Photoreactions of Halogeno-1,4-naphthoquinones with Electron-rich Alkenes

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Photochemical reactions of 2,3-dichloro-1,4-naphthoquinone with 1,1-diarylethylenes or the related electron-rich alkenes have been investigated by steady-state photoreactions, flash photolysis, and kinetic analyses based on the Stern–Volmer experiment and concentration dependence of quantum yields; there is reasonable agreement between them. In acetonitrile a radical ion pair composed of a quinone radical anion and a 1,1-diarylethylene radical cation was observed, while no intermediate was observed in benzene. Dimerization products derived from radical cations were obtained only in the photoreaction of quinone with 1,1-bis(4-methoxyphenyl)ethylene.

Electron-transfer photochemistry is one of the most intriguing fields in organic chemistry.[1] The combination of a variety of donors and acceptors has provided us with a number of novel reactions including isomerizations, rearrangements, dimerizations, additions, substitutions, and oxygenations.

In our previous papers we described the results on the basis of electron transfer in the photoreactions of halogeno-1,4-naphthoquinones with 1,1-diarylethylenes.[2,3] The results suggested that photoreactions in these systems could be promoted by excitation of a quinone and that the intermediate radical pair produced by electron transfer from alkene to the excited quinone is converted into the substitution product at a halogen atom by the ethylenic group (ethylene adduct) *via* radical or ionic coupling and the following dehalogenation (Scheme 1). Furthermore, subsequent photocyclization results in the formation of 5-phenylbenz[*a*]anthracene-7,12-diones (BAD), which has been extended to the synthetic application of polyaromatic compounds.[3–5] Photoreactions of halogeno-1,4-naphthoquinones with 2-alkoxy-1-alkenes such as 2-methoxy-1-alkenes[6] and 2-trimethylsiloxy-1-alkenes[7] afforded 2-(2-oxoalkyl)-1,4-naphthoquinones derived from ethylene adduct (Scheme 1).

Since the proposed nature of the intermediates in quinone–electron-rich alkene system stems largely from indirect measurements, we have extended our study in order to consolidate the reaction mechanism in the formation of the ethylene adduct. In this article, details from a mechanistic point will be discussed in the light of steady-state photoreactions, kinetic analyses, and flash photolysis results.

Results

Photoreactions of 2,3-*Dichloro*-1,4-*naphthoquinone* (**1a**) *with* 1,1-*Diphenylethylenes* (**2a–c**) *in Acetonitrile.*—We have reported that formation of ethylene adduct is suppressed as the polarity of a solvent increased:[3] in benzene the most efficient formation of ethylene adducts was observed and well studied.[2–7] On the other hand, the photoreaction in polar solvents such as acetonitrile has been rather inadequately investigated.

We report that in the benzene photoreaction of 2,3-dichloro-1,4-naphthoquinone (**1a**) with 1,1-diphenylethylene (**2a**) gives both cyclobutane adduct (**8a**) and ethylene adduct (**3a**) [and 5-phenylbenz[*a*]anthracene-7,12-dione (BAD) (**4a**)], while photoreactions of quinone (**1a**) with 1,1-bis(4-methylphenyl)ethylene (**2b**) or 1,1-bis(4-methoxyphenyl)ethylene (**2c**) gives only ethylene adduct (**3b**) or (**3c**) [and corresponding BAD (**4b**) or (**4c**)] (Scheme 2). Irradiation of an acetonitrile solution containing quinone (**1a**) (0.02), alkene (**2a**) (0.04), and pyridine (0.04 mol dm^{-3}; hydrochloric acid scavenger) under argon through an aqueous $CuSO_4$ filter for 6 h gave cyclobutane adduct (**8a**) (14), ethylene adduct (**3a**) (4), and BAD (**4a**) (15%) (Table 1). The absence of pyridine causes decomposition of photoproducts due to the evolution of hydrochloric acid. Similarly, photoreaction of quinone (**1a**) with alkene (**2b**) in acetonitrile afforded cyclobutane adduct (**8b**) (5), ethylene adduct (**3b**) (9), and BAD (**4b**) (21%). Photoproducts obtained in acetonitrile are similar to those obtained in benzene[3] except with the cyclobutane adduct (**8b**) which was obtained only in acetonitrile, but the yields in acetonitrile are lower than those in benzene. Interestingly, photoreaction of quinone (**1a**) with alkene (**2c**) in acetonitrile afforded diene (**9c**) (62) and dihydronaphthalene (**10c**) (14) mainly in addition to ethylene adduct (**3c**) (2%) and BAD (**4c**) (trace). Photoreaction of quinone (**1a**) with 2-methoxy-hept-1-ene (**5a**) and subsequent hydrolysis gave only 2-(2-oxoalkyl)-1,4-naphthoquinone (**7a**) in both benzene and acetonitrile.[6]

Mechanistic Studies.—Kinetic analysis and flash photolysis of the photoreactions were carried out in order to study these reaction processes in details. Photoreactions of quinone (**1a**) with alkene (**2c**) or (**5a**) were chosen for this study because cyclobutane adducts were not obtained in these cases. It is said that the $S_1 \longrightarrow T_1$ process for quinones generally occurs with a high efficiency (Φ_{ST} *ca.* 1.0).[8] Since singlet states of halogeno-1,4-naphthoquinones easily turn to the triplet states *via* intersystem crossing due to the heavy atom effect by halogen atoms,[9] these reactions probably occur *via* the lowest triplet state. Indeed, quinone (**1a**) showed no fluorescence in benzene or hexane and formation of ethylene adducts at the initial stage was suppressed by a triplet quencher O_2 or fluoranthene (E_T 53 kcal mol^{-1}).[10,*] The first triplet level of quinone (**1a**) is reported to be at 56 kcal mol^{-1} on the basis of the measured phosphorescence spectra in deaerated ethanol at 77 K.[11] Dependence of the quantum yields, Φ for the formation of ethylene adducts (**3c**) or (**6a**) upon the concentration of fluoranthene (F) as a triplet quencher was estimated in the photoreactions of quinone (**1a**) with alkene (**2c**) or (**5a**) (>405 nm).† The Stern–Volmer plots are shown in Figure 1. The straight line for the formation of ethylene adducts in both benzene and acetonitrile indicates that ethylene adducts

