

ALLYLSTANNANE PHOTOADDITIONS TO IMINIUM SALTS.
EFFICIENCIES OF SEQUENTIAL ELECTRON TRANSFER DESTANNATION
VERSUS DESILYLATION PATHWAYS

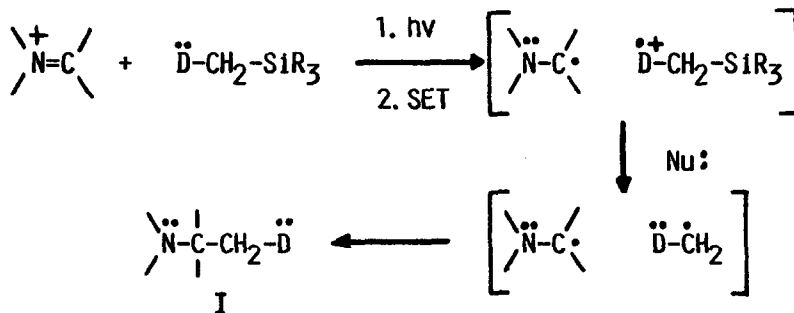
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SUMMARY. Electron transfer induced, photoadditions of allyltins to 1-methyl-2-phenyl-1-pyrrolinium perchlorates have been probed. The quantum efficiencies of these processes are larger than that for photoaddition of the corresponding allylsilane.

In previous investigations, we have explored the photochemistry of iminium salt-allyl and benzylsilane systems.¹ These efforts have established that electron transfer mechanisms (Scheme 1) are operable for generation of the adducts I. Continuing studies focused on preparative applications of these processes have demonstrated their utility as photocyclization methodologies in synthetic approaches to members of the harringtonine,^{2a,b} erythrina,^{2c} and protoberberine and spirobenzylisoquinoline^{2d} alkaloid families.

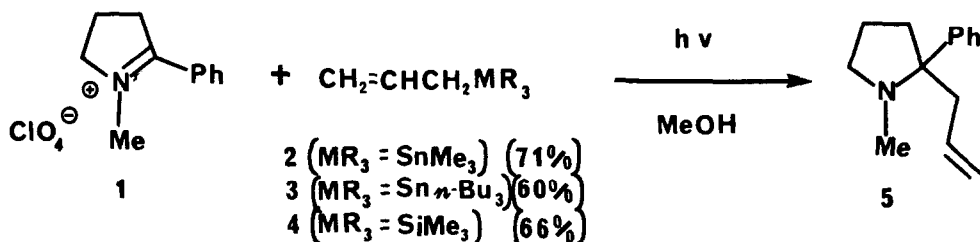
The key step in these photochemical reactions is proposed to be nucleophile induced elimination of the trialkylsilyl moiety, located β to the positively charged radical site. The facility of this elimination is most probably due to the large interaction between the σ_{C-Si} and π orbitals which results in delocalization of the positive charge density into the C-Si σ -bond. This feature, while leading to thermodynamic stabilization of the radical cation function,³ results in a kinetic instability similar to that possessed by β -silyl carbocations.⁴ Thus, the low ionization potential⁵ and facile



electrophilic substitution reactions of allylsilanes⁶ are both rationalized on the basis of these features. Orbital interactions of this type exist to a greater extent in allylstannane systems. In fact, the ionization potential of the tin-substituted propenes are lower than those for the silicon analogs,⁷ and allylstannanes are known to readily participate in allylation reactions with carbon electrophiles.⁸

On the basis of these observations, we felt that the electron transfer induced, photoreaction pathways followed by organosilanes as outlined in Scheme 1 might be also followed by the corresponding tin-species. In addition, we anticipated that the enhanced σ (metal-carbon) π -orbital interaction in the stannane cases could lead to higher photoaddition reaction efficiencies. Preliminary studies have confirmed these postulates.

