Regioselective Reduction of 1-Methylquinolinium lons by Tributyltin Hydride and Tris(trimethylsilyl)silane via Photoinduced Electron Transfer

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Thermal reduction of 1-methylquinolinium ion by tributyltin hydride occurs *via* a polar mechanism to yield 1-methyl-1,2-dihydroquinoline selectively, while the photoreduction of 1-methylquinolinium ion derivatives by tributyltin hydride and tris(trimethylsilyl)silane proceeds *via* photoinduced electron transfer from the metal hydrides to the singlet excited states of 1-methylquinolinium ion derivatives to yield the corresponding 1,4-dihydroquinolines exclusively.

Tributyltin hydride (Bu₃SnH) is the reducing agent commonly used to conduct radical chain reactions being applied to reductions of a variety of functional groups and the C-C bond formation in organic synthesis.¹ Recently, tris(trimethylsilyl)silane $[(Me_3Si)_3SiH]$ has also emerged as a useful alternative to Bu_3SnH .² Although metal hydrides are regarded as potential hydride donors as well as electron donors,³ little is known about the mechanisms of the hydride- and electron-transfer reactions. On the other hand, nicotinamide adenine dinucleotide (NAD⁺) and analogues are biologically important oxidizing agents. The regioselective reduction of NAD+ analogues has attracted considerable interest in relation with the biological hydride reduction occurring selectively at the C-4 position.⁴ This study reports that the thermal reduction of 1-methylquinolinium ion derivatives (X-QuH⁺) by Bu₃SnH occurs via a polar mechanism to yield mixtures of the corresponding 1,2- and 1,4-dihydroquinolines in which the 1,2-dihydro derivatives predominate but the photochemical reduction by Bu₃SnH and (Me₃Si)₃SiH proceeds via photoinduced electron transfer from the metal hydrides to the singlet excited states of X-QuH+ to yield the corresponding 1,4-isomers exclusively.

Upon mixing QuH⁺ (8.0×10^{-5} mol) with Bu₃SnH (1.9×10^{-4} mol) in acetonitrile (0.80 cm³) at 298 K, QuH⁺ was readily reduced to yield initially 1-methyl-1,2-dihydroquinoline (1,2-QuH₂: 80% in 30 min), which was gradually isomerized to the corresponding 1,4-isomer (1,4-QuH₂: 70% in 70 min) as shown in Scheme 1. The reduction of 1,4-dimethylquinolinium ion (4-Me-QuH⁺) by Bu₃SnH also occurs efficiently to yield exclusively the corresponding 1,2-isomer (4-Me-1,2-QuH₂) which does not isomerizes to the 1,4-isomer. These products were well identified from their ¹H NMR spectra.[†] The isomerization from 1,2-QuH₂ to 1,4-QuH₂ has been reported to occur by the reaction of the 1,2-isomer with QuH⁺ in reduction of quinolinium salts with NaBH₄.⁵ When QuH⁺ is replaced by 1,2-dimethylquino-linium ion (2-MeQuH⁺) in which the C-2 position is blocked

(2-Me-1,4-QuH₂)

Scheme 2

by the methyl group, no reaction with Bu₃SnH has occurred at 298 K (Scheme 2). Irradiation of the absorption band of 2-MeQuH⁺ ($\lambda_{max} = 315$ nm) in deaerated MeCN containing Bu₃SnH with monochromatized light of $\lambda = 315$ nm, however, results in efficient reduction of 2-MeQuH⁺ to yield the corresponding 1,4-isomer (2-Me-1,4-QuH₂) exclusively (Scheme 2).[†] No 1,2-isomer has been formed during the photochemical reaction.

When Bu₃SnH is replaced by $(Me_3Si)_3SiH$, no thermal reduction of X-QuH⁺ (X = H, 2-Me and 4-Me) by $(Me_3-Si)_3SiH$ has occurred at 298 K. As is the case of the photochemical reaction of 2-MeQuH⁺ with Bu₃SnH, irradiation of the absorption band of X-QuH⁺ in deaerated MeCN containing $(Me_3Si)_3SiH$ and H_2O (5.0 mol dm⁻³) results in the efficient reduction of X-QuH⁺ to yield the corresponding 1,4-isomer (X-1,4-QuH₂) exclusively (H₂O is added to trap the silvl cation).

The one-electron oxidation potential (E°_{ox} vs. SCE) (SCE) = standard calomel electrode) of (Me₃Si)₃SiH is 1.30 V by applying the Rehm and Weller free energy relation for electron transfer⁶ as described previously.⁷ Thus, the photoinduced electron transfer from (Me₃Si)₃SiH to the singlet excited states 1X-QuH+* is highly exergonic judging from the much less positive value of the E°_{ox} value of (Me₃Si)₃SiH than those of the one-electron reduction potentials ($E^{\circ}_{red} vs.$ SCE) of ${}^{1}X$ -QuH+* (2.54, 2.46 and 2.51 V for X = H, 2-Me and 4-Me, respectively). In fact, the fluorescence of ¹X-QuH^{+*} is quenched efficiently by (Me₃Si)₃SiH with the quenching rate constants (k_q) in the range of 1.0×10^{10} – 1.3×10^{10} $dm^3 mol^{-1} s^{-1}$, being close to the diffusion limit in MeCN at 298 K.6 Thus, the photoreduction of X-QuH+ by (Me₃Si)₃SiH may occur via photoinduced electron transfer from (Me₃Si)₃SiH to ¹X-QuH^{+*} as shown representatively for the reaction between (Me₃Si)₃SiH and QuH⁺ in Scheme 3.