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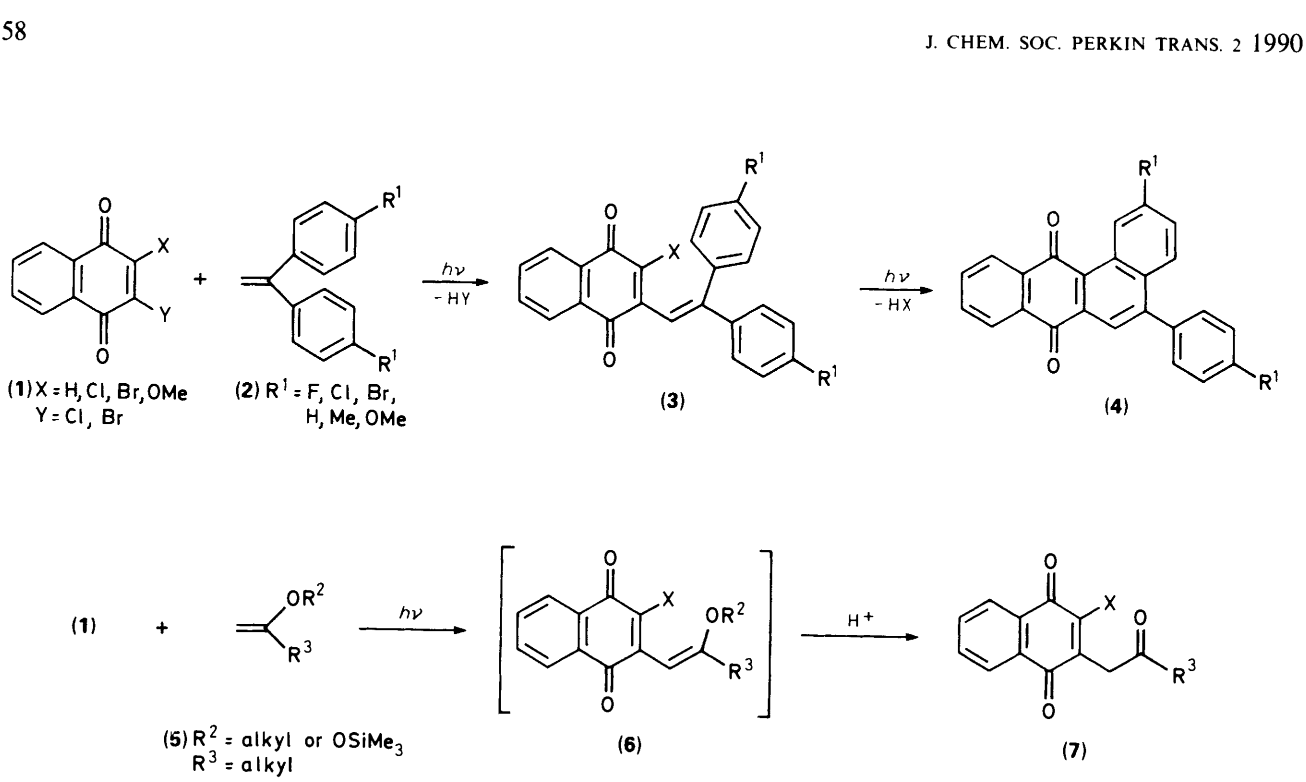
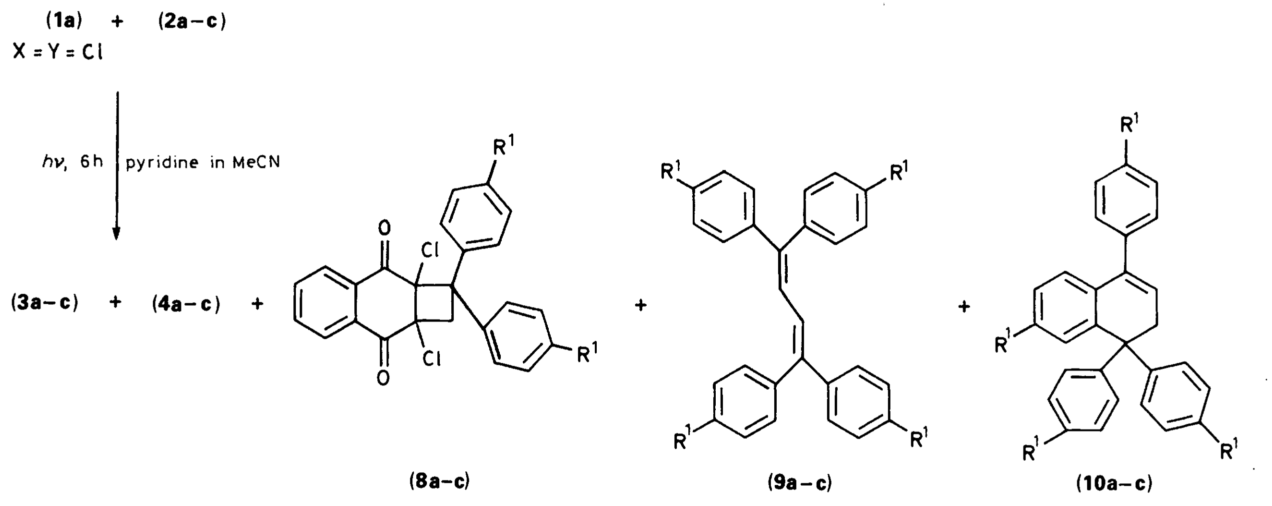
* 1 cal = 4.184 J.

† Since triplet quenchers, even fluoranthene (≤400 nm), show too wide-spread absorption in UV–VIS spectra, it was difficult to excite only quinone (**1a**) in the presence of triplet quencher except for the case of fluoranthene.



Scheme 1.

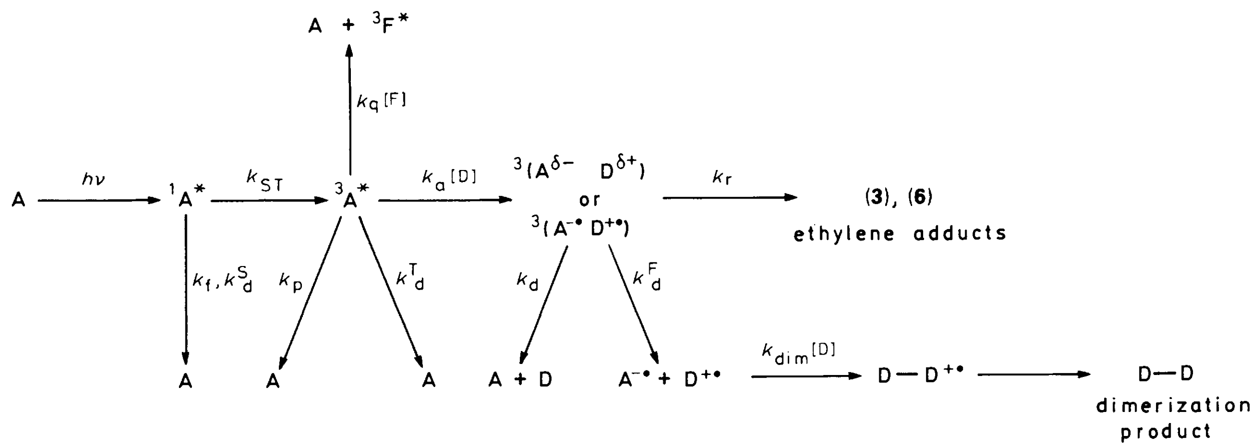


Scheme 2. Z represents compound number. (**Za**) (Z = 2–4, 8–10): R_1 = H; (**Zb**) (Z = 2–4, 8–10): R^1 = Me: (**Zc**) (Z = 2–4, 8–10): R^1 = OMe; (**Za**) (Z = 5–7): R^2 = Me, R^3 = C_5H_{11}.

Table 1. Photochemical reactions of 2,3-dichloro-1,4-naphthoquinone (**1a**) with 1,1-diphenylethylene (**2a–c**) in acetonitrile.

Alkene	Quinone conversion (%)	Alkene conversion (%)	Yield of products (%)[a] (3)	(4)	(8)	(9)	(10)
(**2a**): R^1 = H	100	96	(**3a**): 4	(**4a**): 15	(**8a**): 14	(**9a**): 0	(**10a**): 0
(**2b**): R^1 = Me	74	39	(**3b**): 9	(**4b**): 21	(**8b**): 5	(**9b**): 0	(**10b**): 0
(**2c**): R^1 = OMe	50	80	(**3c**): 2	(**4c**): trace	(**8c**): 0	(**9c**): 62	(**10c**): 14

[a] An acetonitrile solution containing (**1a**) (0.02), (**2**) (0.04), pyridine (0.04 mol dm^{-3}) was irradiated for 6 h under argon.



Scheme 3. A: quinone, D: alkene, F: triplet quencher.

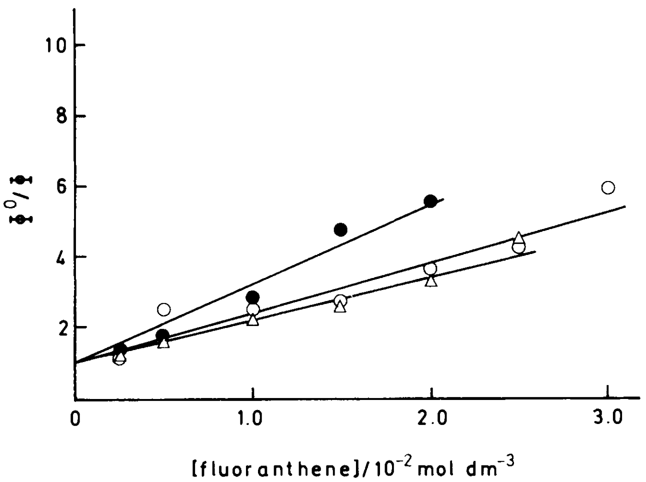


Figure 1. Stern–Volmer plot for quenching of formation of ethylene adducts (**3c**) (△ in benzene) or (**6a**) (○ in benzene: ● in acetonitrile) by fluoranthene under an argon atmosphere. ([**1a**] = 1.0 × 10^{-2}, [(**2c**)] = [(**5a**)] = 2.0 × 10^{-2}, [pyridine] = 2.0 × 10^{-2} mol dm^{-3}, λ > 405 nm).

