Reduction of 10-Methylacridinium Ion by Alkenes *via* Photoinduced Electron Transfer

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The photoaddition reactions of various alkenes with 10-methylacridinium ion occur efficiently in methanol to yield the adducts in which the methoxy group from methanol is generally introduced in the less substituted sp^2 carbon under irradiation of the visible light. In the case of photochemical reaction of cyclohexene with AcrH$^+$, however, cyclohexene adduct with no incorporation of methoxy group from methanol was obtained as well as the methoxy-incorporated adduct. When a sterically hindered alkene, 2,3-dimethylbut-2-ene is employed, no methoxy group is incorporated in the adduct. On the other hand, the photoaddition of but-2-ene affords two regioisomers, the ratio of which varies slightly depending on the *cis*- and *trans*-isomers as well as reaction temperature. The reaction mechanism involving photoinduced electron transfer from alkenes to the singlet excited state of 10-methylacridinium ion provides a comprehensive and confirmative basis for understanding the product distributions, the fluorescence quenching by alkenes, and the dependence of quantum yields on the alkene concentrations.

Arnold *et al.* have discovered that photoinduced electron transfer from the excited state of methyl *p*-cyanobenzoate to 1,1-diphenylethylene results in the anti-Markovnikov addition of methanol to the olefin.[1] Photoaddition of such nucleophiles to a wide variety of alkenes is also known to proceed *via* photoinduced electron transfer.[2,3] Another pioneering work by Mariano *et al.* has revealed that the photoreduction of pyrrolinium ions by alkenes occurs *via* photoinduced electron transfer from alkenes to the singlet excited states of pyrrolinium ions to yield the adducts.[4-6] Such photoinduced electron transfer has also been invoked as the primary step in the photochemistry of pyridinium and quinolinium ions with alkenes.[7] The photosubstitution reaction between dicyanobenzenes and alkyl olefins as well as the photoaddition of alkenes to cyanoaromatic compounds is also known to be initiated by photoinduced electron transfer.[8-11] However, most of the photoinduced electron transfer reactions of alkenes have so far been limited to those having high energy excited states such as dicyanobenzenes and pyrrolinium ions, requiring irradiation with UV light. Such high energy photochemistry has usually afforded a mixture of various products.[1-11]

This study reports that 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$, green colour) which has an absorption maximum at 358 and 417 nm[12] is highly effective for the selective photoaddition of various alkenes. The clean and simple products formed by the photoreduction of AcrH$^+$ by alkenes disclosed in this study together with the well characterized excited state properties of 10-methylacridinium ion[13,14] provide a nice opportunity to gain more comprehensive and confirmative understanding for the photoinduced electron transfer reactions of alkenes.

Experimental

Materials.—10-Methylacridinium iodide was prepared by the reaction of acridine with methyl iodide in acetone, and it was converted to the perchlorate salt ($AcrH^+ClO_4^-$) by addition of magnesium perchlorate to the iodide salt, and purified by recrystallisation from methanol.[15] Alkenes were obtained commercially. Methanol used as a solvent was purified and dried by the standard procedure.[16] [$^2H_4$]methanol (99.8%, Wako Pure Chemicals) was used without further purification.

Reaction Procedure.—A [$^2H_4$]methanol (CD_3OD) solution (0.8 cm^3) containing AcrH$^+$ (8×10^{-3} mol dm^{-3}) in an NMR tube sealed with a rubber septum was deareated by bubbling with argon gas through a stainless steel needle for 5 min. After an alkene (2 mm^3) was added to the solution by means of a microsyringe and mixed, the solution was irradiated with a high pressure mercury lamp through acetophenone–methanol filter transmitting λ >300 nm at room temp. or in an ice–water bath. The gaseous alkene was introduced into the NMR tube through a stainless steel needle. After the reaction was complete, when the solution became colourless, the reaction solution was analysed by ^{1}H NMR spectroscopy. The ^{1}H NMR measurements were performed using Japan Electron Optics JNM-PS-100 (100 MHz) and JNM-GSX-400 (400 MHz) NMR spectrometers (*J*-values in Hz).