The reaction is initiated by photoinduced electron transfer from (Me₃Si)₃SiH to ¹QuH^{+*} to give the metal hydride radical cation-quinolinyl radical pair, followed by the hydrogen transfer in the cage in competition with the back-electron transfer to the reactant pair to yield the hydride adduct selectively without dimerization of free QuH radicals escaped from the cage.

According to Scheme 3, the dependence of Φ on the (Me₃Si)₃SiH concentration may be expressed by eqn. (1),

$$\Phi = [k_{\rm H}k_{\rm et} \, \tau/(k_{\rm H} + k_{\rm b})][({\rm Me}_{3}{\rm Si})_{3}{\rm SiH}]/ \{1 + k_{\rm et} \, \tau[({\rm Me}_{3}{\rm Si})_{3}{\rm SiH}]\} \quad (1)$$

where k_{et} and k_b are the rate constants of photoinduced electron transfer and the back-electron transfer, τ is the lifetime of ¹X-QuH^{+*}, $k_{\rm H}$ is the rate costant of hydrogen transfer from (Me₃Si)₃SiH⁺⁺ to X-QuH⁺, respectively. The fluorescence lifetimes τ of ¹X-QuH^{+*} (X = H, 2-Me and 4-Me) were determined as 29, 15 and 19 ns in MeCN by single photon counting using a Horiba NAES-1100 time-resolved spectrofluorophotometer, respectively. The dependence of Φ on [(Me₃Si)₃SiH] was confirmed by the linear plots between Φ^{-1} and $[(Me_3Si)_3SiH]^{-1}$, from which were determined the $k_{\rm et}$ values by using the τ values. The $k_{\rm et}$ values are also diffusion-limited, consistent with the k_q values determined independently, demonstrating the validity of the electrontransfer mechanism in Scheme 3. The existence of the rate-determining hydrogen transfer step following the photoinduced electron transfer in Scheme 3 is confirmed by the deuterium isotope effect determined as $\Phi_{\rm H}/\Phi_{\rm D} = 1.9$ from the ratio of the limiting quantum yields (Φ_{∞}) of $(Me_3Si)_3SiH$ and $(Me_3Si)_3SiD$, which corresponds to $(k_H/k_D)[(k_D +$ $(k_{\rm b})/(k_{\rm H} + k_{\rm b})$ in eqn. (1). In contrast, no kinetic isotope effects have been observed in the k_q and k_{et} values. The Φ_{∞} values of photoreduction of QuH+, 2-MeQuH+ and 4-MeQuH+ by (Me₃Si)₃SiH are 8.0×10^{-2} , 9.6×10^{-2} and 7.6×10^{-2} , respectively. Similar Φ_{∞} values irrespective of methyl substituents show sharp contrast with the diminished reactivity of 2-MeQuH+ in the thermal reduction by Bu₃SnH (Scheme 2). Thus, the thermal reduction of X-QuH+ by Bu₃SnH may proceed via a polar mechanism exhibiting the significant steric effect of methyl group at the C-2 carbon where the C-H bond is formed with X-QuH+. In contrast, no significant steric effects have been observed in the photochemical reactions via the photoinduced electron transfer. Since the spin density of X-QuH is greatest at the C-4 position (0.33) as compared with that at the C-2 position (0.23),⁸ the hydrogen

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transfer from the metal hydride radical cation to QuH may occur at the C-4 position to yield the corresponding 1,4-isomer predominantly.

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† The 1H NMR measurements were performed using a Japan Electron Optics JNM-GSX-400 (400 MHz) NMR spectrometer. ¹H NMR spectra in CD₃CN: 1,2-QuH₂ δ 3.00 (s, 3H), 4.20 (m, 2H), 5.8–6.0 (m, 1H), 6.4-7.2 (m, 5H); 1,4-QuH₂ δ 3.18 (s, 3H), 3.40 (m, 2H), 6.6-7.2 (m, 6H); 4-Me-1,2-QuH₂ δ 2.80 (s, 3H), 3.04 (s, 3H), 4.04 (m, 2H), 5.62 (m, 1H), 6.4-7.2 (m, 4H); 2-Me-1,4-QuH₂: 8 3.05 (s, 3H), 3.20 (s, 3H), 3.48 (m, 2H), 5.9-6.0 (m, 1H), 6.8-7.4 (m, 4H); 4-Me-1,4-QuH₂: δ 3.02 (s, 3H), 3.18 (s, 3H), 3.40 (m, 1H), 6.6-7.4 (m, 6H). The 1,2- and 1,4-isomers also can be differentiated by their absorption spectra ($\lambda_{max} = 350$ and 250 nm, respectively).

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