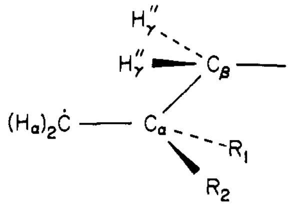
Table I. Comparison of Measured γ-Hydrogen Hyperfine Splittings with Values Calculated for *n*-Propyl in the Appropriate Conformation (hfs in G)

radical	θ_{Me}, deg	$H'\gamma$ ($\theta_\gamma = 180°$) measd	$H'\gamma$ ($\theta_\gamma = 180°$) calcd[a]	$H''\gamma$ ($\theta_\gamma = 60°$) measd	$H''\gamma$ ($\theta_\gamma = 60°$) calcd[a]
1	90	+0.10[b]	−0.26	−0.59	−0.27
2	60	+1.45	+0.89	−0.72	−0.49[b]
3	45	+4.04	+2.06[c]	−0.62	−0.48[c]
	0		4.37		−0.69

[a] From Table XIV of ref 5. [b] For $\theta_\gamma = -60°$ the calculated value is −0.23. [c] Estimated from data in Table XIV.

is expected to be somewhat larger than that found for CH_3 rotation in *n*-propyl, viz.,[7] 3.7 kcal/mol.[20] The CH_3 groups in **2** and **3** are therefore expected to be frozen (on the EPR time scale) into the conformation (**4**) having minimum steric interaction at temperatures above that at which the methyl of *n*-propyl freezes out, i.e. at ca. 110 K.[7] For all three radicals the preferred conformation of each methyl should have one hydrogen (H'_γ) with $\theta_\gamma = 180°$ and two hydrogens (H''_γ) with $\theta_\gamma = 60°$, see **4**.



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As we expected, the neopentyl radical (generated photochemically from di-*tert*-butyl peroxide, triethylsilane, and neopentyl bromide in *n*-propane) at 96 K gave an EPR spectrum (Figure 1) in which the nine γ hydrogens were not all equivalent: $a^{H_\alpha}(2H) = 21.4$ G; $|a^{H'_\gamma}(3H)| = 4.04$ G; $|a^{H''_\gamma}(6H)| = 0.62$ G. As the temperature is raised the lines broaden until at 175 K only a broad triplet remains. At higher temperatures, a new γ structure appears and sharpens until at ca. 225 K hfs's from nine equivalent γ-H can, as previously reported,[21,22] be observed: $|a^{H_\gamma}(9H)| = 0.96$ G. Similarly, isobutyl (generated by the same technique) at 90 K gave an EPR spectrum having the following hfs's:[23] $a^{H_\alpha}(2H) = 21.3$ G; $a^{H_\beta}(1H) = 35.3$ G; $|a^{H'_\gamma}(2H)| = 1.45$ G; $|a^{H''_\gamma}(4H)| = 0.72$ G (see Figure 2). At temperatures above 125 K the γ structure broadens and coalesces into a single line. The septet splitting from six equivalent γ-H cannot be resolved.[23]

For neopentyl the spectral width due to the γ hydrogens is 15.84 G at low and 9.64 G at high temperatures. *The signs of the H′ and H″ hfs's must therefore be different*, which confirms the fact that a^{H_γ} is strongly dependent on θ_γ. Following Ellinger et al.[4,5] we assign H′ a positive and H″ a negative sign, i.e., a^{H_γ} (high temperature, 9H) $= (3a^{H'_\gamma} + 6a^{H''_\gamma})/9 = (12.12 - 3.72)/9 = +0.93$ G, which is in satisfactory agreement with the experimental value of 0.96 G. Similarly, for isobutyl we assign $a^{H'} = +1.45$ G and $a^{H''} = -0.72$ G; this yields a^{H_γ} (high temperature, 6H) = +0.003 G; which serves to explain why the γ hydrogens of this radical cannot be resolved at high temperatures! Finally, from our own data for *n*-propyl we assign $a^{H''_\gamma} = -0.59$ and from our $|a^{H_\gamma}$ (high temperature, 3H)$| = 0.36$ G we conclude that $a^{H'_\gamma} = +0.10$ G.