The isolation of products was carried out with 100 ~ 50 times as large scale as compared to the procedure mentioned above. For example, a deaerated methanol solution containing $AcrH^+ClO_4^-$ (50 mg) and MeCH=CMe$_2$ (1.5 cm^3) was irradiated with a high pressure mercury lamp through an acetophenone–methanol filter transmitting λ > 300 nm at room temp. After the reaction was complete, water was added to the resulting solution. Vacuum concentration resulted in precipitation of the products, which were readily isolated by the filtration. The isolated products were analysed by ^{1}H NMR spectroscopy in CDCl$_3$ solution; $\delta_H(CD_3OD)$ **1**, 0.66 (s, 6 H), 2.91 (s, 2 H), 3.31 (s, 3 H), 3.33 (s, 3 H), 4.00 (s, 1 H) and 6.9–7.3 (m, 8 H); **2**: 0.49 (s, 3 H), 0.71 (t, 3 H, *J* 7.8), 1.06–1.15 (m, 1 H), 1.37–1.52 (m, 1 H), 2.90 (d, 1 H, *J* 8.8), 2.96 (d, 1 H, *J* 8.8), 3.31 (s, 3 H), 3.32 (s, 3 H), 4.04 (s, 1 H) and 6.9–7.2 (m, 8 H); **3**, 0.41 (s, 3 H), 0.72 (s, 3 H), 1.01 (d, 3 H, *J* 5.9), 3.12 (q, 1 H, *J* 6.4), 3.31 (s, 3 H), 3.32 (s, 3 H), 4.17 (s, 1 H) and 6.86–7.23 (m, 8 H); **4**, 0.6–2.3 (m, 9 H), 2.95 (dt, 1 H, *J* 3.3, 10.3), 3.30 (s, 3 H), 3.31 (s, 3 H), 4.51 (d, 1 H, *J* 3.3) and 6.8–7.3 (m, 8 H); **5**, 0.6–2.3 (m, 7 H), 3.36 (s, 3 H), 3.65 (d, 1 H, *J* 8.3), 5.4–5.5 (m, 1 H), 5.6–5.7 (m, 1 H) and 6.8–7.3 (m, 8 H); **6**, 0.85 (s, 3 H), 0.9–2.0 (m, 8 H), 2.97 (dd, 1 H, *J* 4.4, 11.2), 3.31 (s, 3 H), 3.36 (s, 3 H), 4.22 (s, 1 H) and 6.8–7.2 (m, 8 H); **7**, 0.9–2.0 (m, 10 H), 3.31 (s, 3 H), 3.62 (d, 1 H, *J* 8.3), 5.17 (m, 1 H) and 6.8–7.2 (m, 8 H); **8**, 0.9–2.0 (m, 10 H), 3.31 (s, 3 H), 4.18 (d, 1 H, *J* 5.7), 5.45–5.48 (m, 1 H) and 6.8–7.2 (m, 8 H); **9**, 1.01 (s, 3 H), 1.51 (s, 3 H), 1.58 (s, 3 H), 2.19 (d, 2 H, *J* 7.8), 3.39 (s, 3 H), 3.89 (t, 1 H, *J* 7.8) and 6.84–7.20 (m, 8 H). $\delta_H(CDCl_3)$ **1**, 0.71 (s, 6 H), 3.12 (s, 2 H), 3.50 (s, 3 H), 3.52 (s, 3 H), 4.17 (s, 1 H) and 6.8–7.4 (m, 8 H); **3**, 0.40 (s, 3 H), 0.74 (s, 3 H), 0.98 (d, 3 H), 3.30 (q, 1 H), 3.30 (s, 3 H), 3.54 (s, 3 H), 4.36 (s, 1 H) and 6.8–7.4 (m, 8 H); **4**, 0.6–2.3 (m, 9 H), 2.9–3.0 (m, 1 H), 3.32 (s, 3 H), 3.48 (s, 3 H), 4.61 (d, 1 H, *J* 3.4) and 6.8–7.3 (m, 8 H); **5**, 0.6–2.3 (m, 7 H), 3.38 (s, 3 H), 3.65 (d, 1 H, *J* 8.3), 5.4–5.5 (m, 1 H), 5.6–5.7 (m, 1 H) and 6.8–7.3 (m, 8 H); **6**, 0.90 (s, 3 H), 0.8–2.2 (m, 8 H), 2.95–2.99 (m, 1 H), 3.32 (s, 3 H), 3.41 (s, 3 H), 4.30 (s, 1 H) and 6.8–7.2 (m, 8 H); **7**, 0.8–2.2 (m, 10 H), 3.37 (s, 3 H), 3.61 (d, 1 H, *J* 8.5), 5.19 (m, 1 H) and 6.8–7.2 (m, 8 H); **8**, 0.8–2.2 (m, 10 H), 3.37 (s, 3 H), 4.19 (d, 1 H, *J* 5.7), 5.49 (m, 1 H) and 6.8–7.2 (m, 8 H); **9**, 1.04 (s, 3 H), 1.56 (s, 3 H), 1.60 (s, 3 H), 2.46 (d, 2 H), 3.55 (s, 3 H), 4.03 (t, 1 H) and 6.8–7.4 (m, 8 H); **A**, 0.56 (d, 3 H, *J* 7.0), 1.07 (d, 3 H, *J* 6.1), 1.82–1.85 (m, 1 H), 3.06–3.08 (m, 1 H), 3.29 (s, 3 H), 3.35 (s, 3 H), 4.18 (d, 1 H, *J* 6.0), 6.69–7.25 (m, 8 H) and **B**, 0.73 (d, 3 H, *J* 6.9), 0.96 (d, 3 H, *J* 6.3), 1.45–1.48 (m, 1 H), 3.06–3.08 (m, 1 H), 3.29 (s, 3 H), 3.37 (s, 3 H), 3.89 (d, 1 H, *J* 9.9) and 6.69–7.25 (m, 8 H). The elemental analysis of the products gave satisfactory results (**1**: Calc. for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 80.61; H, 8.19; N, 4.91%. **3**: Calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.39; H, 8.52; N, 4.67%).

Quantum Yield Determinations.—A standard actinometer (potassium ferrioxalate)[17] was used for the quantum yield determination of the photoreduction of $AcrH^+$ by alkenes. A square quartz cuvette (10 mm i.d.) which contained a methanol solution (3.0 cm^3) of $AcrH^+$ (3.1×10^{-4} mol dm^{-3}) and alkenes (2×10^{-3}–3×10^{-2} mol dm^{-3}) was irradiated with monochromatized light of $\lambda = 358$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and $AcrH^+$ absorbed essentially all the incident light of $\lambda = 358$ nm. The light intensity of monochromatized light of $\lambda = 358$ nm was determined as 1.83×10^{-8} and 5.35×10^{-8} einstein s^{-1} with the slit width of 10 and 20 nm, respectively. The photochemical reaction was monitored by using a Shimadzu UV-160A spectrophotometer. The quantum yields were determined from the decrease in absorbance due to $AcrH^+$ ($\lambda = 396$ nm, $\varepsilon = 3.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}).