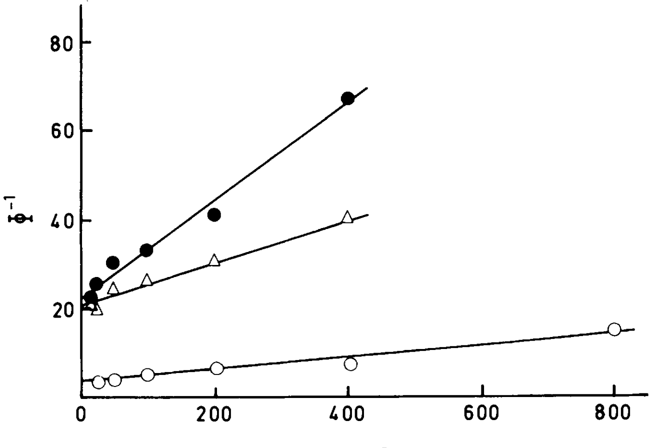


Figure 2. Plot of Φ^{-1} *vs.* $[D]^{-1}$. The data were obtained upon irradiation (λ 366 nm) of benzene or acetonitrile solutions containing quinone (**1a**) (1.0 × 10^{-2}), alkenes (**2c**) (△ in benzene) or (**5a**) (○ in benzene; ● in acetonitrile), and pyridine (2.0 × 10^{-2} mol dm^{-3}) under an argon atmosphere.

are formed *via* the lowest triplet excited state (T_1) of quinone (**1a**). On the other hand, plots of reciprocal quantum yields Φ^{-1} *vs.* reciprocal alkene (D) concentration $[D]^{-1}$ were found to be linear in the photoreactions of quinone (**1a**) with alkene (**2c**) or (**5a**) (Figure 2). The quantum yields of ethylene adduct (**3c**) or (**6a**) in acetonitrile are lower than those in benzene.

Scheme 3 shows the reaction pathways for the formation of ethylene adduct, involving unimolecular deactivation steps of the excited state of quinone (A) (k_f, k_d^s, k_p, k_d^T), intersystem crossing (k_{ST}), formation of exciplex or ion radical pair (k_a), the triplet quenching of quinone A by fluoranthene (k_q), deactivation of exciplex or ion radical pair (k_d), separation from ion pair to free ions (k_d^F), dimerization of alkene cation radical with neutral alkene (k_{dim}), and formation of ethylene adducts (k_r). The quantum yields Φ for the formation of ethylene adducts are expressed in equations (1) and (2).

$$\Phi = \Phi_{ST}\{k_a[D]/(k_p + k_d^T + k_q[F] + k_a[D])\}\{k_r/(k_d + k_d^F + k_r)\} \quad (1)$$

$$\Phi^0 = \Phi_{ST}\{k_a[D]/(k_p + k_d^T + k_a[D])\} \times \{k_r/(k_d + k_d^F + k_r)\} \quad (2)$$

The relative ratio Φ^0/Φ derived from equations (1) and (2) is expressed in equation (3).

$$\Phi^0/\Phi = 1 + k_q[F]/(k_p + k_d^T + k_a[D]) = 1 + k_q\tau[F] \quad (3)$$

From the slope and the intercept of the plots shown in Figures 1 and 2, the following rate constants and the ratios can be evaluated: k_d^T, k_a, and k_d/k_r, assuming Φ_{ST} *ca.* 1, $k_p \ll k_a[D]$, $k_p \ll k_d^T$,* $k_d^F \ll k_d$, $k_d^F \ll k_r$, $k_q = 5.0 \times 10^9$ for a benzene solution, and $k_q = 1.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1} for an acetonitrile solution.[10],† The rate constants and the ratios are summarized in Table 2.

Rate constants k_d^T and k_a obtained are reasonable as discussed later. The reaction ratio k_d/k_r in acetonitrile is larger than that in benzene for the photoreaction of (**1a**) with (**5a**) (*ca.* eight times), and this indicates that deactivation of radical ion pair or exciplex including back electron transfer is more effective in acetonitrile as reported previously by us.[3] These results are consistent with the CIDNP results between quinone (**1a**) and alkenes (**2b**) or (**2c**).[2,3] That is, strong polarization signals of starting reactants, quinone (**1a**) and alkenes (**2b**) or (**2c**), due to back electron transfer were observed in polar solvents such as CD_3CN and CD_3OD, but not in C_6D_6 nor $CDCl_3$.

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* Phosphorescence spectra of (**1a**) were not observed at room temperature and were weak even under deaerated conditions at 77 K.

† Direct measurement of k_q value could not be carried out because of the overlapping of the absorption between quinone (**1a**) and fluoranthene at 347.2 nm.

Table 2. Rate constants obtained by kinetic analysis and flash photolysis.

		Kinetic analysis				Flash photolysis	
Alkene	Solvent	$k_q\tau/10^2$ mol dm^{-3}	$k_d^T/10^6$ s^{-1}	$k_a/10^9$ dm^3 mol^{-1} s^{-1}	k_a/k_r	$k_d^T/10^5$ s^{-1}	$k_a/10^9$ dm^3 mol^{-1} s^{-1}
(2c)	PhH	1.2	4.4	1.9	20	5.6	4.9
(2c)	MeCN	—[a]	—[a]	—[a]	—[a]	5.9	—[b]
(5a)	PhH	1.4	5.4	1.5	2.7		—[c]
(5a)	MeCN	2.2	8.9	1.8	22		—[c]

[a] Formation of benz[*a*]anthracene-7,12-dione derivative **(4c)** was too fast to determine the yield of ethylene adduct **(3c)**. [b] Because the decay kinetics at 500 nm in the presence of alkene **(2c)** were not single exponential, k_a could not be determined. [c] Since the plots of k *vs.* [D] deviated from the straight line, the correct value of k_a could not be determined.

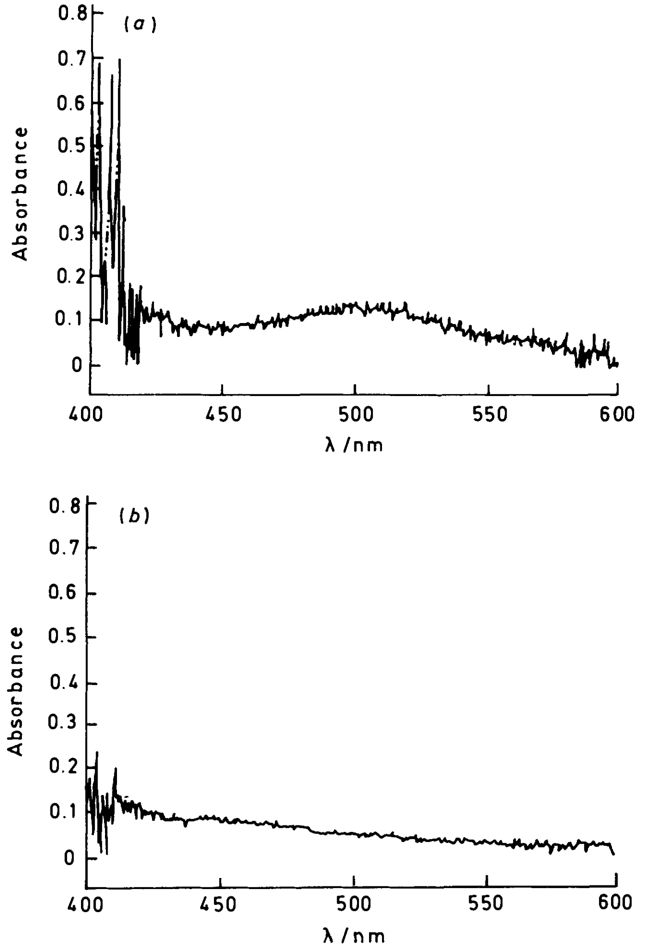

Figure 3. Transient absorption spectra (*a*) of **(1a)** and (*b*) of **(1a)**–**(5a)** in benzene obtained by picosecond photolysis. [**(1a)**] = 1.8 × 10^{-3}, [**(5a)**] = 1 mol dm^{-3} at 40 ps–2 ns after flashing.