The foregoing results are summarized in Table I, where they are compared with the results computed by Ellinger et al.[5] for *n*-propyl in the appropriate conformation. Four facts are clear: (i) a^{H_γ} is strongly dependent on θ_γ for all three radicals; (ii) $a^{H'_\gamma}$ ($\theta_\gamma = 180°$) is strongly dependent on θ_{Me}, rising from near zero for *n*-propyl ($\theta_{Me} = 90°$) to a predicted maximum of ca. 8 G in the ideal W-plan[25] ($\theta_{Me} = 0°$) arrangement; (iii) $a^{H''_\gamma}(\theta_\gamma = 60°)$ is virtually independent of θ_{Me}; (iv) ab initio calculations give an excellent qualitative and a satisfactory quantitative description of our experimental results.

Registry No. 1, 2143-61-5; 2, 4630-45-9; 3, 3744-21-6.

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Electron Transfer Initiated Photoaddition of Allylsilanes to 1-Methyl-2-phenylpyrrolinium Perchlorate. A Novel Allylation Methodology

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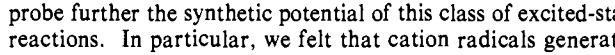
In previous reports[1-3] we have described our initial exploratory and mechanistic studies of olefin iminium salt photochemistry. In these we described irradiations of 2-phenyl-1-pyrrolinium perchlorate (**1**) in the presence of electron-rich olefins and methanol which lead to formation of interesting adducts. The stuctural, regiochemical, and stereochemical characteristics of these processes are best rationalized by mechanisms involving one electron transfer from the olefins to the singlet excited state of **1** followed by nucleophilic capture of the derived cation radical **3** and coupling, as outlined for isobutylene addition in Scheme I. In some cases the intermediate cation radicals undergo another characteristic reaction involving deprotonation. This is demonstrated in the photochemistry of **1** with cyclohexene which produces the allylic addition product **6** via deprotonation of **4** as outlined in Scheme I. Analogous electron–proton-transfer pathways operate in additions of alcohols and ethers to iminium salts[2] as well as in amine–ketone reductions[4] and amine–aromatic hydrocarbon additions.[5] Another route open to the oxygen-based cation radical generated by electron transfer from 1,1,2-trimethylcyclopropanol is cleavage of the weak, alkyl-substituted cyclopropane bond leading to the 4-butan-2-onyl radical.[2]

Thus, the results of these preliminary studies suggest that cation radicals, generated by one electron transfer from n- and π-electron donors to iminium salts excited states, undergo predictable transformations leading to radical precursors of addition products. We felt that this postulate might be useful in designing new systems to test the validity of the mechanistic rationale and to probe further the synthetic potential of this class of excited-state reactions. In particular, we felt that cation radicals generated by electron transfer from allylsilanes would undergo ready desilylation in the presence of even weak nucleophiles to produce allyl radicals (reaction 1).[6] This pathway should compete ef-



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† Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University, Oita, Japan.

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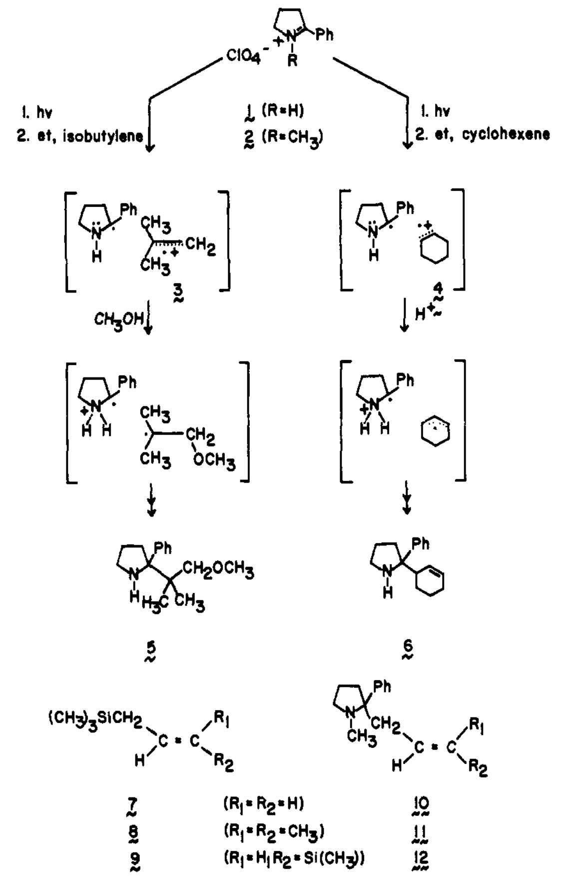
Table I. Electron Transfer and Fluorescence Quenching Rate Constants for Pyrrolinium Salt (1 and **2**) and Allylsilane (7–9) Systems

