

Regio-reversal in Thermal and Photochemical Reduction of 10-Methylacridinium Ion by Allylic Silanes and Stannanes

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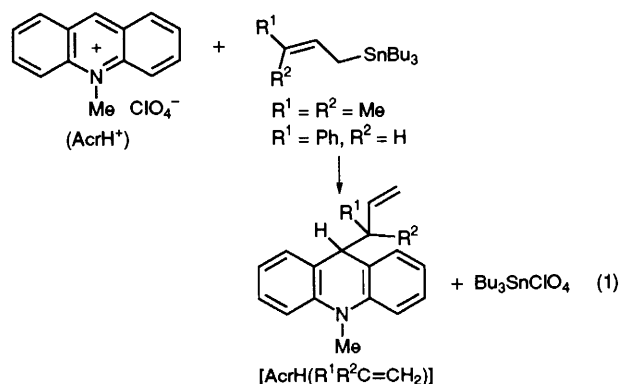
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Thermal reduction of 10-methylacridinium ion by allylic stannanes occurs *via* a polar mechanism to yield the dihydroacridines allylated at the γ -position exclusively, while the photoallylation of 10-methylacridinium ion proceeds *via* the photoinduced electron transfer from allylic silanes and stannanes to the singlet excited state of 10-methylacridinium ion to yield mainly the α -adducts.

Organo-silanes and -stannanes have been frequently used as key reagents for many synthetically important transformations.^{1,2} On the other hand, carbon-carbon bond formation *via* photoinduced electron-transfer reactions of organo-silanes and -stannanes has recently attracted growing interest not only because of the mechanistic aspects but also in view of synthetic utility.³⁻⁶ However, no mechanistic comparison has so far been made for the thermal and photochemical carbon-carbon bond formation reactions of organo-silanes and -stannanes with the same substrates.

This study reports that the photochemical reduction of 10-methylacridinium perchlorate ($\text{AcrH}^+\text{ClO}_4^-$) by allylic silanes and stannanes occurs efficiently and regioselectively to yield the allylated dihydroacridines and that the thermal reduction of the same oxidants by allylic stannanes also occurs with the reversed regioselectivities. Thus, these reaction systems provide a nice opportunity to compare directly the chemoselectivities as well as the regioselectivities in both the thermal and photochemical C-C bond formation reactions of the organometallic compounds and to gain comprehensive and confirmative understanding for their mechanistic difference.

Upon mixing AcrH^+ (4.8×10^{-5} mol) with allyltributyltin ($\text{CH}_2=\text{CHCH}_2\text{SnBu}_3$; 6.4×10^{-5} mol) in acetonitrile (0.80 cm^3), AcrH^+ was readily reduced to yield selectively 9-allyl-10-methyl-9,10-dihydroacridine [$\text{AcrH}(\text{CH}_2\text{CH}=\text{CH}_2)$; 100% yield]. When unsymmetrical allylic stannanes, *i.e.* prenyltributyltin ($\text{Me}_2\text{C}=\text{CHCH}_2\text{SnBu}_3$) and tributyl-*trans*-cinnamylstannane ($\text{PhCH}=\text{CHCH}_2\text{SnBu}_3$) were employed, the allylic group was introduced exclusively at γ -position [eqn. (1)]. These products were well identified from their ^1H NMR spectra.[†] No thermal reduction of AcrH^+ has occurred when allylic silanes are employed instead of allylic stannanes.