Flash photolysis experiments were carried out in order to make a comparison with the results obtained by the kinetic treatment. Figure 3(*a*) shows the transient absorption spectra of quinone **(1a)** in benzene, observed by picosecond laser photolysis. Upon excitation of quinone **(1a)**, absorption at λ_{max} 500 nm built up within the first 40 ps delay and this band did not decay up to 2 ns. On the other hand, no absorption band was observed in the presence of alkene **(2c)** or **(5a)** (1 mol dm^{-3}) from 40 ps–2 ns [Figure 3(*b*)]. That is, this absorption at 500 nm is quenched by alkene **(2c)** or **(5a)**.* The transient species absorbing at 500 nm is ascribed to the triplet absorption of quinone **(1a)** on the basis of these results and similarity between this transient absorption and triplet absorption of other quinones.[12–14] The decay kinetics at 500 nm fitted a practically single exponential [Figure 4(*a*)],† and the value of the decay constant of this curve (k_d^T = 5.6 × 10^5 s^{-1}) is reasonable as a triplet decay constant of quinones.[8,12–14]

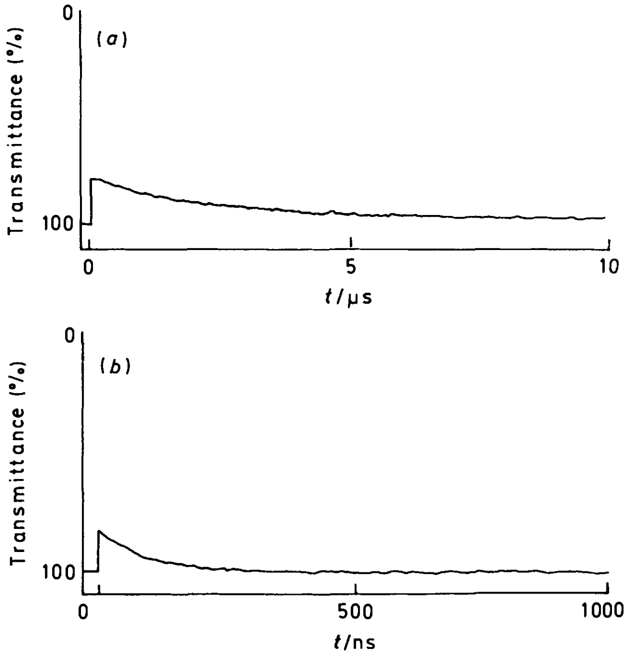

Figure 4. Oscilloscope traces of the transmittance at 500 nm of (*a*) **(1a)** (3.6 × 10^{-4}) and of (*b*) **(1a)** (3.6 × 10^{-4}) and **(2c)** (2.0 × 10^{-3} mol dm^{-3}) in benzene at room temperature by nanosecond laser photolysis.

In the presence of alkene **(2c)** the decay of ^{3}**(1a)**‡ follows the first-order rate law [Figure 4(*b*)], the decay constant k obeys equation (4).

$$k = K_d^T + k_a[D] \qquad (4)$$

The plots of k *vs.* [D] were found to be linear with k_d^T = 5.6 × 10^5 s^{-1} and k_a = 4.9 × 10^9 dm^3 mol^{-1} s^{-1} [Figure 5], roughly consistent with the values obtained by the kinetic treatment (Table 2). The value k_a obtained is approximately equal to those obtained for carbonyl compound–electron-rich

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* Since in picosecond photolysis alkene concentration is high (*ca.* 1 mol dm^{-3}), the probability of collision between the quinone and the alkene is much higher and the excited triplet state of quinone **(1a)** is quenched rapidly by the alkene (within 40 ps) compared with that in low concentration of alkene (10^{-4} to *ca.* 10^{-2} mol dm^{-3}).

† Since oscilloscope traces of the transmittance at 380 nm by nanosecond photolysis did not reach to 100%, the k_d^T and k values at 380 nm could not be determined.

‡ See the footnote * on p. 261.

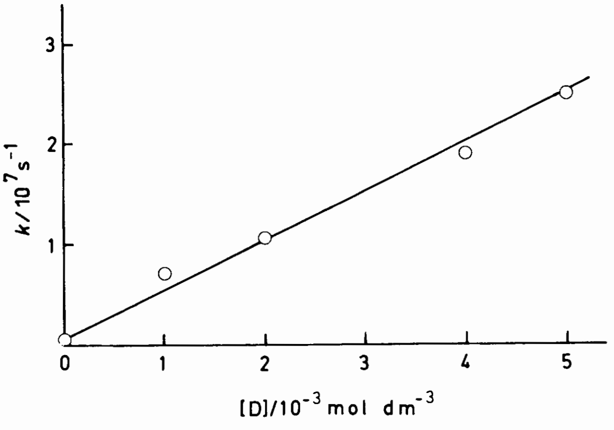

Figure 5. Plot of *k vs.* [D]. The data were obtained by nanosecond photolysis (347.2 nm) in a benzene solution containing quinone (**1a**) (3.6×10^{-4} mol dm^{-3}) and alkene (**2c**).

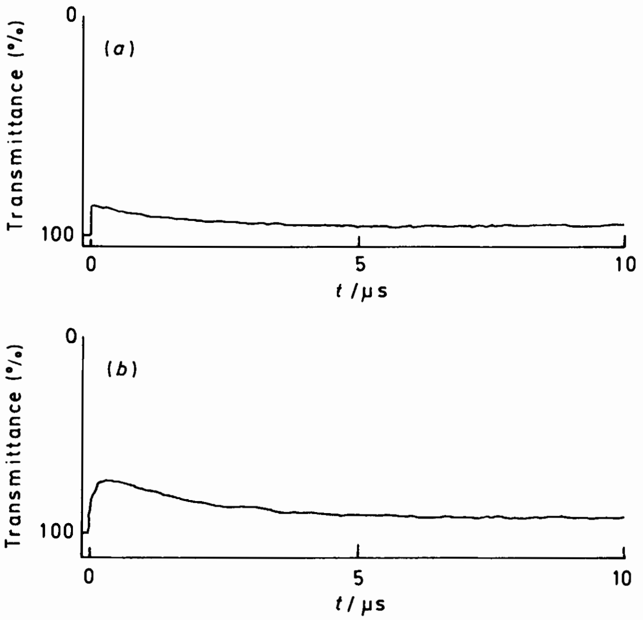

Figure 6. Oscilloscope traces of the transmittance at 500 nm of (*a*) (**1a**) (3.6×10^{-4}) and of (*b*) (**1a**) (3.6×10^{-4}) and (**2c**) (2.0×10^{-3} mol dm^{-3}) in acetonitrile at room temperature by nanosecond laser photolysis.

donors such as anthraquinone (AQ)/triethylamine (TEA) in ethanol, *i.e.* 2.5×10^9,[15] and benzophenone/TEA in benzene, *i.e.* 3×10^9,[16] *p*-chloranil (CA)/naphthalene in propyl cyanide, *i.e.* 7.0×10^9,[14] CA/durene in 1,2-dichloroethane, *i.e.* 2.5×10^9 dm^3 mol^{-1} s^{-1}.[17]

In non-polar solvents such as hexane and benzene, the reactive intermediate produced from the donor and the acceptor is considered to be an exciplex.[1] In our previous studies, we have demonstrated that formation of the ethylene adduct occurs *via* an exciplex or radical ion pair in the photoreactions of halogeno-1,4-naphthoquinone with electron-rich alkenes. We have tried to find this intermediate directly by flash photolysis, but were not successful in non-polar solvents. This may be ascribed to the small molar absorption coefficients, short lifetimes (<40 ps), and the too wide-spread absorption (>680 nm) of the exciplex.