Fluorescence Quenching.—Fluorescence measurements were carried out on a Shimadzu RF-5000 spectrofluorophotometer. The excitation wavelength of $AcrH^+$ was 360 nm in MeOH. The monitoring wavelength was that corresponding to the maximum of the emission band at 488 nm. The solution was deoxygenated by argon purging for 10 min prior to the measurements. Relative emission intensities were measured for an MeOH solution containing $AcrH^+$ (3.0×10^{-5} mol dm^{-3}) with an alkene at various concentrations (3×10^{-3}–2×10^{-2} mol dm^{-3}). There was no change in the shape but there was a change in the intensity of the fluorescence spectrum by the addition of an alkene. The Stern–Volmer relationship [eqn. (1)]

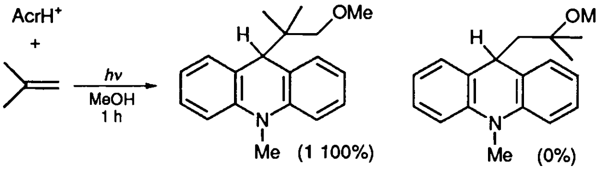
$$I_0/I = 1 + K_{SV}[D] \qquad (1)$$

was obtained for the ratio of the emission intensities in the absence and presence of an alkene (I_0/I) and the concentrations of alkene [D]. The observed quenching rate constants k_q ($= K_{SV}\tau^{-1}$) were obtained from the Stern–Volmer constants K_{SV} and the fluorescence lifetime ($\tau = 31$ ns)[18] of $AcrH^+$.

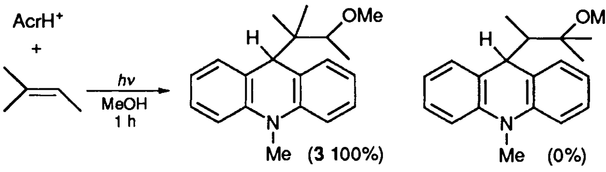
Theoretical Calculations.—The theoretical studies were performed using the PM3 molecular orbital method.[19] The MOPAC program (QCPE No. 455), which was revised as OS/2 Version 5.01 to adapt for the use on a NEC PC computer was obtained through the Japan Chemistry Program Exchange (JCPE).[20] The calculations were also performed by using MOL-GRAPH program Ver. 2.8 by Daikin Industries Ltd. Final geometry and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The geometries of the radical cation ($CH_2{=}CMeEt^{+\bullet}$) and the radical ($^\bullet CH_2CMe{=}CMe_2$) were optimized using the half-electron (HE) method with the restricted Hartree–Fock (RHF) formalism.[21]

Results and Discussion

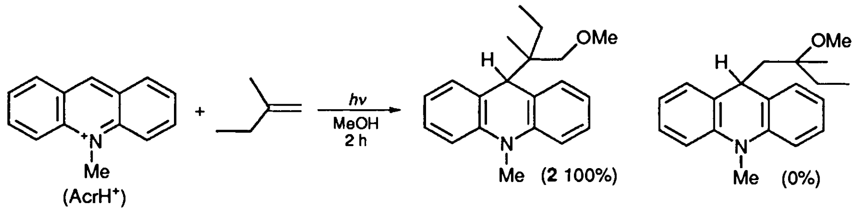
Photoaddition of 10-*Methylacridinium Ion to Alkenes.*—Irradiation of the absorption band of 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) in deaerated methanol solution containing 2-methylpropene for 1 h gave an adduct (**1**) in which methoxy group from methanol is incorporated at the least substituted carbon (Scheme 1). The products are well identified by the ^1H NMR spectra and elemental analysis (see Experimental section). The NMR yield of **1** was 100% and **1** was readily isolated as the sole product (the isolated yield was 79%, see Experimental section) and no other product has been obtained as shown in Scheme 1. Likewise the photoaddition of 2-methylbut-1-ene and 2-methylbut-2-ene occurs efficiently to yield the adducts **2** and **3** as shown in Schemes 2 and 3, respectively. In each case the methoxy group from methanol is selectively introduced in the less substituted sp^2-carbon, and no other products have been obtained (Schemes 2 and 3). Such anti-Markovnikov addition of methanol to alkenes has also been observed in the electron transfer photosensitized addition of nucleophile to styrene derivatives[1,2] as well as the photoaddition reactions of alkenes to pyrrolinium salts.[4–6] Anodic oxidation of alkenes in methanol is also known to result in the methoxylation.[22] In the case of photochemical reaction of cyclohexene with $AcrH^+$, however, cyclohexene adduct (**5**:



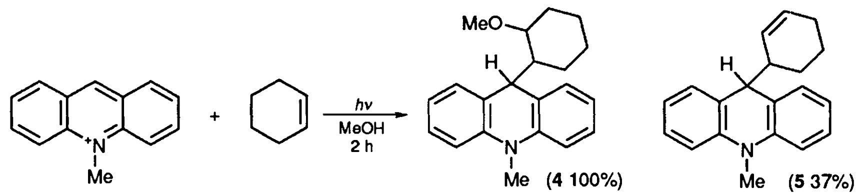
Scheme 1



Scheme 3



Scheme 2



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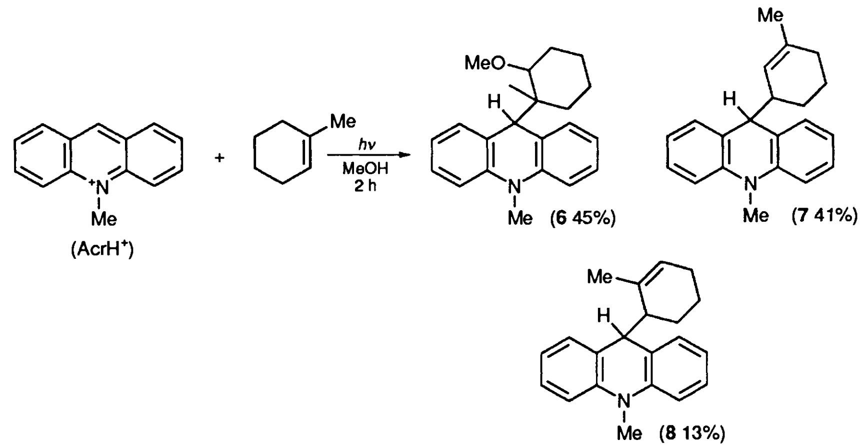

