Mechanism of the Photocycloaddition of 1-Aminoanthraquinones to Olefins by Visible Light Irradiation; Oxetan Formation *via* an Exciplex

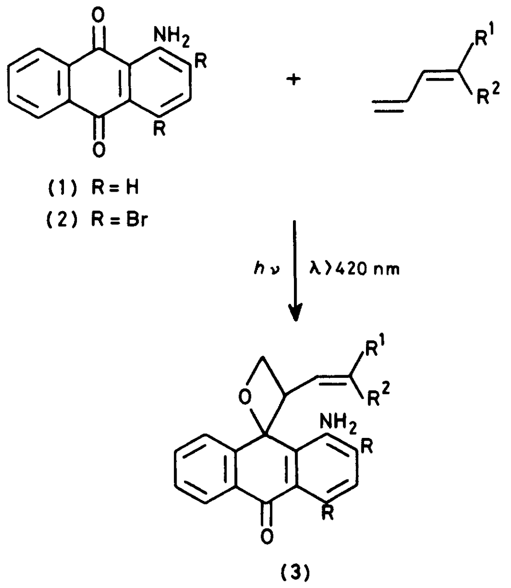
By **Haruo Inoue,* Atsuo Ezaki, and Mitsuhiko Hida,** Department of Industry, Faculty of Technology, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan

The mechanisms of the photocycloadditions of 1-aminoanthraquinone (1) and 1-amino-2,4-dibromoanthraquinone (2) to olefins by visible light irradiation have been investigated. Fluorescence of compound (1) was quenched by olefins without the appearance of a new emission and the Stern–Volmer constants accorded well with those obtained from the double reciprocal plots of the quantum yield against the concentration of olefin. The rate constant for the reaction was larger for olefins with lower ionization potentials, and was one order of magnitude larger in ethanol than in benzene. Exciplex quenching effects caused by amines such as triethylamine, butylamine, piperidine, and pyridine were also observed. All the results indicate that the reaction proceeds *via* exciplex formation between compound (1) in its excited singlet charge-transfer state and the olefin. The photocycloaddition of compound (2) in benzene was quenched by oxygen and gave a linear Stern–Volmer plot; the reaction in ethanol was only partially quenched. Detailed kinetic studies indicated that, in benzene, compound (2) had a single mode of reaction *via* the excited triplet charge-transfer state, while in ethanol it had a dual mode of reaction *via* both the singlet and triplet charge-transfer states.

THE photochemical cycloaddition of anthraquinone to olefins is known to produce the corresponding oxetans *via* the excited triplet $n\pi^*$ state of the quinone.[1] On the other hand, anthraquinone derivatives with electron-donating substituents such as an amino-group have long been accepted as not having any reactivity toward olefins since their lowest excited triplet state is an intramolecular charge-transfer ($\pi\pi^*$) state.[2,3] However, we have found that photocycloadditions of 1-aminoanthraquinones to dienes are effectively induced by visible light irradiation.[4] This reaction does not appear to be a conventional photocycloaddition *via* the $n\pi^*$ triplet state of the quinone, but a new type occurring *via* the intramolecular charge-transfer ($\pi\pi^*$) state.[5] We report here on detailed mechanistic studies of the photocycloaddition of 1-aminoanthraquinone (1) and 1-amino-2,4-dibromoanthraquinone (2). It has been shown that the photocycloaddition of compound (1) proceeds *via* exciplex formation between the aminoanthraquinone in its excited singlet charge-transfer (^{1}CT) state and the olefin. A striking solvent effect occurred in the reaction of compound (2) and indicated that in benzene there was a single mode *via* the triplet charge-transfer (^{3}CT) state and in ethanol a dual mode of reaction *via* both the ^{3}CT and ^{1}CT states.

EXPERIMENTAL

1-Aminoanthraquinone (1),[6] 1-amino-2,4-dibromoanthraquinone (2),[7] and the olefins[5] were purified as reported previously. A Shimadzu U.V.-200 spectrophotometer was used for the measurement of visible and u.v. spectra, and a Hitachi MPF-4 spectrofluorometer for the fluorescence spectra. The quantum yield of the photocycloaddition was determined using a potassium tris(oxalato)ferrate(III) chemical actinometer. The reaction mixture in a quartz cell (optical length 4 cm) was irradiated with a 500 W xenon lamp (USHIO UXL-500 DXO) through the following filter system: a Toshiba interference filter (KL-47) and a glass filter (VY-45) for monochromatic light of λ 470 nm, together with a benzene solution of the aminoanthraquinone (1) (1.0×10^{-3} mol dm^{-3}; optical length 1 cm), for irradiation with light of wavelength $340 < \lambda < 390$ nm.