In acetonitrile, a drastic change appeared. The decay kinetics at 500 nm in the presence of alkene (**2c**) was not single exponential and the curve was composed of fast rise (*ca.* 0.1 μs) and slow decay [Figure 6(*b*)], while the decay kinetics at 500 nm in the absence of alkene (**2c**) ($k_d^T = 5.9 \times 10^5$ s^{-1}) fitted a practically single exponential [Figure 6(*a*)] and the value obtained in acetonitrile was almost equal to that obtained in benzene. The slow decay (6×10^5 s^{-1}) showed little dependence upon the concentration of alkene (**2c**) ($10^{-4} \sim 10^{-2}$ mol dm^{-3}). Time-resolved absorption spectra (Figure 7) showed that a new absorption band (λ_{max} 535 nm) appeared with a delay time of 2 μs and decayed with a delay time of 10 μs. This absorption band corresponds to the slow decay measured at 500 nm. Assignment of this spectrum due to the transient species was carried out by optical studies of anion radical (**1a**)$^{-\bullet}$ (in 2-methyltetrahydrofuran at 77 K) and cation radical (**2c**)$^{+\bullet}$ (in trichlorofluoromethane at 77 K) generated by γ-irradiation (Figure 8) according to results given elsewhere.[18] It is apparent that the band with λ_{max} 535 nm is derived from cation radical (**2c**)$^{+\bullet}$,* and the spectra observed at a delay time of 2 μs may be regarded as the superposition of the spectrum of anion radical (**1a**)$^{-\bullet}$ and cation radical (**2c**)$^{+\bullet}$. In CD_3CN and CD_3OD, but not in C_6D_6, the CIDNP signals for quinone (**1a**) and alkene (**2c**) due to back electron transfer were observed, indicating that this absorption band is due to the radical ion pair. Taking account of the agreement of the decay time of the curve at 500 nm in a benzene solution containing quinone (**1a**) and alkene (**2c**) with the build-up time of the corresponding curve in an acetonitrile solution containing (**1a**) and (**2c**) and also of the above results, it seems that in acetonitrile the triplet state of quinone (**1a**) is quenched rapidly by alkene (**2c**) and simultaneously the ion pair [(**1a**)$^{-\bullet}$ + (**2c**)$^{+\bullet}$] is generated and then decays slowly. Thus, the fast rise at 500 nm in acetonitrile could be due to formation of the ion pair, although it includes the contribution of the triplet absorption of quinone (**1a**).

Discussion

We have reported that photoreactions of halogeno-1,4-naphthoquinones with 1,1-diphenylethylenes gave cyclobutane adducts ($\Delta G > 0$) and ethylene adducts ($\Delta G < 0$). Formation of the ethylene adduct occurred *via* photoinduced electron transfer which was supported by the relationship between formation of ethylene adducts and the free-energy changes (ΔG) in benzene together with substituent effects in the photoreactions of quinone (**1a**) with *p*-disubstituted 1,1-diphenylethylenes, solvent effects for the formation of ethylene adduct, and CIDNP.[2,3] Direct unambiguous evidence for electron-transfer processes comes from the flash photolysis results. In the photoreaction of quinone (**1a**) with 1,1-bis(4-methoxyphenyl)ethylene (**2c**), a radical ion pair composed of a quinone radical anion and an alkene radical cation was observed in acetonitrile. The decay constant of the ion pair is independent of alkene concentration, indicating that the ion pair is not dissociated to free ion, but is solvent-separated.† Otherwise, free alkene radical cation produced would be quenched rapidly by the neutral alkene and thus the decay constant would be dependent on the alkene concentration.[19] ‡ Accordingly, decay constant of the solvent-separated ion pair is estimated to be 6×10^5 s^{-1} and the value is nearly equal to that for AQ–TEA in toluene, *i.e.* 1.9×10^5 s^{-1},[15] benzophenone–1,4-diazabicyco[2,2,2]octane in benzene or acetonitrile–benzene, *i.e.*

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* T. Shida at Kyoto University suggested in a personal communication that the absorption with λ_{max} 535 nm may well be a cation radical of (**2c**)$^{+\bullet}$ the geometry of which is considerably different from that of the neutral molecule of (**2c**).

† Since the decay constant of the ion pair is independent of the alkene concentration, no interception of the ion pair by the alkene occurs.

‡ Free alkene radical cation dissociated from the ion pair is quenched rapidly by the neutral alkene and a dimer radical cation is produced.

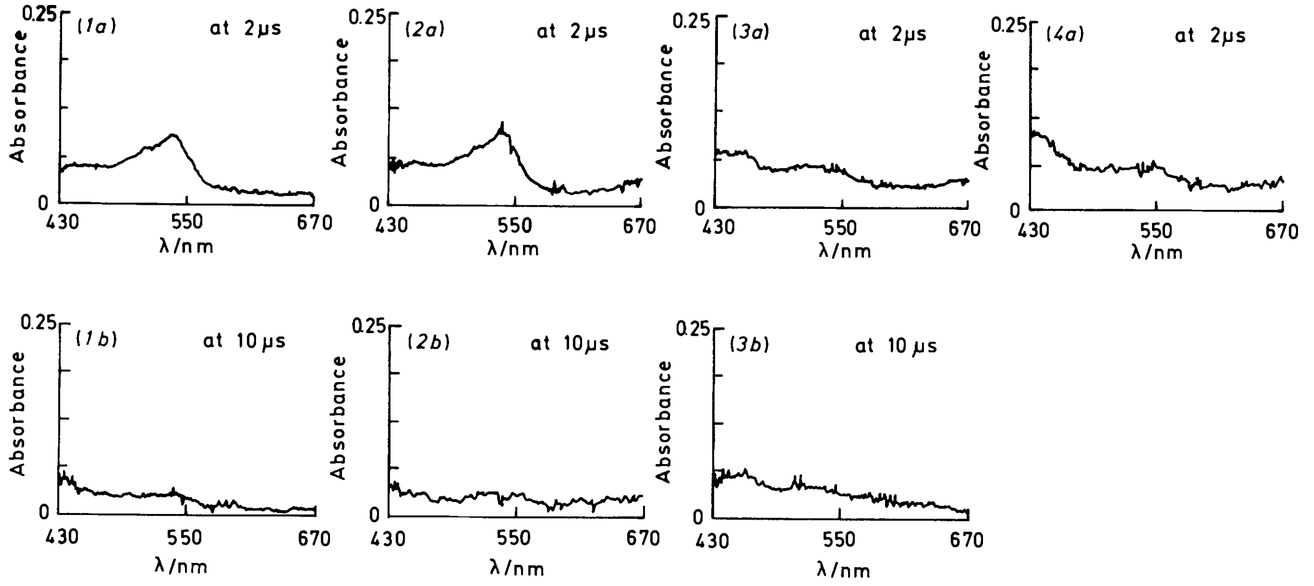


Figure 7. Transient absorption spectra of quinone (**1a**) (3.6 × 10^{-4} mol dm^{-3})/alkene (**2c**) in acetonitrile at room temperature (*a*) at 2 μs delay and (*b*) at 10 μs delay by nanosecond laser photolysis. [(*i*) [(**2c**)] = 1.0 × 10^{-2}; (*ii*) [(**2c**)] = 1.0 × 10^{-3}; (*iii*) [(**2c**)] = 1.0 × 10^{-4}; (*iv*) [(**2c**)] = 0 mol dm^{-3}).