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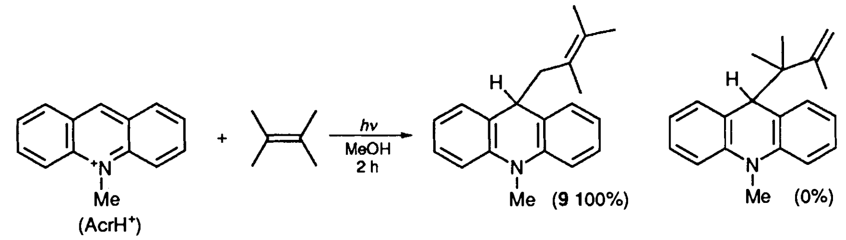
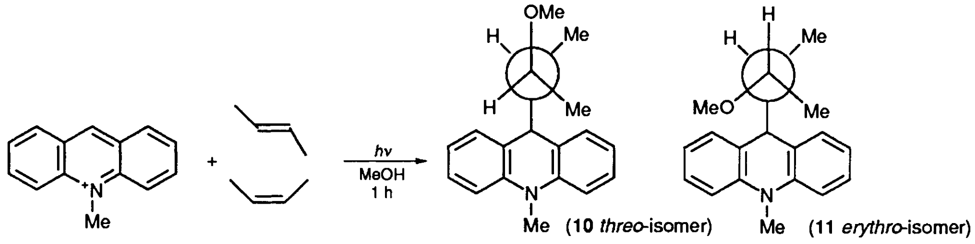


Scheme 6



Scheme 7

37% yield) without incorporation of methoxy group from methanol was obtained as well as the methoxy-incorporated adduct (**4**: 63% yield) as shown in Scheme 4. Mariano *et al.*[4-6] also reported that both the methoxy-incorporated adduct and the cyclohexene adduct without incorporation of methoxy group are obtained in the photoaddition reaction of cyclohexene to pyrrolinium salts. When cyclohexene is replaced by methylcyclohexene, two regioisomers of the methylcyclohexene adduct (**7** and **8**) are obtained as well as the methoxy-incorporated adduct (**6**), Scheme 5. The two regioisomers can be distinguished by the ^{1}H NMR spectra (see Experimental section). When a sterically hindered alkene, 2,3-dimethylbut-2-ene is employed, no methoxy group is incorporated in the adduct, and the alkene adduct (**9**) is obtained as the sole product (Scheme 6). The C–C bond formation in **9** occurs selectively at the sp^3 carbon of methyl group of 2,3-dimethylbut-2-ene and no adduct at the sp^2 carbon has been obtained (Scheme 6).

The photoaddition of (*Z*)-but-2-ene and (*E*)-but-2-ene gives the methoxy-incorporated adducts exclusively. In this case two diastereoisomers (*threo* and *erythro*) are obtained in comparable yields (Scheme 7). The 400 MHz ^{1}H NMR spectra of the products show different signals due to 9-H attached to the dihydroacridine ring of *threo* and *erythro* isomers (see Experimental section). One shows a low field shift with a smaller spin–spin coupling constant (**A**: δ 4.18, J 6.0) as compared to the other (**B**: δ 3.89, J 9.9). Although the assignment of the two isomers is difficult at present in the absence of X-ray data, the isomer distribution (**A** and **B**) depending on (*Z*)-and (*E*)-but-2-ene was examined at different temperatures as shown in Table 1. The isomer distribution is largely the same irrespective of the starting isomer (*Z*)- and [(*E*)-but-2-ene] at 298 K. However, there is a noticeable difference in the isomer distribution: the isomer **A** is somewhat larger than **B** in the case of (*Z*)-but-2-ene and the opposite trend is observed in the case of (*E*)-but-2-ene (Table 1). Such a difference is increased by lowering the reaction temperature. As such the isomer **B** (65% yield) is dominated as compared to **A** (35%) when the photochemical reaction of (*E*)-but-2-ene is carried out in methanol at 273 K (Table 1).

Table 1 Ratios of diastereoisomers in the photoreduction of $AcrH^+$ by but-2-ene in deaerated CD_3OD

		Yield (%)		
Z/*E*	*T*/K	**A**	**B**	**A**/**B**
Z and *E*	298	40	60	0.7
Z	298	56	44	1.3
E	298	42	58	0.8
Z	273	58	42	1.4
E	273	35	65	0.5

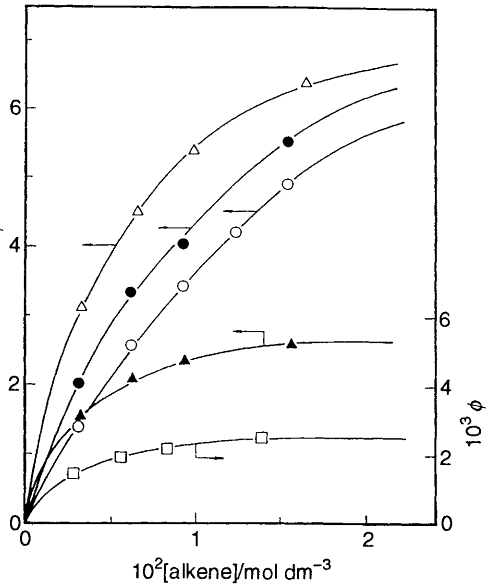


Fig. 1 Dependence of the quantum yields (Φ) on [alkene] for the photoreduction of $AcrH^+$ (3.1×10^{-4} mol dm^{-3}) by alkenes [$CH_2{=}CMeEt$ (○), $MeCH{=}CHEt$ (●), cyclohexene (△), $MeCH{=}CMe_2$ (▲), $Me_2C{=}CMe_2$ (□)] in deaerated MeOH at 298 K

