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

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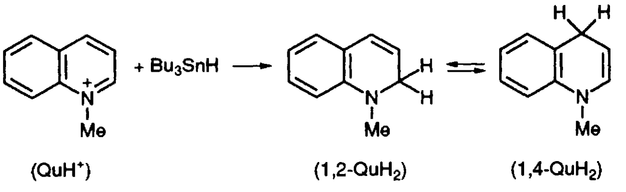
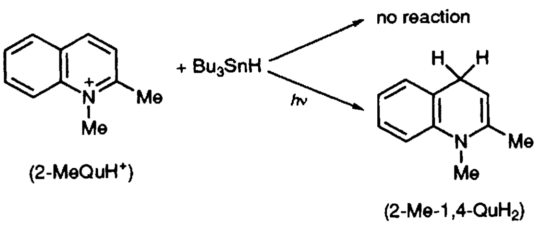
Thermal reduction of 1-methylquinolinium ion by tributyltin hydride occurs *via* a polar mechanism to yield 1-methyl-1,2-dihydroquinoline selectively, while the photoreduction of 1-methylquinolinium ion derivatives by tributyltin hydride and tris(trimethylsilyl)silane proceeds *via* photoinduced electron 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 (Bu_3SnH) 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 ($X\text{-}QuH^+$) by Bu_3SnH 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 Bu_3SnH and $(Me_3Si)_3SiH$ proceeds *via* photoinduced electron transfer from the metal hydrides to the singlet excited states of $X\text{-}QuH^+$ to yield the corresponding 1,4-isomers exclusively.

Upon mixing QuH^+ (8.0×10^{-5} mol) with Bu_3SnH (1.9×10^{-4} mol) in acetonitrile (0.80 cm^3) at 298 K, QuH^+ was readily reduced to yield initially 1-methyl-1,2-dihydroquinoline ($1,2\text{-}QuH_2$: 80% in 30 min), which was gradually isomerized to the corresponding 1,4-isomer ($1,4\text{-}QuH_2$: 70% in 70 min) as shown in Scheme 1. The reduction of 1,4-dimethylquinolinium ion ($4\text{-}Me\text{-}QuH^+$) by Bu_3SnH also occurs efficiently to yield exclusively the corresponding 1,2-isomer ($4\text{-}Me\text{-}1,2\text{-}QuH_2$) which does not isomerizes to the 1,4-isomer. These products were well identified from their ^1H NMR spectra.† The isomerization from $1,2\text{-}QuH_2$ to $1,4\text{-}QuH_2$ has been reported to occur by the reaction of the 1,2-isomer with QuH^+ in reduction of quinolinium salts with $NaBH_4$.[5] When QuH^+ is replaced by 1,2-dimethylquinolinium ion ($2\text{-}MeQuH^+$) in which the C-2 position is blocked by the methyl group, no reaction with Bu_3SnH has occurred at 298 K (Scheme 2). Irradiation of the absorption band of $2\text{-}MeQuH^+$ (λ_{max} = 315 nm) in deaerated MeCN containing Bu_3SnH with monochromatized light of λ = 315 nm, however, results in efficient reduction of $2\text{-}MeQuH^+$ to yield the corresponding 1,4-isomer ($2\text{-}Me\text{-}1,4\text{-}QuH_2$) exclusively (Scheme 2).† No 1,2-isomer has been formed during the photochemical reaction.



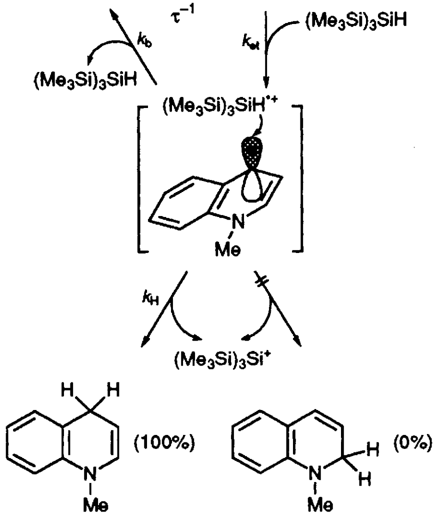
Scheme 1



Scheme 2

When Bu_3SnH is replaced by $(Me_3Si)_3SiH$, no thermal reduction of $X\text{-}QuH^+$ (X = H, 2-Me and 4-Me) by $(Me_3Si)_3SiH$ has occurred at 298 K. As is the case of the photochemical reaction of $2\text{-}MeQuH^+$ with Bu_3SnH, irradiation of the absorption band of $X\text{-}QuH^+$ in deaerated MeCN containing $(Me_3Si)_3SiH$ and H_2O (5.0 mol dm^{-3}) results in the efficient reduction of $X\text{-}QuH^+$ to yield the corresponding 1,4-isomer ($X\text{-}1,4\text{-}QuH_2$) exclusively ($H_2O$ is added to trap the silyl cation).

The one-electron oxidation potential (E°_{ox} *vs.* SCE) (SCE = standard calomel electrode) of $(Me_3Si)_3SiH$ is 1.30 V by applying the Rehm and Weller free energy relation for electron transfer[6] as described previously.[7] Thus, the photoinduced electron transfer from $(Me_3Si)_3SiH$ to the singlet excited states $^1X\text{-}QuH^{+*}$ is highly exergonic judging from the much less positive value of the E°_{ox} value of $(Me_3Si)_3SiH$ than those of the one-electron reduction potentials (E°_{red} *vs.* SCE) of $^1X\text{-}QuH^{+*}$ (2.54, 2.46 and 2.51 V for X = H, 2-Me and 4-Me, respectively). In fact, the fluorescence of $^1X\text{-}QuH^{+*}$ is quenched efficiently by $(Me_3Si)_3SiH$ 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 $X\text{-}QuH^+$ by $(Me_3Si)_3SiH$ may occur *via* photoinduced electron transfer from $(Me_3Si)_3SiH$ to $^1X\text{-}QuH^{+*}$ as shown representatively for the reaction between $(Me_3Si)_3SiH$ and QuH^+ in Scheme 3.