Irradiation ($\lambda > 250\text{nm}$) of 1-methyl-2-phenyl-1-pyrrolinium perchlorate (1)^{1a,9} in the presence of allyltrimethylstannane (2)¹⁰ (0.20M) in methanol, followed by basic work-up and chromatographic purification (silica gel) led to isolation of the known¹ pyrrolidine 5. Similar results were obtained when allyltri-n-butylstannane was used as substrate or when acetonitrile was employed as solvent. Control experiments established that addition reactions did not occur in the absence of light. Importantly, the yields for production of the isolated adduct 5 from the allylstannanes 2(71%) and 3(60%) are nearly the same as that from the analogous silicon species 4 (66%).¹¹



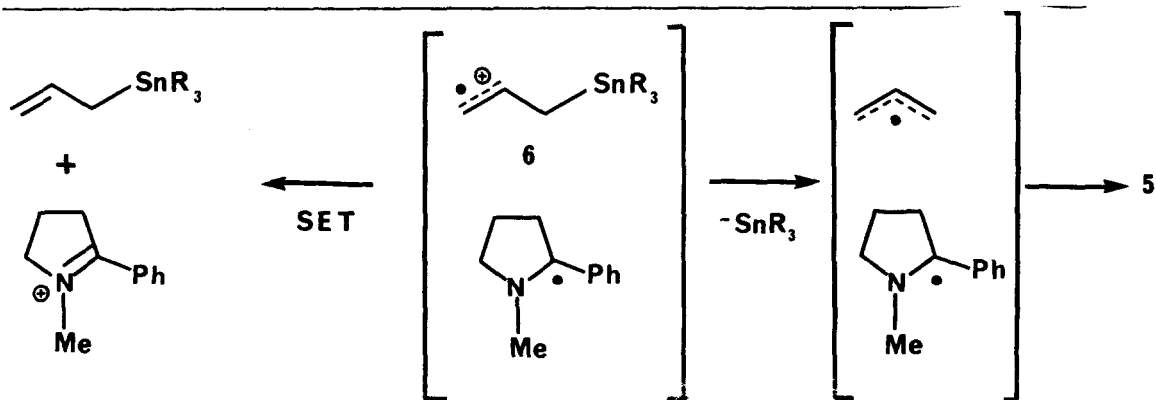
Quantum yield measurements reveal a more dramatic difference between the efficiencies for electron transfer induced photoadditions of the allylstannanes and allylsilane to pyrrolinium salt 1. The limiting quantum yields (α_T) for adduct formation were determined by measuring the quantum efficiencies at varying concentrations of the allylmetallic substrate in acetonitrile (Table 1).¹² The intercepts of $1/\phi$ vs. $1/[\text{allylmetallic}]$ plots correspond to quantum yields at infinite allylmetallic concentration and reflect the relative rates of cation radical pair demetallation vs. back electron transfer. As is evident from inspection of the data in Table 1, the efficiencies for allylstannane photoadditions are approximately one order of magnitude greater than that for the allylsilane photoaddition. This difference can be attributed to the greater interaction occurring between the $\sigma_{\text{Sn-C}}$ and π -orbital in the cation radical 6 which causes a greater rate of demetallation relative to back electron transfer.

Table 1. Limiting Quantum Yields for Photoadditions of Allylmetallics 2-4 to Pyrrolinium Perchlorate 1.

Allylmetallic	α_f
2	0.23 ± 0.03^a
3	0.21 ± 0.03^a
4	0.02 ± 0.002^b

(a) Obtained at low allylmetallic concentration, due to competitive light absorption, by the method described in ref. 1a.

(b) This value was determined in previous work, ref. 1a.



The lower ionization potential of allylstannanes as compared to allylsilanes contributes to the observed differences in fluorescence quenching rate constants. Accordingly, the k_q -values (MeCN, 25°C) for quenching of 1 fluorescence by 2 and 4 are $6.8 \pm 0.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $4.1 \pm 0.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively, reflecting the respective ionization potentials of 8.7eV⁷ and 9.0 eV⁵ for 2 and 4.