Photoinduced Electron Transfer.—Irradiation of the absorption bands of $AcrH^+$ causes fluorescence at 488 nm in MeOH. The fluorescence of $^1AcrH^{+*}$ is quenched efficiently by alkenes. The quenching rate constants k_q are determined from the slopes of the Stern–Volmer plots and lifetime of the singlet excited state $^1AcrH^{+*}$ ($\tau = 31$ ns).[18] The k_q values thus determined are listed in Table 2, where the k_q values vary depending on alkenes. The Gibbs energy change of photoinduced electron transfer from alkenes to $^1AcrH^{+*}$ (ΔG^0_{et}) is given by eqn. (2), where E^0_{ox} and E^0_{red} are the one-electron oxidation potentials of alkenes

$$\Delta G^0_{et} = F(E^0_{ox} - E^0_{red}) \qquad (2)$$

and the one-electron reduction potential (E^0_{red}) of $^1AcrH^{+*}$ (2.32 V).[13] Since the one-electron oxidation potentials of various alkenes can be estimated by using the empirical relationship between E^0_{ox} and the adiabatic ionization potentials (I_a) of alkenes;[23,24] E^0_{ox}(*vs.* SCE) = $0.89\,I_a - 5.74$,[25] the ΔG^0_{et} values are determined from the I_a and E^0_{red} values by using eqn. (2). The dependence of the activation Gibbs energy of photoinduced electron transfer $\Delta G^{\ddagger}$ on the Gibbs energy change of electron transfer (ΔG^0_{et}) has been well established as given by the Marcus equation [eqn. (3)],[26] where λ is the reorganization energy for

$$\Delta G^{\ddagger} = (\lambda/4)[1 + (\Delta G^0_{et}/\lambda)]^2 \qquad (3)$$

the electron transfer. The λ value of alkene–$AcrH^+$ system is taken as 9.6 kcal mol^{-1}, which is a typical value of various organic electron donors and acceptors.[27] On the other hand $\Delta G^{\ddagger}$ values are related to the rate constant of electron transfer (k_{et}) as given by eqn. (4), where *Z* is the collision frequency that

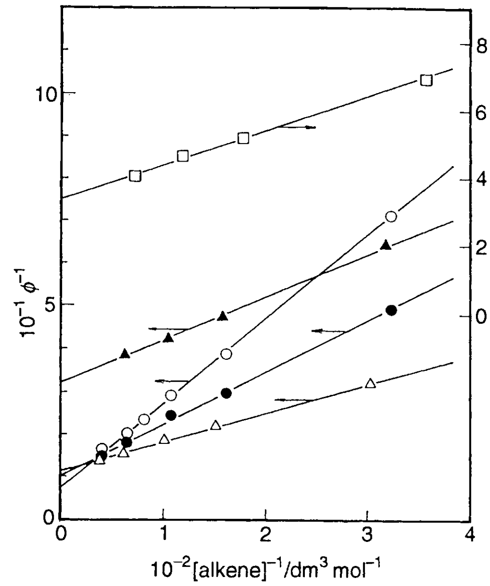


Fig. 2 Plots of Φ^{-1} *vs.* [alkene]$^{-1}$ for the data in Fig. 1

$$\Delta G^{\ddagger} = 2.3RT\log[Z(k_{et}^{-1} - k_{diff}^{-1})] \qquad (4)$$

is taken as 1×10^{11} dm^3 mol^{-1} s^{-1}, and k_{diff} is the diffusion rate constant in MeCN (2.0×10^{10} dm^3 mol^{-1} s^{-1}).[27] Then, the k_{et} values can be calculated from the ΔG^0_{et} and $\Delta G^{\ddagger}_0$ values by using eqns. (3) and (4). The k_{et} values thus obtained are also listed in Table 2, where the k_{et} values agree well with the observed k_q values. The use of the empirical Rehm–Weller equation[27] instead of the Marcus equation [eqn. (3)], which has a theoretical background,[26] gave essentially the same results. Thus, the fluorescence quenching of $^1AcrH^{+*}$ by alkenes may occur *via* photoinduced electron transfer from alkenes acting as electron donors (D) to the singlet excited state $^1AcrH^{+*}$ (Scheme 8).

$$D + {}^1AcrH^{+*} \longrightarrow D^{+\bullet} + AcrH^{\bullet}$$

Scheme 8

Quantum Yields.—Irradiation of the absorption band of $AcrH^+$ (λ_{max} = 358 nm) in deaerated methanol containing an alkene results in the decrease in the absorption band of $AcrH^+$ and the concomitant increase in the absorption band (λ_{max} 285 nm) due to the adduct. The quantum yields (Φ) of the photoaddition reactions of alkenes with $AcrH^+$ were determined from the spectral change under irradiation of monochromatized light of λ_{max} 358 nm (see Experimental section). The Φ value increases with an increase in the concentration of the alkene [D], to approach a limiting value (Φ_∞) in accordance with eqn. (5) as shown in Fig. 1. Eqn. (5) is rewritten

$$\Phi = \Phi_\infty K_{obs}[D]/(1 + K_{obs}[D]) \qquad (5)$$

as eqn. (6) and the linear plots of Φ^{-1} *vs.* $[D]^{-1}$ are shown in Fig. 2. From slopes and intercepts are obtained the Φ_∞ and K_{obs}