Scheme 3

The reaction is initiated by photoinduced electron transfer from $(Me_3Si)_3SiH$ 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 $QuH^{\bullet}$ radicals escaped from the cage.

According to Scheme 3, the dependence of Φ on the $(Me_3Si)_3SiH$ concentration may be expressed by eqn. (1),

$$\Phi = [k_H k_{et}\,\tau/(k_H + k_b)][(Me_3Si)_3SiH]/\{1 + k_{et}\,\tau[(Me_3Si)_3SiH]\} \quad (1)$$

where k_{et} and k_b are the rate constants of photoinduced electron transfer and the back-electron transfer, τ is the lifetime of $^1X\text{-}QuH^{+*}$, k_H is the rate cosntant of hydrogen transfer from $(Me_3Si)_3SiH^{\bullet+}$ to $X\text{-}QuH^{\bullet}$, respectively. The fluorescence lifetimes τ of $^1X\text{-}QuH^{+*}$ (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 $[(Me_3Si)_3SiH]$ was confirmed by the linear plots between Φ^{-1} and $[(Me_3Si)_3SiH]^{-1}$, from which were determined the k_{et} values by using the τ values. The k_{et} values are also diffusion-limited, consistent with the k_q values determined independently, demonstrating the validity of the electron-transfer 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 $\Phi_H/\Phi_D = 1.9$ from the ratio of the limiting quantum yields (Φ_∞) of $(Me_3Si)_3SiH$ and $(Me_3Si)_3SiD$, which corresponds to $(k_H/k_D)[(k_D + k_b)/(k_H + k_b)]$ 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^+, $2\text{-}MeQuH^+$ and $4\text{-}MeQuH^+$ by $(Me_3Si)_3SiH$ 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 $2\text{-}MeQuH^+$ in the thermal reduction by Bu_3SnH (Scheme 2). Thus, the thermal reduction of $X\text{-}QuH^+$ by Bu_3SnH 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 $X\text{-}QuH^+$. In contrast, no significant steric effects have been observed in the photochemical reactions *via* the photoinduced electron transfer. Since the spin density of $X\text{-}QuH^{\bullet}$ is greatest at the C-4 position (0.33) as compared with that at the C-2 position (0.23),[8] the hydrogen transfer from the metal hydride radical cation to $QuH^{\bullet}$ 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 CD_3CN: $1,2\text{-}QuH_2$ δ 3.00 (s, 3H), 4.20 (m, 2H), 5.8–6.0 (m, 1H), 6.4–7.2 (m, 5H); $1,4\text{-}QuH_2$ δ 3.18 (s, 3H), 3.40 (m, 2H), 6.6–7.2 (m, 6H); $4\text{-}Me\text{-}1,2\text{-}QuH_2$ δ 2.80 (s, 3H), 3.04 (s, 3H), 4.04 (m, 2H), 5.62 (m, 1H), 6.4–7.2 (m, 4H); $2\text{-}Me\text{-}1,4\text{-}QuH_2$: δ 3.05 (s, 3H), 3.20 (s, 3H), 3.48 (m, 2H), 5.9–6.0 (m, 1H), 6.8–7.4 (m, 4H); $4\text{-}Me\text{-}1,4\text{-}QuH_2$: 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 (λ_{max} = 350 and 250 nm, respectively).

References

1 W. P. Neumann, *Synthesis*, 1987, 665; C. P. Jasperse, D. P. Curran and T. L. Fevig, *Chem. Rev.*, 1991, **91**, 1237; B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon, Oxford, 1986.

2 C. Chatgilialoglu, *Acc. Chem. Res.*, 1992, **25**, 188 and references cited therein.

3 J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic, New York, 1978, p. 501; R. J. Klingler, K. Mochida and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 6626; D. Yang and D. D. Tanner, *J. Org. Chem.*, 1986, **51**, 2267.

4 D. M. Stout and A. Meyer, *Chem. Rev.*, 1982, **82**, 2235; J. W. Bunting, *Bioorg. Chem.*, 1991, **19**, 456; S. Fukuzumi, in *Advances in Electron Transfer Chemistry*, ed. P. S. Mariano, JAI Press, Greenwich, 1992, vol. 2, p. 65..

5 R. M. G. Roberts, D. Ostović and M. M. Kreevoy, *J. Org. Chem.*, 1983, **48**, 2053; T. T. Romoff, N. S. Sampson and P. van Eikeren, *J. Org. Chem.*, 1987, **52**, 4454; D. Kim, I.-S. H. Lee and M. M. Kreevoy, *J. Am. Chem. Soc.*, 1990, **112**, 1889.

6 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.

7 S. Fukuzumi and T. Tanaka, in *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, part C, ch. 10; S. Fukuzumi, M. Fujita, J. Otera and Y. Fujita, *J. Am. Chem. Soc.*, 1992, **114**, 10271.

8 S. Fukuzumi and T. Kitano, *J. Chem. Soc., Perkin Trans. 2*, 1991, 41.