

Selective Photoalkylation of 10-Methylacridinium Ion with Tetra-alkylstannanes or Diethylmercury using Visible Irradiation

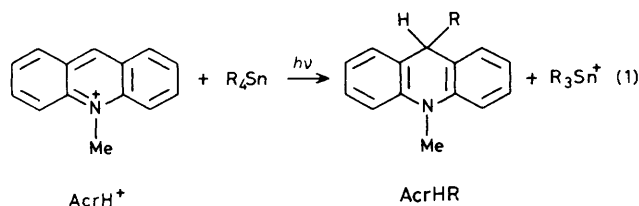
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Efficient and selective photoalkylation of 10-methylacridinium ion with tetra-alkyltin compounds and diethylmercury is initiated by electron transfer from the alkylmetals to the singlet excited state of 10-methylacridinium ion in acetonitrile under irradiation with visible light.

Photoinduced electron-transfer reactions between electron donors and acceptors have attracted growing interest recently not only because of the mechanistic aspects but also in view of their synthetic utility.¹⁻⁴ However, most photochemical electron-transfer-induced reactions so far reported have afforded a mixture of various products.¹⁻⁴ Moreover, most of the photoexcited reagents have so far been limited to those having high energy excited states such as dicyanoarenes¹ and iminium salts,^{2,3} and so the photochemical reactions require irradiation with u.v. light.

We now report a reagent which is photoreducible with visible light irradiation ($\lambda > 390$ nm), the 10-methylacridinium ion (AcrH^+), the 9-position of which can be alkylated selectively by photoinduced electron-transfer reactions with tetra-alkyltin compounds [equation (1)] and dimethylmercury.



10-Methylacridinium perchlorate (green) has an absorption maximum at 417 nm and irradiation of the absorption band causes fluorescence at 490 nm in acetonitrile (MeCN). The fluorescence of AcrH^+ is quenched by tetra-alkyltin compounds R_4Sn ($\text{R} = \text{Me}, \text{Et}, \text{Bu}^n, \text{and Pr}^i$) as well as diethylmercury in MeCN at 298 K. Little quenching of the fluorescence of AcrH^+ was observed using Et_4Si , however. The quenching rate constants k_q were determined from the slopes of the Stern-Volmer plots and the lifetime of the singlet excited state $^1\text{AcrH}^{+*}$ (τ 31 ns).⁵ Table 1 lists the k_q values, which increase with increasing donor ability of the alkyl group of R_4Sn to reach the diffusion limit, $2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.⁶ By applying the Marcus theory,^{7,8} the rate constants, k_{et} , of electron transfer from R_4Sn or Et_2Hg to $^1\text{AcrH}^{+*}$ can be calculated from the one-electron oxidation potentials E_{ox}^0 of R_4Sn and Et_2Hg ^{9,10} and the one-electron reduction potential E_{red}^0 of $^1\text{AcrH}^{+*}$.⁵ The k_{et} values thus obtained are in reasonable agreement with the k_q values (Table 1). Thus, the fluorescence quenching of $^1\text{AcrH}^{+*}$ by R_4Sn and Et_2Hg may occur by electron transfer from the alkylmetals RM to $^1\text{AcrH}^{+*}$ [equation (2)].



Irradiation of the absorption band (λ_{max} , 417 nm) of AcrH^+ ($5.0 \times 10^{-2} \text{ mol dm}^{-3}$) in CD_3CN containing Et_4Sn ($4.1 \times 10^{-2} \text{ mol dm}^{-3}$) under degassed conditions resulted in the formation of 9-ethyl-10-methylacridan and Et_3Sn^+ as shown in Figure 1, the time course of the reaction being monitored by

^1H n.m.r. spectroscopy. Likewise, the photochemical reaction of AcrH^+ with other tetra-alkyltin compounds R_4Sn ($\text{R} = \text{Me}, \text{Bu}^n, \text{and Pr}^i$) gave the corresponding 9-alkyl-10-

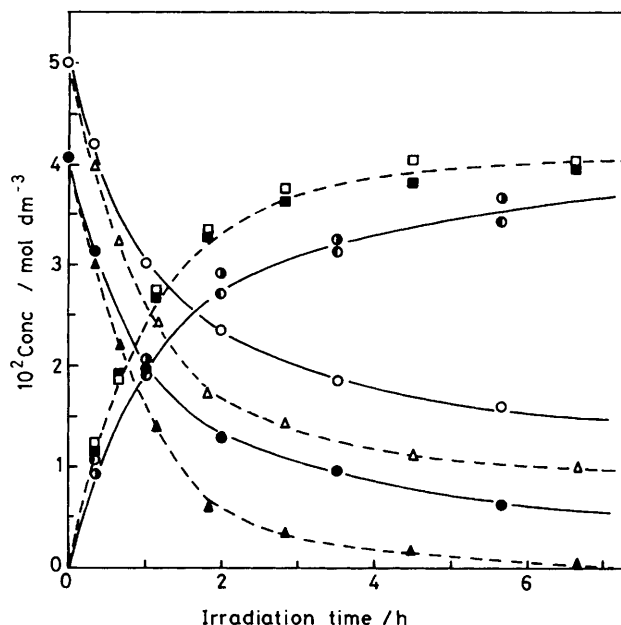
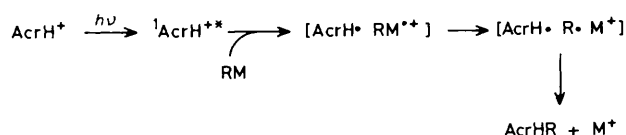