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + (K_{obs}[D])^{-1}] \qquad (6)$$

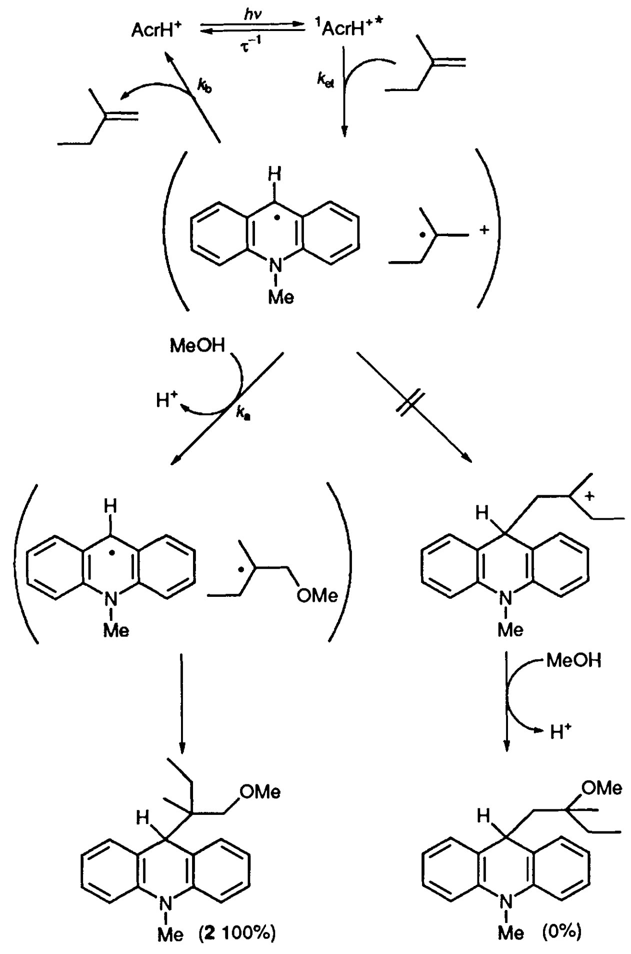
values. The Φ_∞ and K_{obs} values thus determined are summarized in Table 2.

The K_{obs} values can be converted to the corresponding rate constants (k_{obs}) provided that the excited state of $AcrH^+$ involved in the photochemical reaction is singlet ($^1AcrH^{+*}$;

Table 2 Limiting quantum yields Φ_∞, the observed quenching constants K_{obs}, and the rate constants k_{obs} in the photoreduction of AcrH$^+$ by alkenes, the fluorescence quenching rate constants k_q of ^{1}AcrH^{+*} by alkenes in MeOH at 298 K, and the calculated rate constants k_{et} of electron transfer from alkenes to ^{1}AcrH^{+*}

Alkene	Φ_∞	K_{obs}/dm^3 mol^{-1}	k_{obs}/dm^3 mol^{-1} s^{-1}	k_q/dm^3 mol^{-1} s^{-1}	k_{et}[a]/dm^3 mol^{-1} s^{-1}
CH_2=CHPr	[b]	[b]	[b]	$< 10^7$	7.7×10^3 (9.7)
CH_2=CMeEt	0.13	3.3×10	1.2×10^9	1.6×10^9	4.8×10^8 (1.4)
MeCH=CHEt	0.10	8.3×10	2.7×10^9	3.1×10^9	1.9×10^9 (−0.2)
Cyclohexene	0.087	1.7×10^2	5.5×10^9	6.2×10^9	5.9×10^9 (−2.1)
1-Methylcyclohexene	0.020	2.4×10^2	7.9×10^9	9.6×10^9	—
MeCH=CMe_2	0.031	3.1×10^2	1.0×10^{10}	1.1×10^{10}	1.7×10^{10} (−8.8)
Me_2C=CMe_2	0.003	3.3×10^2	1.1×10^{10}	1.2×10^{10}	8.8×10^9 (−16.1)

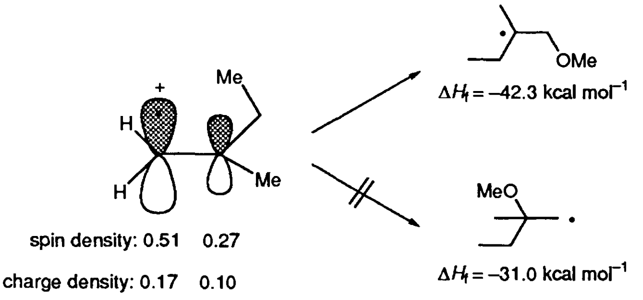
[a] Calculated by using eqns. (2)–(4), see text. The values of parentheses correspond to the Gibbs energy change of electron transfer (ΔG^0_{et}/kcal mol^{-1}).
[b] No reaction.



Scheme 9

$k_{obs} = K_{obs}\,\tau^{-1}$, $\tau = 31$ ns).[18] As shown in Table 2 the k_{obs} values agree well with the k_q values determined independently by the fluorescence quenching of ^{1}AcrH^{+*}, indicating that the photoreduction of AcrH$^+$ by alkenes proceed *via* photoinduced electron transfer from alkenes to the singlet excited state, ^{1}AcrH^{+*} (Scheme 8).