We are continuing our investigations of the allyltin and related benzytin electron transfer induced, photoaddition reactions in order to evaluate their synthetic potential.¹³

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References

- (1) (a) Ohga, K.; Yoon, U.C.; Mariano, P.S., *J. Org. Chem.*, **1984**, *49*, 213; (b) Ohga, K.; Mariano, P.S., *J. Am. Chem. Soc.*, **1982**, *104*, 617; (c) Lan, A.J.Y.; Quillen, S.; Heuckeroth, R.O.; Mariano, P.S., *J. Am. Chem. Soc.*, **1984**, *106*, 6439.
- (2) (a) Tiner-Harding, T.; Ullrich, J.W.; Chiu, F.T.; Chen, S.F.; Mariano, P.S., *J. Org. Chem.*, **1982**, *47*, 3360; (b) Chiu, F.T.; Ullrich, J.W.; Mariano, P.S., *J. Org. Chem.*, **1984**, *49*, 228; (c) Ahmed-Schofield, R.; Mariano, P.S., *J. Org. Chem.*, **1985**, *50*, 5667; (d) Ho, G.Y.; Lan, A.J.Y.; Mariano, P.S., *Tetrahedron Lett.*, **1985**, 5867.

- (3) (a) Bock, H.; Kaim, W., Acc. Chem. Res., **1982**, 159 and references therein; (b) Traylor, T.G.; Berwin, H.J.; Jerkunica, J.; Hall, M.L., Pure Appl. Chem., **1972**, 30, 399 and references therein.
- (4) Colvin, E.W., "Silicon in Organic Synthesis", Butterworth, London, **1981**, pp. 97-124.
- (5) Weidner, U.; Schweig, A., J. Organometall. Chem., **1972**, 39, 261.
- (6) See for example, Hosomi, A.; Saburen, H., Tetrahedron Lett., **1976**, 1295; **1977**, 4041, **1978**, 2589 and references therein.
- (7) Brown, R.S.; Eaton, D.F.; Hosomi, A.; Traylor, T.G.; Wright, J.M., J. Organometall. Chem., **1974**, 66, 249.
- (8) Hosomi, A.; Iguchi, H.; Endo, M.; Dakumi, H., Chem. Lett., **1979**, 977, Takuwa, A.; Naruta, Y.; Saga, O.; Maruyama, K., J. Org. Chem., **1984**, 49, 1857.
- (9) Mariano, P.S.; Stavinoha, J.; Bay, E., Tetrahedron, **1981**, 37, 3385.
- (10) The trialkylstannanes **2** and **3** were prepared by the method of Jones, W.J.; Davies, W.C.; Bowden, S.T.; Edwards, C.; Davis, V.E.; Thomas, L.H., J. Chem. Soc., **1947**, 1446.
- (11) Note that the yield of adduct **5** production from allylsilane **4** is slightly higher than that previously reported^{1a} owing to yield optimization.
- (12) Quantum yields for photoadditions of the allylstannanes to pyrrolinium salt **1** were measured at varying allylstannane concentrations kept low to avoid competitive light absorption by these donors. Quantum yields for adduct **5** formation from photoreaction of **1** with allylstannane **2** (ϕ and [allylstannane]) are 0.007 ($5.31 \times 10^{-3} M$), 0.009 ($5.99 \times 10^{-3} M$), 0.013 ($7.52 \times 10^{-3} M$), 0.014 ($1.01 \times 10^{-2} M$). A plot of this data (ϕ^{-1} vs [allylstannane] $^{-1}$) gives a reciprocal intercept corresponding to the limiting quantum yield (α_r) of 0.23 and an intercept to slope ratio corresponding to $k_q \tau$ of $3.8 M^{-1}$. The latter value compares favorably with the $k_q \tau$ value of $6.8 M^{-1}$ obtained by Stern-Volmer analysis of fluorescence quenching data.
- (13) Electron transfer induced photoadditions of organostannanes to cyanoaromatics have been previously explored by Eaton, D.F., J. Am. Chem. Soc., **1981**, 103, 7235; **1980**, 102, 3280.

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