(1) R = H
(2) R = Br

(3)

RESULTS AND DISCUSSION

Photocycloaddition of 1-*Aminoanthraquinone* (1) *in Ethanol and Benzene.—Fluorescence quenching.* Irradiation with visible light ($\lambda > 420$ nm) of a mixture of compound (1) and the olefin afforded an oxetan (3) as a stereoselective product. Since visible light irradiation causes an exclusive excitation of the aminoanthraquinone (1) to its intramolecular ^{1}CT level, and triplet quenchers such as oxygen and anthracene did not affect the photocycloaddition, the reaction appears to proceed *via* this excited ^{1}CT level.[5] In order to confirm this postulate, fluorescence quenching and related kinetic studies have been made. As shown in Figure 1 the fluorescence of compound (1) in ethanol was quenched by the addition of *trans*-penta-1,3-diene without the

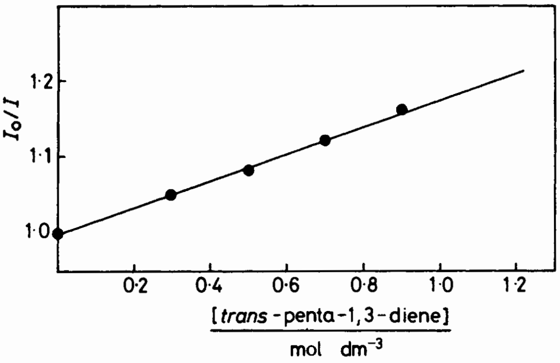


FIGURE 1 Fluorescence quenching of 1-aminoanthraquinone (1) in ethanol by *trans*-penta-1,3-diene; [compound (1)] 1.00 × 10^{-4} mol dm^{-3}; excitation at λ = 470 nm

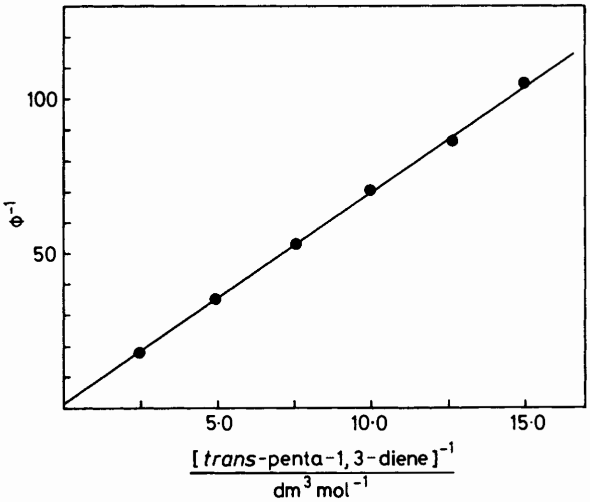


FIGURE 2 Effect of the concentration of *trans*-penta-1,3-diene on the photocycloaddition of 1-aminoanthraquinone (1) in ethanol; [compound (1)] 1.00 × 10^{-4} mol dm^{-3}; λ = 470 nm

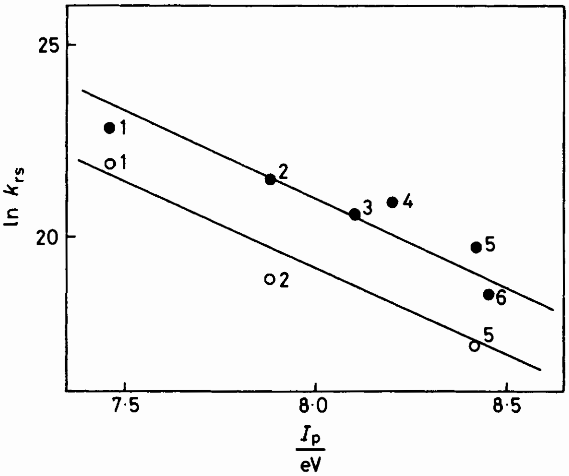


FIGURE 3 Logarithmic plot of k_{rs} in the photocycloaddition of 1-aminoanthroquinone (1) *versus* the ionization potential of the olefin; ●, in ethanol; ○, in benzene; 1, 2,5-dimethylhexa-2,4-diene; 2, cyclohexa-1,3-diene; 3, hexa-2,4-dien-1-ol; 4, cyclopentadiene; 5, *trans*-penta-1,3-diene; 6, *cis*-penta-1,3-diene