Reaction Mechanism via *Photoinduced Electron Transfer.* Based on the above results the reaction mechanism for the photoaddition reactions of 2-methylbut-1-ene with AcrH$^+$ may be summarized as shown in Scheme 9. The reaction is initiated by photoinduced electron transfer from the alkene to the singlet excited state (^{1}AcrH^{+*}) to give the alkene radical cation-acridinyl radical pair. The nucleophilic addition of methanol to the alkene radical cation in competition with the back electron transfer gives the alkoxy-incorporated radical which may be coupled with acridinyl radical to yield the adduct (Scheme 9).



Scheme 10

According to Scheme 9, the quantum yield is expressed by eqn. (7), which agrees well with the experimental result [eqn. (5)]. The limiting quantum yield Φ_∞ is then expressed by eqn. (8), where the competition between the rate of nucleophilic addition

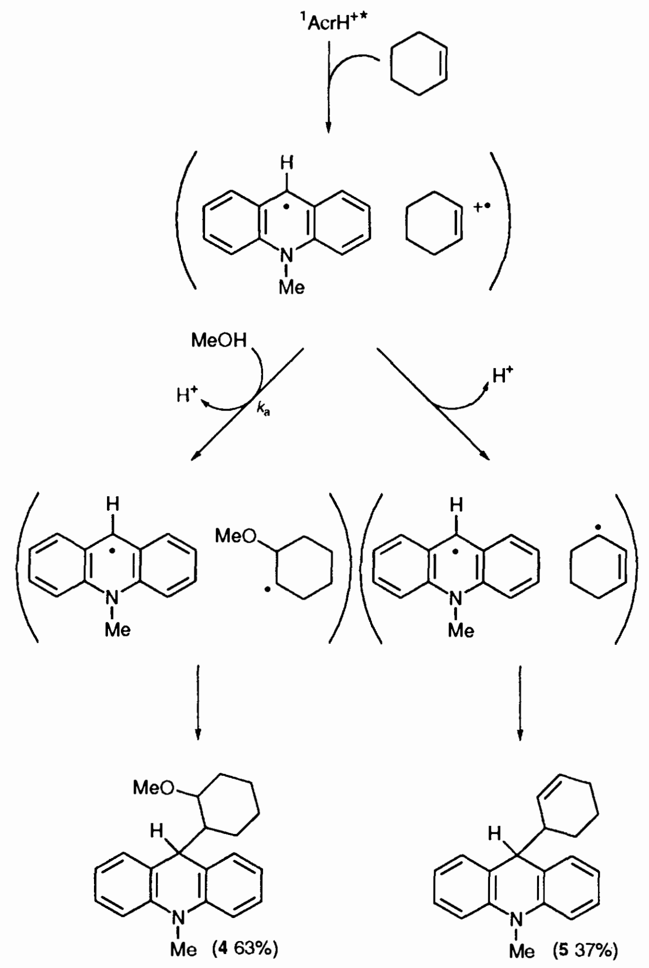
$$\Phi = [k_a k_{et} \tau[D]/(k_a + k_b)]/(1 + k_{et}\tau[D]) \qquad (7)$$

$$\Phi_\infty = k_a/(k_a + k_b) \qquad (8)$$

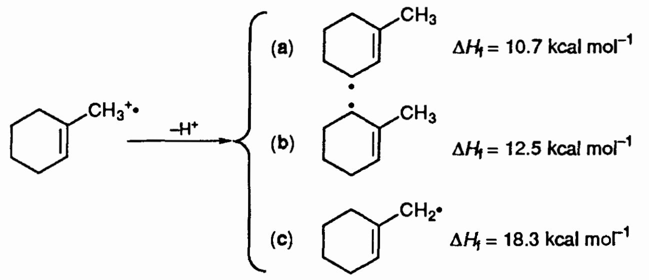
of methoxide ion to the alkene radical cation (k_a) and the back electron transfer (k_b) determines the limiting quantum yield. The nucleophilic addition may occur at the less substituted sp^2 carbon of the alkene radical cation because of the steric effect of the substituent. The PM3 calculation of 2-methylbut-1-ene radical cation also indicates that the charge density at the less substituted sp^2 carbon is larger and thereby more susceptible to the nucleophilic attack (Scheme 10). Moreover, the resulting radical produced by the nucleophilic attack at the less substituted sp^2 carbon is more stable than the other as shown in Scheme 10. Likewise the addition of 2-methylpropene with AcrH$^+$ may proceed *via* photoinduced electron transfer, followed by the nucleophilic addition of methoxide ion to the less substituted sp^2 carbon of the alkene radical cation.

An alternative reaction pathway in which the alkene radical cation adds to AcrH$^\bullet$ first may be unlikely to occur, since such addition would occur at the less substituted sp^2 carbon to yield a different product from **2** (Scheme 9). In fact, the second order rate constant of nucleophilic addition of methanol to the 1,1-diphenylethylene radical cation has been reported as 1.6×10^9 dm^3 mol^{-1} s^{-1} being close to the diffusion limit.[28] Thus, in neat methanol the nucleophilic attack of methanol may precede the radical coupling. In the case of pent-1-ene, however, the one-electron reducing ability is not strong enough to start the photoinduced electron transfer to ^{1}AcrH^{+*} (Table 2).