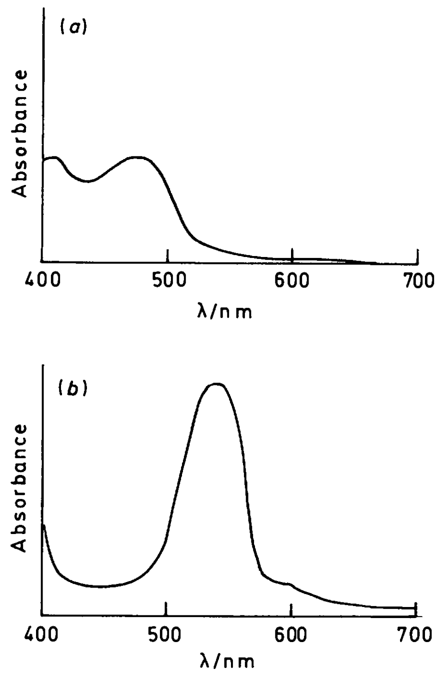
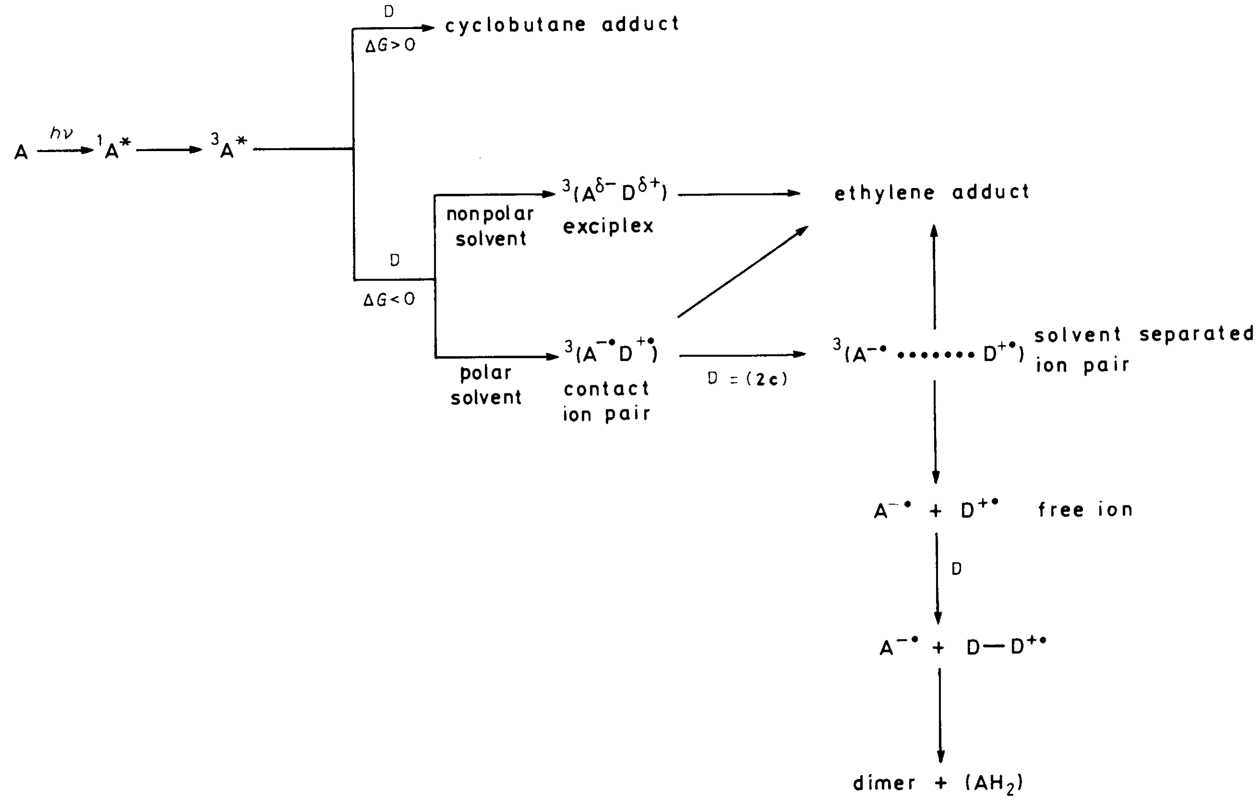
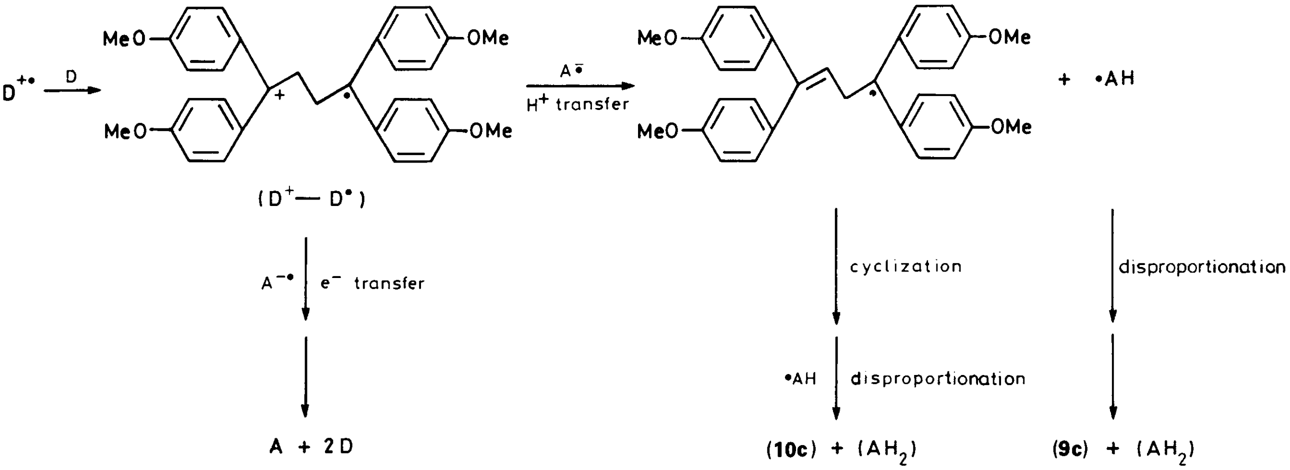


Figure 8. Electronic absorption spectra of (*a*) $(\mathbf{1a})^{-\bullet}$ and (*b*) $(\mathbf{2c})^{+\bullet}$. Spectra were obtained in γ-irradiated frozen matrix (*a*) of 2-methyltetrahydrofuran at 77 K or (*b*) of trichlorofluoromethane at 77 K.

