22.0%, and 24.3% at 15.8%, 24.6%, 38.9%, and 49.8% of the 4 disappearance yield, respectively.

Quantum Yields of Reactions of 1-Methyl-2-phenyl-1-pyrrolinium Perchlorate (4) with Allylsilanes 6 and 8–10. Solutions (6 mL) containing 4 (5.0×10^{-3} M) and allylsilanes 6 and 8–10 (7.50×10^{-3} M) in quartz tubes (7 mm i.d. × 25 cm) were positioned in a circular way around lamp and irradiated with Corex-filtered light for 20 min. For each irradiation, a solution (6 mL) containing 4 (5.0×10^{-3} M) and 3-(trimethylsilyl)propene (0.2 M) in CH_3CN was used as the actinometer. Aliquots (0.3 mL) of the photolysates were diluted (25 mL) with CH_3CN prior to measurements of UV absorbances at 254 nm. Quantum yields for disappearance of 4 were calculated from decreases in absorbances at this wavelength. Aliquots (5 mL) of the photolysates were concentrated under reduced pressure to yield residues to which 0.5 mL of 2-methoxynaphthalene in $CHCl_3$ (15 mg/25 mL) as an internal standard, 0.1 mL of saturated $NaHCO_3$, and 0.1 mL of water were added. These $CHCl_3$ solutions were washed with 0.2 mL of water, dried by passing them through a column containing anhydrous Na_2SO_4 (4 mm i.d. × 2 cm), and analyzed by GLC (5% OV-101, 6 ft × $^1/_8$ in. column) for the amounts of 1-methyl-2-phenyl-2-(4-2-methyl-2-butenyl)pyrrolidine (13) (150 °C, 35-mL flow rate) and 1-methyl-2-phenyl-pyrrolidine (14) (120 °C, 35-mL flow rate) produced.

Detection of 2,5,5-Trimethylhepta-2,6-diene (17) and 2,7-Dimethylocta-2,6-diene (16). Solutions (6 mL) containing 4 (5.0×10^{-3} M) and the allylsilanes 6 and 8–10 (7.5×10^{-3} M) in quartz tubes were irradiated with Corex-filtered light for 20 min. Aliquots of the photolysates were directly analyzed by GLC (5% OV-101, 6 ft × $^1/_8$ in. column, 80 °C, 35-mL flow rate). The 1,5-hexadienes 16 and 17 were found to be present in each photolysate in a ratio of ca. 1:1 and in yields of ca. 5%.

Product Yields from Photolysis of Pyrrolinium Perchlorate 4 with Allylsilanes 6 and 8–10. Solutions (6 mL) containing 4 (5.0×10^{-3} M) and allylsilanes 6 and 8–10 (7.5×10^{-3} M) in quartz tubes were irradiated with Corex-filtered light. The photolysate was subjected to a normal workup and was analyzed by GLC by using 2-methoxynaphthalene as an internal standard in the same way as described for the determination of quantum yields (vide supra). Conversions were ca. 75% of 4, and yields were calculated on the basis of percent conversion of 4.

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