quencher	$E_{1/2}(+)$,[a] V vs. Ag/Ag$^+$	ΔG_{et},[b] kcal/mol	k_{et}[b] $\times 10^{-10}$, M$^{-1}\cdot$s^{-1}	k_q[c] $\times 10^{-9}$, M$^{-1}\cdot$s^{-1}	
				1	**2**
8	1.07	−34.6	1.5		6.2 ± 0.2
9	1.48	−25.1	1.5		
$PhCH_2Si(CH_3)_3$	1.48	−25.1	1.5	6.22 ± 0.06	5.9 ± 0.2
cyclohexene	2.03	−12.4	1.3	6.00 ± 0.04	4.27 ± 0.06
7	1.94	−14.5	1.4	5.25 ± 0.07	4.10 ± 0.05
1-octene	2.56	−0.22	0.2	4.59 ± 0.05	3.19 ± 0.06
$CH_2{=}CHSi(CH_3)_3$	2.82	+5.8	0.9×10^{-4}	3.16 ± 0.01	1.45 ± 0.03

[a] Oxidation potentials were calculated from known or estimated ionization potentials[9] by use of the relationship of Miller.[15] [b] Calculated by use of the Weller relationship[7] and known emission spectroscopic and electrochemical data for 1 and **2**.[1,2] [c] Concentrations of 1 and 2 in acetonitrile at 25 °C and 1×10^{-4} and 1×10^{-3} M, respectively. τ_0 for 1 is 16 ns and for **2** is 1 ns.

Scheme I



fectively with nucleophilic attack on carbon and deprotonation and, thus, could potentially provide a selective route for allylic photoaddition to iminium salts. In this communication we report results of initial studies which indicate that these thoughts are correct.

Electron transfer from allylsilanes to singlet excited states of the 2-phenylpyrrolinium salts 1 and **2** should be efficient[7] as a result of favorable σ–π interactions[8] between silicon and olefinic groups, leading to low ionization potentials.[9] This feature is reflected in the observation that the allylsilanes 7 and 8 serve as efficient quenchers of the fluorescence of **1** and **2** even though exchange energy transfer in these cases is strongly endoergic. Quenching rate constants obtained from slopes of linear Stern–Volmer plots of ϕ_{f0}/ϕ_f vs. [Q] were near the diffusion-controlled limit and compared favorably with those found for olefin quenching and predicted by electron-transfer theory (Table I).[7] The emission and absorption spectroscopic properties of mixtures of the allylsilanes and pyrrolinium salts do not indicate excited- or ground-state complex formation. It is not possible to obtain fluorescence quenching data for the bis(trimethylsilyl)propene **9** due to its instability, a result of rapid protodesilylation,[10] and poor absorption characteristics.

In order to determine if efficient electron transfer in these systems is translated into useful photochemistry, photoadditions of the allylsilanes of **2** were explored. Irradiation (Corex) of methanolic solutions of **2** with ca. 1 M allylsilane **7** led to production of a single major product, isolated after base treatment of the photolysate, silica gel chromatography, and preparative GLC in a 42% yield. The structure of this material is assigned as the 2-phenyl-2-allylpyrrolidine (**10**) on the basis of characteristic spectroscopic properties and comparisons with those of analogous substances.[1-3] Careful analysis of the crude reaction mixture revealed the absence of products incorporating methoxyl groups or the (trimethylsilyl)propene side chain which would originate by methanol addition to or deprotonation of an intermediate cation radical derived from **7**. The adduct **10** is also produced upon irradiation of **2** and **7** in acetonitrile solution. Furthermore, no reaction producing **10** was observed when **2** and **7** were subjected to dark reaction conditions which mimicked those used for the photoreaction.