$5 \times 10^5 - 3 \times 10^6$ s^{-1}.[16] In non-polar solvents none of the intermediates were observed directly by means of laser flash photolysis and CIDNP. We have demonstrated that formation of the ethylene adduct occurs *via* a charge-transfer complex such as an exciplex or radical ion pair in non-polar solvents by the indirect measurement above. If the intermediate is a radical ion pair in non-polar solvents, the radical ion pair must also be observed in the photoreaction of quinone (**1a**) with alkene (**2c**) similar to that in polar solvents. No detection of intermediate in non-polar solvents suggests that the intermediate is not a radical ion pair, but an exciplex, probably a triplet exciplex because it is generally difficult to observe an exciplex, particularly a triplet exciplex, directly. Therefore, we believe that an exciplex is an intermediate in non-polar solvents such as benzene. In the photoreactions of quinone (**1a**) with 1,1-diphenylethylenes (**2a**–**c**), dimerization products of the alkene were obtained only in the reaction of quinone (**1a**) with alkene (**2c**), when these reactions were undertaken in acetonitrile. It is well known that the electron transfer photosensitized dimerization of 1,1-diphenylethylene (**2a**) occurs mainly in polar solvents such as acetonitrile when electron-accepting sensitizers such as 4-cyanobenzoate,[20] cyanoanthracene,[19] and so on[21–23] were used. In these cases, cage separation of the ion pair and interception of the geminate ion pair by alkene competes with back electron transfer from the radical anion to the radical cation, and alkene dimers are produced. Under our conditions ion pairing in polar solvents may be contact enough and there is not sufficient dissociation to form a solvated ion pair. Thus, back electron transfer and coupling of the ion pair to products are more effective processes than interception of an ion pair by an alkene and cage separation of an ion pair, and no dimerization of alkene (**2a**) or (**2b**) sensitized by quinone (**1a**) occurs. In the photoreaction of quinone (**1a**) with 1,1-bis(4-methoxyphenyl)ethylene (**2c**), the ion pair could be drawn apart due to the delocalization of the positive charge in the methoxy group of $(\mathbf{2c})^{+\bullet}$. Thus, free ion $(\mathbf{2c})^{+\bullet}$, on escape from the solvent-separated ion pair is easily attacked by alkene (**2c**), which results in the formation of dimers, diene (**9c**) and dihydronaphthalene (**10c**), though naphthalene-1,4-diol derived from the free radical anion of quinone was not detected probably due to decomposition (Scheme 4).[1] The fact that strong CIDNP signals responsible for back electron transfer were observed in the photoreaction of quinone (**1a**) with alkene (**2c**) is consistent with the solvent-separated character of the ion pair. Cation radicals produced in polar solvents can be trapped as methanol or cyanide adducts.[19–21] As previously reported by us,[3] similar methanol adducts could not be detected in methanol for the photoreaction of quinone (**1a**) with alkenes (**2a**–**c**), which supports the fact that the radical ion pair is in contact and back electron transfer is effective. It is known that nucleophilic addition of methanol to the radical cation $(\mathbf{2c})^{+\bullet}$ is much slower than the dimerization between alkene (**2c**) and alkene radical cation $(\mathbf{2c})^{+\bullet}$.[19] Thus, free radical cation $(\mathbf{2c})^{+\bullet}$ is not trapped by methanol even in the photoreaction of quinone (**1a**) with alkene (**2c**). Mattes and Farid reported the photodimerization of alkene (**2c**), using 9,10-dicyanoanthracene (DCA) as a



Scheme 4. A: quinone, D: alkene.



Scheme 5.

sensitizing acceptor.[19] The diene (**9c**) and dihydronaphthalene (**10c**) were obtained in addition to the reduced acceptor and tetrahydronaphthalene analogue. The effect of added quinones such as benzoquinone, 1,4-naphthoquinone, and 2,3-dichloro-1,4-naphthoquinone (**1a**) on the quantum yield of dimerization of alkene (**2c**) sensitized by DCA was investigated by them. Irradiation in the presence of low concentrations of quinone increases product quantum yields, accompanied by an increase in the ratio of [(**9**)] : [(**10**)]. Under our conditions high yields of diene (**9**), dihydronaphthalene (**10**) and a high ratio of [(**9**)] : [(**10**)] were obtained. Considering the similar reaction mechanism proposed by them (Scheme 5), our results are explained by the stronger basicity of the quinone radical anion over that of DCA.

In conclusion, electron-transfer photoreactions of halogeno-1,4-naphthoquinones with electron-rich alkenes gives ethylene adducts *via* an exciplex in non-polar solvents, and a contact ion pair in polar solvents, whereas on the whole dimerization of the alkene sensitized by cyanoaromatics occurs mainly. Solvent-separated ion pairs were not produced unless stabilized cation radicals, such as those derived from 1,1-bis(4-methoxyphenyl)ethylene (**2c**), were used.

Experimental

General Methods.—All melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. Mass spectra were taken on a JEOL JMS-DX300 mass spectrometer. The electronic spectra were obtained using a Shimadzu UV-100 spectrometer. ^{1}H NMR spectra (CD_3Cl, $SiMe_4$ as an internal reference) were recorded by using a JEOL (PS-100 spectrometer or JEOL DX-400 spectrometer. IR spectra were obtained by using a JASCO IRA-1 spectrometer with KBr pellets. Fluorescence and phosphorescence spectra were taken by using a Shimadzu RF-502A spectrometer. Elemental analyses were performed at the Micro Analytical Center of Kyoto University.

Starting Materials.—2,3-Dichloro-1,4-naphthoquinone (**1a**) was commercially available from Nacalai Tesque Co. and used after recrystallization and sublimation. 1,1-Diphenylethylene derivatives (**2a–c**) were prepared from the corresponding acetophenone and phenylmagnesium bromide followed by dehydration in dimethyl sulphoxide and used after distillation or recrystallization and sublimation. 2-Methoxyhept-1-ene (**5a**) was prepared according to the published procedure[24] and used after distillation. All solvents and pyridine were used after distillation. Spectroscopic grade benzene and acetonitrile (Nacalai Tesque Co.) were used without further purification. Fluoranthene (Nacalai Tesque Co.) was commercially available and purified by recrystallization and sublimation.

General Procedure for the Preparative Photochemical Reaction.—An acetonitrile solution (25 cm^3 in a Pyrex tube) containing quinone (**1a**) (0.02), alkene (**2a–c**) or (**5a**) (0.04), and pyridine (0.04 mol dm^{-3}) was irradiated through an aqueous $CuSO_4$ filter for 6 h under an argon atmosphere at room temperature with a high-pressure mercury lamp (300 W). After irradiation, the reaction mixture was concentrated *in vacuo* and separated by flash column chromatography on silica gel (Merck Kieselgel 60H), developing with hexane–benzene (3:1), benzene subsequently and chloroform finally. The first band contained unchanged alkane (**2**), second one contained unchanged quinone (**1**), third one contained cyclobutane adduct (**8**), fourth one contained BAD (**4**), and final one contains ethylene adduct (**3**). In the photoreaction of quinone (**1a**) with alkene (**2c**), the first band contained diene (**9c**), second one contained unchanged alkene (**2c**), third one contained unchanged quinone (**1a**), fourth one contained dihydronaphthalene (**10c**), fifth one contained BAD (**4c**), and final one contained ethylene adduct (**3c**). In the photoreaction of quinone (**1a**) with alkene (**5a**), the first band contained unchanged alkene (**5a**), the second one contained unchanged quinone (**1a**), and the final one contained 2-oxoalkylated quinone (**7a**). These products were identified by comparison with the previously reported data[3,7,19] and spectroscopic data.

1,6-*Dichloro*-8,8-*bis*(4-*methylphenyl*)-3,4-*benzbicyclo*-[4,2,0]*octa*-3-*ene*-2,5-*dione* (**8b**).—Colourless crystals from hexane–chloroform, m.p. 135 °C. *m/z* 434, 436, 438 (M^+). (Found: C, 71.47; H, 4.39; Cl, 16.56. Calc. for $C_{26}H_{20}Cl_2O_2$: C, 71.73; H, 4.63; Cl, 16.39%); ν_{max}(KBr) 1 690 (C=O) cm^{-1}. δ_H($CDCl_3$) 1.97 (3 H, s), 2.28 (3 H, s), 3.48 (1 H, d, *J* 11.9 Hz), 4.34 (1 H, d, *J* 11.9 Hz), 6.70 (2 H, d, *J* 7.9 Hz), 7.12 (2 H, d, *J* 8.2 Hz), 7.15 (2 H, d, *J* 8.6 Hz), 7.30 (2 H, d, *J* 8.2 Hz), 7.61 (1 H, td, dd, *J* 7.3, 1.4 Hz), 7.67 (1 H, td, *J* 7.3 Hz), 7.87 (1 H, dd, *J* 7.3, 1.2 Hz), and 8.11 (1 H, dd, *J* 7.3, 1.2 Hz).