Figure 1. Photoalkylation of AcrH^+ with R_4Sn with visible light irradiation ($\lambda > 390$ nm) in CD_3CN ; $\text{R} = \text{Et}$ (—): AcrH^+ (○), Et_4Sn (●), AcrHEt (◐), Et_3Sn^+ (◑); $\text{R} = \text{Pr}$ (---): AcrH^+ (△), Pr_4Sn (▲), AcrHPr (◒), Pr_3Sn^+ (◓).

Table 1. Rate constants $k_q/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ of the fluorescence quenching of $^1\text{AcrH}^{+*}$ by alkylmetals and the calculated rate constants $k_{et}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ of the electron-transfer reactions from alkylmetals to $^1\text{AcrH}^{+*}$ in MeCN at 298 K.

Alkylmetal	$\log k_q^a$	$\log k_{et}^b$
Et_4Si	c	
Me_4Sn	8.34	8.46
Et_4Sn	10.00	9.91
Bu^n_4Sn	10.08	10.01
Pr^i_4Sn	10.32	10.14
Et_2Hg	10.30	10.14

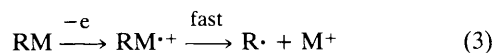
^a The experimental errors of k_q are within $\pm 10\%$. ^b Calculated by applying the Marcus theory (refs. 7 and 8), using the one-electron oxidation potentials of the alkylmetals (refs. 9 and 10) and the one-electron reduction potential of $^1\text{AcrH}^{+*}$, the latter being determined from the one-electron reduction potential of AcrH^+ (-0.43 V vs. standard calomel electrode) and the excitation energy (energy midpoint between the emission and absorption maxima: 2.75 eV); the reorganization energy of the electron transfer (λ 170 kJ mol^{-1}) was taken from ref. 10. ^c Too small to be determined accurately.



Scheme 1

methylacridan (AcrHR) and R_3Sn^+ [equation (1)]. The selective formation of AcrHR was confirmed by ^1H n.m.r. comparison with authentic materials independently prepared.† The use of Et_2Hg in place of Et_4Sn gave the same product, 9-ethyl-10-methylacridan, but this photochemical reaction was hardly detectable when Et_4Si was used as photo-oxidizable reagent. The rates of reaction of the alkylmetals are in the order $\text{Et}_2\text{Hg} \sim \text{Pr}^i_4\text{Sn} > \text{Bu}^n_4\text{Sn} > \text{Et}_4\text{Sn} \gg \text{Me}_4\text{Sn} \gg \text{Et}_4\text{Si}$, as observed for the electron transfer from alkylmetals to ${}^1\text{AcrH}^{+\ast}$ (Table 1).

One-electron oxidation of alkylmetals such as R_4Sn , R_2Hg , and R_4Si has been reported to result readily in the cleavage of the metal-carbon bond, generating the alkyl radical [equation (3)].^{11,12} Thus, the mechanism of the present reaction may be formulated as shown in Scheme 1. Irradiation with visible light ($\lambda > 390$ nm) leads to the excited singlet state of AcrH^+ which is quenched by electron transfer from the alkylmetals to ${}^1\text{AcrH}^{+\ast}$ to generate the radical pair $[\text{AcrH}\cdot \text{RM}^{\ast+}]$. The facile cleavage of the metal-carbon bond of $\text{RM}^{\ast+}$ gives the alkyl



radical [equation (3)] which may combine with $\text{AcrH}\cdot$ to yield 9-alkyl-10-methylacridan selectively.

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† 9-R-10-methylacridan derivatives were prepared by the reduction of 9-R-10-methylacridinium compounds by 1-benzyl-1,4-dihydronicotinamide: ^1H n.m.r. (CD_3CN , 100 MHz) R = Me: δ 1.24 (3H, d), 3.35 (3H, s), 3.99 (1H, q), and 6.8–7.3 (8H, m); R = Et: δ 0.75 (3H, t), 1.46 (2H, q), 3.32 (3H, s), 3.83 (1H, t), and 6.8–7.3 (8H, m); R = Bu^n : δ 0.78 (3H, m), 1.19 (4H, m), 1.49 (2H, m), 3.34 (3H, s), 3.84 (1H, t), and 6.8–7.3 (8H, m); R = Pr: δ 0.70 (6H, d), 1.62 (1H, m), 3.32 (3H, s), 3.57 (1H, d), and 6.8–7.3 (8H, m). The 9-R-10-methylacridinium compounds were prepared by the reaction of methyl iodide or dimethyl sulphate with the 9-R-10-methylacridines which were obtained by the Bernthsen reaction from diphenylamine and the carboxylic acids.