When cyclohexene is employed, the nucleophilic attack to the radical cyclohexene radical cation may be disfavoured as compared to the non-substituted sp^2 carbons of the radical cations of 2-methylpropene and 2-methylbut-1-ene. In fact, the



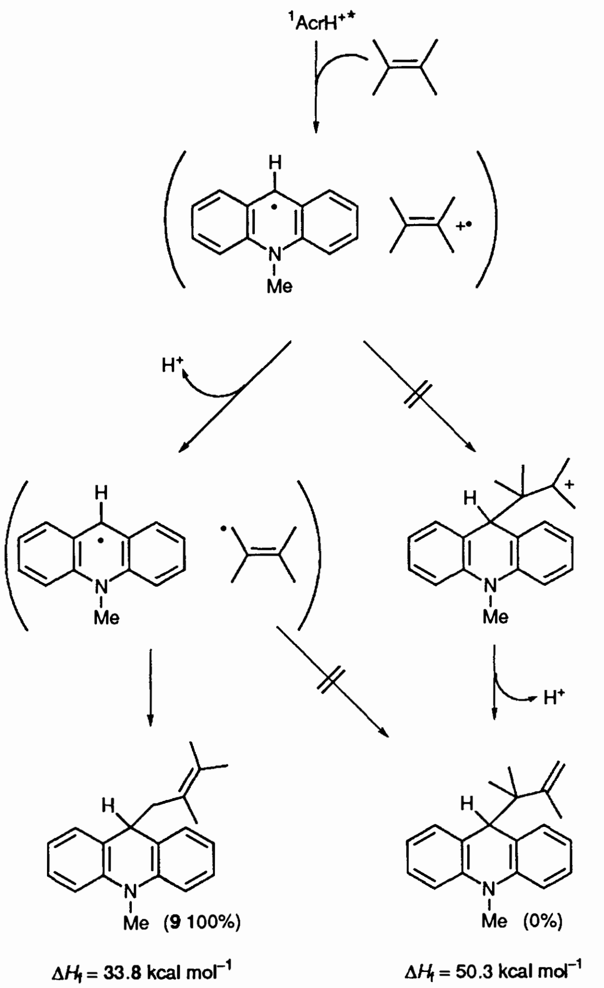
Scheme 11



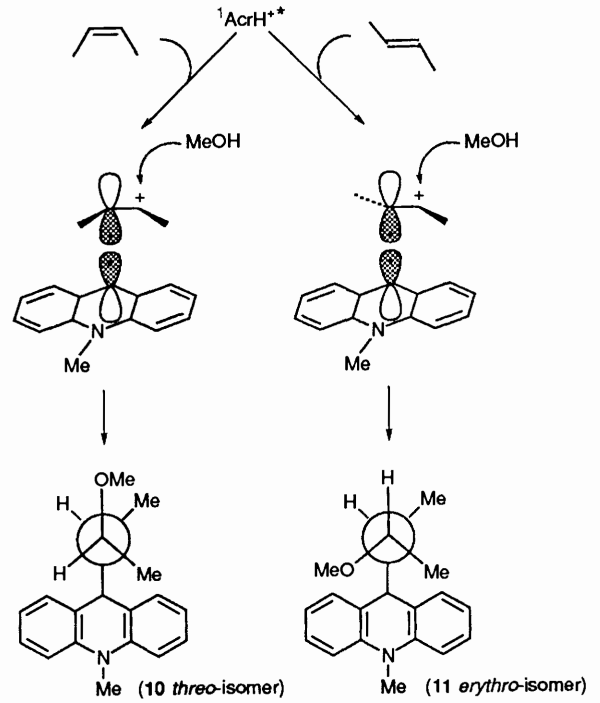
Scheme 12

limiting quantum yield of cyclohexene is smaller than that of 2-methylbut-1-ene (Table 2). In such a case, the deprotonation of the cyclohexene radical cation may well compete with the nucleophilic attack of methoxide ion as shown in Scheme 11. The deprotonation gives a cyclohexenyl radical that is coupled with acridinyl radical to yield the adduct with no incorporation of methoxide group from methanol as well as the methoxide-incorporated product (Scheme 11). In the case of methylcyclohexene, the deprotonation of the radical cation may produce three isomer radicals (**a**, **b**, **c**) depending on the position of the deprotonation. The ΔH_f values of deprotonated radicals calculated by the PM3 method indicate that the thermodynamic stability decreases in order **a** > **b** ≫ **c** as shown in Scheme 12, being consistent with the product distribution in Scheme 5.

When the sterically hindered 2,3-dimethylbut-2-ene is employed, the nucleophilic attack of methoxide ion may be completely blocked by the two methyl groups, when the limiting quantum yield is the smallest (0.003) among alkenes in Table 2.



Scheme 13



Scheme 14

Thus, the deprotonation of the radical cation is the only choice to give the alkenyl radical that is coupled with acridinyl radical to yield the adduct as shown in Scheme 13. It should be noted that there is no adduct which could arise from the radical coupling between 2,3-dimethylbut-2-ene radical cation and acridinyl radical followed by the deprotonation, since such an adduct may be much more unstable than the adduct **9** as indicated by the significantly larger ΔH_f value in Scheme 13.

In the photoreduction of $AcrH^+$ by alkenes described above no homocoupling products of free radicals such as 10,10′-dimethyl-9.9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$] have been obtained, indicating that no free radicals outside the reaction cage are involved. If the photoinduced electron transfer from (*Z*)- and (*E*)-but-2-ene to $^1AcrH^{+*}$, followed by the nucleophilic attack of methanol and the subsequent C–C bond formation occurs by a completely concerted manner, it would be expected that the stereoselective photoaddition of (*Z*)- and (*E*)-but-2-ene occurs, leading to the *threo*- and *erythro*-isomer, respectively (Scheme 14). Although the assignment of two stereoisomers (**A** and **B**) is not clear at present, the different isomer distribution depending on the starting isomers (*E* and *Z*), which is enhanced by lowering the reaction temperature (Table 1), indicates the nucleophilic addition and the subsequent C–C bond formation occur by at least partially concerted manner. Thus, the C–C bond formation is fast enough not to allow the escape of free radicals outside the cage, but not fast enough to gain the complete stereoselection.

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