Similarly, the photoadduct **11** was obtained (47%) from irradiation of **2** in acetonitrile containing 0.2 M prenylsilane **8**, followed by basic workup and molecular distillation. The presence of the 3,3-dimethylprop-2-en-1-yl rather than the 1,1-dimethylprop-2-en-1-yl side chain in **11** is easily determined by ^{1}H NMR [δ 1.64 (gem-dimethyl), 5.02 (br t, J = 6.8 Hz, vinyl)] and ^{13}C NMR [vinyl carbons at 132.3 (s) and 121.2 ppm (d)] analysis. The regioisomeric adduct could not be detected by ^{1}H NMR inspection of the crude photolysate. An analogous process, capable of providing similar mechanistic information, is found in the photoreaction of **2** with bis(trimethylsilyl)propene (**9**). Accordingly, photoaddition occurs upon irradiation of **2** in acetonitrile solutions of **9** (0.27 M) to yield (85%) the adduct **12** after purification by molecular distillation. The ^{1}H NMR spectrum of **12** which contains two vinyl hydrogen resonances at δ 5.74 (dt, J = 18.5, 1.0 Hz) and δ 5.96 (dt, J = 18.5, 6.2 Hz) reveals the presence of the trans-disubstituted olefinic moiety.

Quantum yields for disappearance of **2** (ϕ_{dis}) and formation of **10** (ϕ_r) as a function of allylsilane **7** concentration in acetonitrile were determined in order to gain information about the nature of the excited state of **2** responsible for photoaddition and the detailed mechanism of the process. Steady-state analysis of the kinetic sequence shown in Scheme II gives $\phi_{dis}{}^{-1} = \alpha^{-1} + k_{dis}\tau_0$-$[7])^{-1}$ and $k_{dis} = k_c\alpha k_{et}/(k_{et} + k_{-c})$ where the limiting ([7] →

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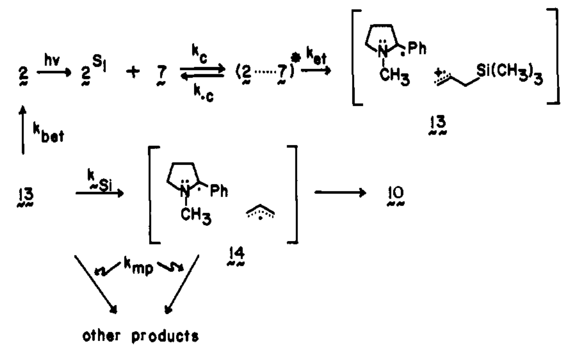
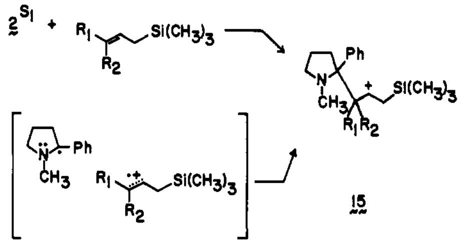
Scheme II



Scheme III



$\infty)\phi_{dis}$ and rate constant for disappearance of **2** are represented by $\alpha = k_{Si} + k_{mp})/(k_{bet} + k_{Si} + k_{mp})$ and k_{dis}, respectively. Thus, the ratio of the intercept to slope from a plot of $\phi_{dis}{}^{-1}$ vs. $[7]^{-1}$ found to be 3.4 ± 0.6 M^{-1} is equal to $k_{dis}\tau_0/\alpha$. The slope of $k_q\tau_0$ obtained from the Stern–Volmer plot of fluorescence quenching data is experimentally 3.8 ± 0.1 M^{-1} and mathematically $k_{dis}\tau_0/\alpha$. Thus, the close agreement of the quantities obtained from these separate experiments suggests that fluoresence quenching and photoreaction are kinetically coupled and, thus, that photoaddition is a singlet excited-state process of **2**. ϕ_{dis} is twice as great as ϕ_r at equal [**7**], suggesting that alternative, as yet unidentified, reaction pathways are available to this system (k_{mp}). If the products of these alternate pathways arise via the cation radical pair **13** or an ensuing intermediate such as **14**, we can estimate that $k_{Si} \sim k_{mp}$ and $k_{bet} \sim 34k_{Si}$. Therefore, the quantum inefficiency of the photoadditions (ϕ_r = 0.01 at [**7**] = 0.2 M) is due mainly to back-electron-transfer from **13**, a process expected to be rapid.