Stern–Volmer Experiment.—Various amounts of fluoranthene were dissolved into a benzene or an acetonitrile solution (3 cm^3) containing quinone (**1a**) (1×10^{-2} mol dm^{-3}), alkene (**2c**) or (**5a**) (2×10^{-2} mol dm^{-3}), and pyridine (2×10^{-2} mol dm^{-3}), respectively. Each sample purged with argon for 5 min in a UV cell was irradiated with a high-pressure mercury lamp through a glass filter (Toshiba VY42) and water filter. No change in the light intensity was detected during these experiments. After irradiation, an appropriate substrate as an internal standard was added into the reaction mixture for the GC analyses, carried out on a JEOL-1100 Gas Chromatograph using a 100–200 cm × 0.3 cm stainless-steel column packed with 5–20% Silicone DC-550 on 60–80 mesh Celite 545. For all quantitative determinations, the GC analyses were carried out in triplicate. In these experiments, conversion of the substrate was always kept below 10%, and within this limit formation of ethylene adduct (**3c**) or (**7a**) increased linearly with time of irradiation. The quantitative yield for the formation of ethylene adduct (**6a**) was determined by conversion of (**6a**) into (**7a**) with treatment of dilute hydrochloric acid solution after irradiation.

Experiment for Investigating Concentration Effect of Alkene (**2c**) *or* (**5a**).—Various amounts of alkene (**2c**) or (**5a**) (10^{-3}–10^{-2} mol dm^{-3}) were dissolved in a benzene or an acetonitrile solution containing quinone (1.0×10^{-2} mol dm^{-3}) and pyridine (2.0×10^{-2} mol dm^{-3}). The sample purged with argon for 5 min in a UV cell was irradiated with high-pressure mercury lamp (366 nm). After irradiation, an appropriate internal standard was added into the reaction mixture for the GC or high-pressure liquid chromatography (HPLC) analyses. The HPLC analyses were carried out using Waters Model 440 absorbance detector equipped with an Altex pump Model 110A and Waters micro-Porasil analytical column. Quantum yields were determined by using a ferrioxalate actinometer.[10] The quantum yields were determined by the mean values of three experiments.

Flash Photolysis.—All transient absorption spectra were measured at room temperature. The second harmonics (347.2 nm) of a picosecond mode-locked[25] and a nanosecond Q-switch[26] ruby laser were used for excitation of sample, and the resolution was 30 ps and 20 ns, respectively. The sample solutions in a cell of 2 mm path length were not deaerated in the picosecond photolysis, while those in a cell of 10 mm path length for the nanosecond photolysis were degassed by several freeze–pump–thaw cycles. A time-resolved absorption spectrum was recorded in the 240 nm scanning region by using a multichannel analyser system (an ISD detector system), where a pulsed xenon flash lamp with a pulse width of 1.7 μs was used as a probing light source. The details of the ISD detector system have been given elsewhere.[27]

Optical Studies of Radical Anion and Radical Cation.—The substrates were dissolved in 2-methyltetrahydrofuran or in trichlorofluoromethane (to 1 mmol dm^{-3}). The degassed solutions were frozen to a glassy solid at 77 K in a 1.5 mm thick optical cell and irradiated. A Cary 17I spectrophotometer was used. All the optical spectra were plotted by subtracting the background absorption of samples before irradiation, so that the spectra are attributable to the species produced upon irradiation. The mechanism of the radical cation or radical anion formation in the irradiated matrix is described elsewhere.[18]

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References

1 (*a*) S. L. Mattes and S. Farid, in 'Organic Photochemistry,' ed. A. Padwa, Marcel Dekker, New York, 1983, vol. 6; (*b*) P. S. Mariano and J. L. Stavinoha, in 'Synthetic Organic Photochemistry,' ed. W. M. Horspool, Plenum Press, New York, 1984, p. 145; (*c*) G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401; (*d*) J. Mattay,

Angew. Chem., Int. Ed. Engl., 1987, **26**, 825, and references cited therein.

2 K. Maruyama, T. Otsuki, and S. Tai, *Chem. Lett.*, 1983, 843.

3 K. Maruyama, T. Otsuki, and S. Tai, *J. Org. Chem.*, 1985, **50**, 52.

4 (*a*) K. Maruyama, T. Otsuki, and K. Mitsui, *J. Org. Chem.*, 1980, **45**, 1424; (*b*) K. Maruyama and H. Imahori, *Dyestuffs and Chemicals*, 1988, **33**, 15; (*c*) K. Maruyama and H. Imahori, *J. Org. Chem.*, 1989, **54**, 2692.

5 K. Maruyama and A. Osuka, in 'The Chemistry of the Quinonoid Compounds,' ed. S. Patai and Z. Rappoport, Wiley, New York, 1988; vol. 2, part 1, ch. 13.

6 K. Maruyama, T. Otsuki, and S. Tai, *Chem. Lett.*, 1984, 371.

7 K. Maruyama, S. Tai, and H. Imahori, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1777.

8 J. M. Bruce, in 'The Chemistry of the Quinonoid Compounds,' ed. S. Patai, Wiley, New York, 1974; vol. 1, part 1, ch. 9.

9 N. J. Turro, in 'Modern Molecular Photochemistry,' the Benjamin–Cummings Publishing Co., Inc., Menlo Park, CA, 1978.

10 S. L. Murov, in 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973.

11 K. Maruyama and H. Imahori, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 816.

12 D. R. Kemp and G. Porter, *Proc. R. Soc. London, Ser. A*, 1971, **326**, 117.

13 K. Hamanoue, Y. Kajiwara, T. Miyake, T. Nakayama, S. Hirase, and H. Teranishi, *Chem. Phys. Lett.*, 1983, **94**, 276.

14 R. Gschwind and E. Haselbach, *Helv. Chim. Acta*, 1979, **62**, 941.

15 K. Hamanoue, K. Yokoyama, Y. Kajiwara, M. Kimoto, T. Nakayama, and H. Teranishi, *Chem. Phys. Lett.*, 1985, **113**, 207; K. Hamanoue, T. Nakayama, Y. Yamamoto, K. Sawada, Y. Yuhara, and H. Teranishi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1121.

16 S. Inbar, H. Linschitz, and S. G. Cohen, *J. Am. Chem. Soc.*, 1981, **103**, 1048.

17 H. Kobashi, M. Funabashi, T. Kondo, T. Morita, T. Okada, and N. Mataga, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3557.

18 (*a*) T. Shida, E. Haselbach, and T. Bally, *Acc. Chem. Res.*, 1984, **17**, 180, and references cited therein; (*b*) T. Shida, in 'Electronic Absorption Spectra of Radical Ions,' Elsevier, 1988, p. 446.

19 S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1986, **108**, 7356, and references cited therein.

20 R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, 1973, **95**, 4080; A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Am. Chem. Soc.*, 1978, **100**, 535.

21 T. Majima, C. Pac, A. Nakasone, and H. Sakurai, *J. Am. Chem. Soc.*, 1981, **103**, 4499.

22 K. Mizuno, J. Ogawa, M. Kamura, and Y. Otsuji, *Chem. Lett.*, 1979, 731.

23 J. C. Moutet and G. Reverdy, *Tetrahedron Lett.*, 1979, 2389.

24 P. F. Hudrlik and A. M. Hudrlik, *J. Org. Chem.*, 1973, **38**, 4254.

25 T. Nakayama, S. Tai, K. Hamanoue, and H. Teranishi, *Mem. Fac. Ind. Arts, Kyoto Tech. Univ., Sci. Technol.*, 1980, **29**, 46; K. Hamanoue, T. Hidaka, T. Nakayama, and H. Teranishi, *Chem. Phys. Lett.*, 1981, **82**, 55.

26 T. Nakayama, T. Miyake, M. Okamoto, K. Hamanoue, and H. Teranishi, *Mem. Fac. Ind. Arts, Kyoto Tech. Univ., Sci. Technol.*, 1980, **29**, 35; K. Hamanoue, K. Yokoyama, Y. Kajiwara, K. Nakajima, T. Nakayama, and H. Teranishi, *Chem. Phys. Lett.*, 1984, **110**, 25.

27 T. Nakayama, T. Yamaguchi, K. Hamanoue, H. Teranishi, T. Nagamura, A. Mugishima, and S. Sakimukai, *J. Spectrosc. Soc. Jpn.*, 1987, **36**, 126.

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