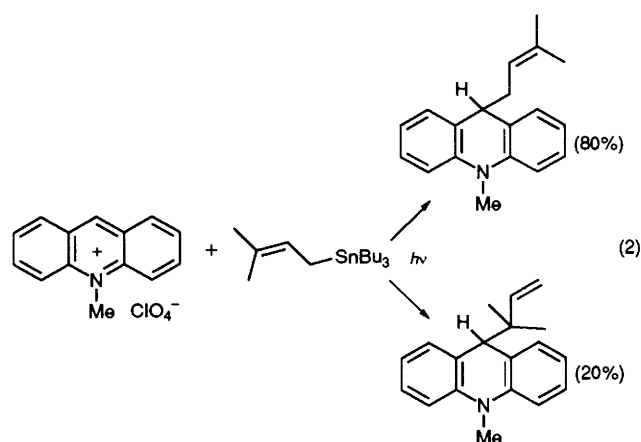


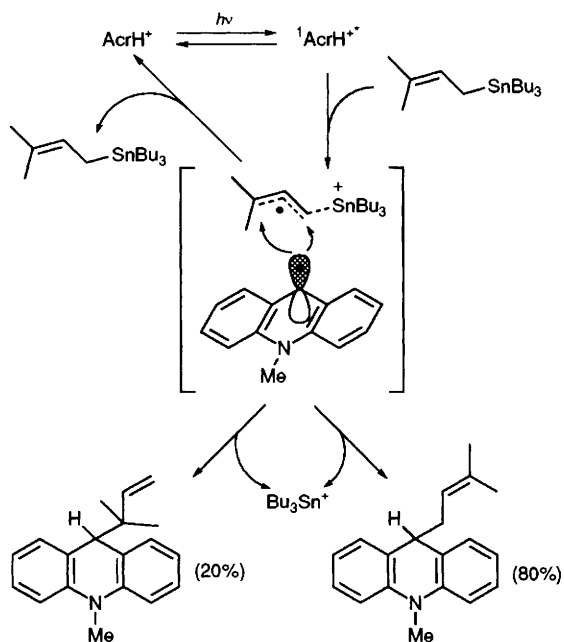
[†] The ^1H NMR measurements were performed using a Japan Electron Optics JNM-GSX-400 (400 MHz) NMR spectrometer. Representative data of ^1H NMR spectra in CD_3CN : $\text{AcrH}(\text{CH}_2\text{CH}=\text{CH}_2)$ δ 2.26 (t, 2H, J 7.3 Hz), 3.36 (s, 3H), 3.96 (t, 1H, J 7.3 Hz), 4.76 (dd, 1H, J 2.0, 17 Hz), 4.87 (dd, 1H, J 2.0, 10.3 Hz), 5.68 (m, 1H), 6.9–7.2 (m, 8H); $\text{AcrH}(\text{CH}_2\text{CH}=\text{CMe}_2)$ δ 0.89 (s, 3H), 0.93 (s, 3H), 2.21 (t, 2H, J 7.3 Hz), 3.40 (s, 3H), 3.89 (t, 1H, J 7.3 Hz), 5.10 (t, 1H, J 7.3 Hz), 6.95–7.29 (m, 8H); $\text{AcrH}(\text{CMe}_2\text{CH}=\text{CH}_2)$ δ 0.84 (s, 6H), 3.30 (s, 3H), 3.73 (s, 1H), 4.45 (dd, 1H, J 2.0, 17.6 Hz), 4.74 (dd, 1H, J 2.0, 10.7 Hz), 5.69 (dd, 1H, J 10.7, 17.6 Hz), 6.9–7.2 (m, 8H).

Rates of reduction of AcrH^+ by allylic stannanes were followed by the disappearance of the absorbance ($\lambda = 415$ nm) due to AcrH^+ . The rates obeyed the ordinary second-order kinetics, showing the first-order dependence on the concentration of each reactant. The observed second-order rate constants ($k_{\text{obs}}/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) at 298 K decreases with the γ -substitution by Ph and Me_2 [6.4×10^{-2} ($\text{CH}_2=\text{CHCH}_2\text{SnBu}_3$) $> 1.4 \times 10^{-2}$ ($\text{PhC}=\text{CHCH}_2\text{SnBu}_3$) $> 5.2 \times 10^{-3}$ ($\text{Me}_2\text{C}=\text{CHCH}_2\text{SnBu}_3$)], demonstrating clearly the presence of steric effect of the substituent at the carbon where the C-C bond is formed with AcrH^+ . In such a case the thermal addition reactions of organostannanes may proceed *via* a polar mechanism in which the C-C bond formation occurs prior to the cleavage of Sn-C bond.