The allylsilane pyrrolinium salt photoadditions represent a potentially interesting class of carbon–carbon bond-forming reactions. Their regio- and stereochemical courses can be understood in terms of pathways involving nucleophile-induced desilylation[11] of initially formed cation radicals followed by coupling at the least substituted allyl radical terminus.[12] Importantly, the regiochemistry observed is inconsistent with alternate mechanisms for these additions in which either attack of the electron-rich allylsilane occurs on the high-energy iminium cation, or cation radical pair coupling occurs prior to desilylation. Both of these routes would produce intermediate **15**, and thus, conjugate addition[13] analogous to that seen in reaction of allyl silanes with electrophiles should predominate due to the efficient σ–π stabilization of cations by adjacent C–Si bonds.[14,8a] Further mechanistic and synthetic aspects of these processes should be uncovered in our continuing studies in this area.[16]

Registry No. 1, 69105-60-8; **2**, 2826-88-2; **7**, 762-7. **8**, 18293-99-7; **9**, 17891-78-0; **10**, 80326-41-6; **11**, 80326-42-7; **12**, 80326-43-8; cyclohexene, 110-83-8; 1-octene, 111-66-0; $PhCH_2Si(CH_3)_3$, 770-09-2; $CH_2{=}CHSi(CH_3)_3$, 754-05-2.

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[11] Weak nucleophiles such as CH_3CN are apparently sufficient for desilylation of the allylsilane-derived cation radicals. Desilylation by this nucleophile follows Ritter-reaction-type pathways leading most probably to acetamide and polysiloxanes upon workup. The low mass balances obtained from irradiations of **2** in the presence of allylsilanes **7** and **8** are most probably due to losses incurred during product purification and to alternate reaction pathways followed by the radical components of the pairs **14** (Scheme II). The alternate pathways must produce volatile products since NMR spectroscopic analyses of the crude photolysates demonstrate the absence of other major components. This speculation is supported by recent, unpublised observations which show that intramolecular counterparts of the reactions described here are exceptionally efficient. Accordingly, photocyclizations of *N*-(trimethylsilylallyl) iminium salts take place in near quantitative yields due to the prohibition of radical cage escape pathways.

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Diverse Mechanisms of Carbon–Hydrogen Bond Formation through Binuclear Reductive Elimination Reactions

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Although binuclear reductive elimination reactions between transition-metal alkyls and hydrides constitute important steps in a variety of stoichiometric and catalytic processes (for example, the product-forming steps in olefin hydrogenation and hydroformylation[1]), only recently have such reactions received direct attention.[2-5] Several recent studies of such reactions have revealed puzzlingly diverse reactivity patterns and yielded disparate mechanistic conclusions.[2-4] We describe here some results of an ongoing study of reactions between several benzylmanganese carbonyls (**1**) and the corresponding hydridomanganese carbonyl complexes (**2**) which reveal clearly the accessibility of several distinct mechanisms for such bimolecular reductive elimination (including a free radical mechanism involving metal–carbon bond homolysis) and identify some of the factors that influence the choice among these mechanisms.

p-X-$C_6H_4CH_2Mn(CO)_4L$(cis)
1a, X = CH_3O;
L = CO
1b, X = CH_3O;
L = $(p\text{-}CH_3OC_6H_4)_3P$
1c, X = H;
L = CO

$HMn(CO)_4L$(cis)
2a, L = CO
2b, L = $(p\text{-}CH_3OC_6H_4)_3P$

Reaction of 1a with 2a in Nonpolar Solvents. The reaction of **1a** (or **1c**)[6] with **2a** in nonpolar solvents such as benzene yielded the corresponding toluene in accord with eq 1 and with the rate law (eq 2) where k_3(65 °C) = (6.0 ± 0.5) × 10^{-4} s^{-1}, k_{-3}/k_4(65 °C) = 8.5 ± 1.0, $\Delta H_3{}^{\ddagger}$ = 23.2 ± 0.3 kcal/mol and $\Delta S_3{}^{\ddagger}$ = –4.8

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[6] The p-CH_3O-substituted derivatives, **1a**, **1b**, and **2b**, were used because of their higher solubilities and because of the convenience of the OCH_3 ^1H NMR signal. Apart from modest rate variations (e.g., k_3 for **1a** ca. 3 times higher than for **1c**), no significant differences were noted between the behavior of **1a** and **1c**.

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