On the other hand, irradiation of the absorption band of AcrH^+ (1.0×10^{-2} mol dm^{-3}) in deaerated MeCN solution (0.8 cm^3) containing $\text{Me}_2\text{C}=\text{CHCH}_2\text{SnBu}_3$ (1.5×10^{-2} mol dm^{-3}) with a xenon lamp in 30 min at 298 K gives an adduct in which the allylic group is introduced mainly at α -position to yield the α -adduct (80%) and γ -adduct (20%), as shown in eqn. (2). The photochemical reaction was performed under the experimental conditions such that the contribution of the thermal reaction can be neglected. In fact, essentially the same ratio of the α - to γ -adduct was obtained at a much lower reaction temperature (233 K) when the contribution of the thermal reaction, if any, should be completely neglected as compared to the reaction at 298 K. When $\text{PhCH}=\text{CHCH}_2\text{SnBu}_3$ is employed at 298 K, the yield of γ -adduct (43%) is compatible with that of α -adduct (57%). The photoallylation of AcrH^+ also occurs efficiently with allylic silanes. In contrast with the case of the stannane counterpart [eqn. (2)], the photoreduction of AcrH^+ with $\text{Me}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$ yields the α adduct exclusively (100%).

The photoinduced electron transfer from allylic silanes and stannanes to the singlet excited state $^1\text{AcrH}^{+\ast}$ is exergonic judging from the less positive values of the one-electron oxidation potentials (E_{ox}^0) of allylic silanes and stannanes than that of the one-electron reduction potential of $^1\text{AcrH}^{+\ast}$ (E_{red}^0 vs. SCE = 2.32 V).^{5,7} In fact, the fluorescence of $^1\text{AcrH}^{+\ast}$ is quenched efficiently by allylic silanes and stan-





nananes with the quenching rate constants in the range of 1.0×10^{10} to $1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, being close to the diffusion limit in MeCN at 298 K.⁸ Thus, the photoaddition reaction may occur *via* photoinduced electron transfer from allylic silanes and stannanes to $^1\text{AcrH}^{+*}$ as shown representatively for the reaction with $\text{Me}_2\text{C}=\text{CHCH}_2\text{SnBu}_3$ in Scheme 1. The reaction is initiated by photoinduced electron transfer from allylic silanes and stannanes to $^1\text{AcrH}^{+*}$ to give the organometallic radical cation-acridinyl radical pair, followed by the radical coupling in the cage in competition with the back electron transfer to the reactant pair to yield the adduct selectively without dimerization of free AcrH[•] radicals escaped from the cage.

A similar mechanism has been proposed by Mariano *et al.*^{3,9} for the photoaddition reaction of allylic silanes with pyrrolinium ions. They proposed that the free allyl radical produced by desilylation of the organosilane radical cation in methanol is responsible for the product-formation step rather than the carbon-carbon bond formation between the organosilane radical cation and pyrrolidinyl radical, based on the identical regiochemical outcome in the photoaddition of 1,1- and 3,3-dimethylallyl silanes giving the same adduct.^{3,9} If free allyl radicals are responsible for the product formation step in the photoaddition reactions with AcrH⁺ in acetonitrile, however, the regioselectivity would be independent of the metal moiety.

The different regioselectivities observed depending on the metal as well as allylic moiety (see above) thereby indicate that the C-C bond formation occurs prior to the complete demetallation from the organometallic radical cations. In fact, the recent EPR work by Rhodes *et al.*¹⁰ has revealed that no fragmentation from the radical cations of allylic silanes and stannanes is observed at 77 K and that the dissociation occurs on annealing to yield allyl radicals. The important point to note from the EPR work is that the organosilane radical cations are shown to be more stable than the corresponding stannane counterparts, in agreement with the stronger Si-C bonds than the Sn-C bonds.¹⁰ On the other hand, acetonitrile employed as a solvent in this study has recently been shown to act as a much less reactive nucleophile in assisting the Si-C bond cleavage of the silane radical cation than other solvents such as methanol.¹¹ Thus, the change in the regioselectivities observed in the photoaddition of unsymmetrical allylic silanes and stannanes is ascribed to the steric and/or electronic effects of the metal and allylic moieties of the radical cations in the C-C bond formation step with AcrH[•] prior to the complete dissociation of the metal-carbon bonds (Scheme 1).

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