appearance of a new emission, and a linear Stern–Volmer plot was obtained with a Stern–Volmer constant of 0.17 dm^3 mol^{-1}. A plot of the reciprocal of the quantum yield for the disappearance of the aminoanthraquinone (1) *versus* the reciprocal of the concentration of the diene also gave a good straight line (Figure 2). The ratio (0.17 dm^3 mol^{-1}) of the intercept to the slope of the plot in Figure 2 agreed well with the Stern–Volmer constant obtained above. These relations are also observed in the photocycloaddition of compound (1) to various olefins both in ethanol and in benzene. The Stern–Volmer constants in the fluorescence quenching and the values of the ratio of the intercept to the slope in the double reciprocal plots are compared in Tables 1 and 2. The good agreement between both sets of values clearly indicates that the photocycloaddition is induced by the reaction of the olefin with compound (1) in its lowest excited ^{1}CT state. Since the lifetime of the S_1 (^{1}CT) state of compound (1) was shown to be 460 ps in ethanol and 1 750 ps in benzene, by a measurement of picosecond fluorescence lifetimes,[6] the rate constant for the reaction (k_{rs}) in each case was calculated from the Stern–Volmer constant in the fluorescence quenching (Tables 1 and 2). The reaction is faster in ethanol than in benzene, and the rate constant k_{rs} in the case of 2,5-dimethylhexa-2,4-diene, which has a rather low ionization potential (7.46 eV), is nearly the diffusion-controlled one. When $\log_e(k_{rs})$ was plotted against the ionization potentials of the olefins, a pair of parallel straight lines was obtained both in ethanol and in benzene (Figure 3). These results strongly suggest that electron transfer interactions between the ground-state olefins and the excited compound (1) in its ^{1}CT state are involved in the

TABLE 1

Kinetic parameters for the photocycloaddition of 1-aminoanthraquinone (1) to olefins in ethanol

Olefin	Φ^{-1} *versus* [Olefin]$^{-1}$ Intercept	Φ^{-1} *versus* [Olefin]$^{-1}$ Intercept/slope (dm^3 mol^{-1})	Stern–Volmer constant for the fluorescence quenching (dm^3 mol^{-1})	$k_{rs} \times 10^{-9}$ [a] (dm^3 mol^{-1} s^{-1})
2,5-Dimethylhexa-2,4-diene	10.0	3.5	3.9	8.5
Cyclohexa-1,3-diene	1.5	0.79	0.83	2.2
Hexa-2,4-dien-1-ol	2.0	0.38	0.39	0.85
Cyclopentadiene	2.0	0.59	0.54	1.2
trans-Penta-1,3-diene	1.2	0.17	0.17	0.37
cis-Penta-1,3-diene	1.1	0.09	0.05	0.11

[a] k_{rs} was calculated from the Stern–Volmer constant for the fluorescence quenching and the lifetime of the S_1 state of compound (1) in ethanol (460 ps).[6]

TABLE 2

Kinetic parameters for the photocycloaddition of 1-aminoanthraquinone (1) to olefins in benzene

Olefins	Φ^{-1} *versus* $[\text{Olefin}]^{-1}$ Intercept	Intercept/slope (dm^3 mol^{-1})	Stern–Volmer constant for the fluorescence quenching (dm^3 mol^{-1})	$k_{rs} \times 10^{-9}$ [a] (dm^3 mol^{-1} s^{-1})
2,5-Dimethylhexa-2,4-diene	2.3	5.6	5.3	3.0
Cyclohexa-1,3-diene	1.3	0.40	0.27	0.15
trans-Penta-1,3-diene	1.3	0.06	0.05	0.029

[a] k_{rs} was calculated from the Stern–Volmer constant for the fluorescence quenching and the lifetime of the S_1 state of compound (1) in benzene (1 750 ps).[6]

reaction process. An exciplex such as $[AQ^{\delta-} \cdots \text{olefin}^{\delta+}]$ may be formed on the reaction pathway. The accelerative effect in ethanol may be rationalized by the stabilization of such a polar intermediate.

Exciplex Quenching.—Recently it has been revealed that exciplex quenching by a third molecule is very useful in ascertaining the presence of an intermediate such as an exciplex on a reaction pathway.[7,8] When hex-2-ene as a potential exciplex quencher was added to the reaction system of compound (1) (1.00×10^{-4} mol dm^{-3}) and *trans*-penta-1,3-diene (1.00×10^{-1} mol dm^{-3}) in ethanol, the photocycloaddition was retarded and gave the same cyclization product as the reaction without hex-2-ene. The Stern–Volmer constant in the linear plot of Figure 4 was found to be 0.28 dm^3 mol^{-1}. Since the fluorescence of the aminoanthraquinone (1) was not affected by the addition of hex-2-ene, the observed quenching effect, although small, can be interpreted as resulting from the interaction of hex-2-ene with an intermediate other than the excited compound (1) in its ^1CT state on the reaction pathway. In the case of triethylamine both the photocycloaddition and the fluorescence of compound (1) were quenched, though to different extents (Figure 5). Although the overall quenching effect on the reaction includes both the effect on the reactive intermediate (such as an exciplex) and that on the fluorescence of compound (1), the former can be distinguished by a plot of the ratio of Φ_0/Φ to I/I' *versus* the concentration of triethylamine, as indicated later. This gives the linear plot of Figure 6 which strongly suggests the presence of a reactive intermediate which can be quenched by the amine. The slope corresponding to the quenching constant was found to be 0.49 dm^3 mol^{-1}. Similar quenching effects by various amines were also observed in the photocycloaddition of compound (1) to cyclohexa-1,3-diene. The quenching constants obtained by the same method as for the plot of Figure 6 are compared in Table 3.

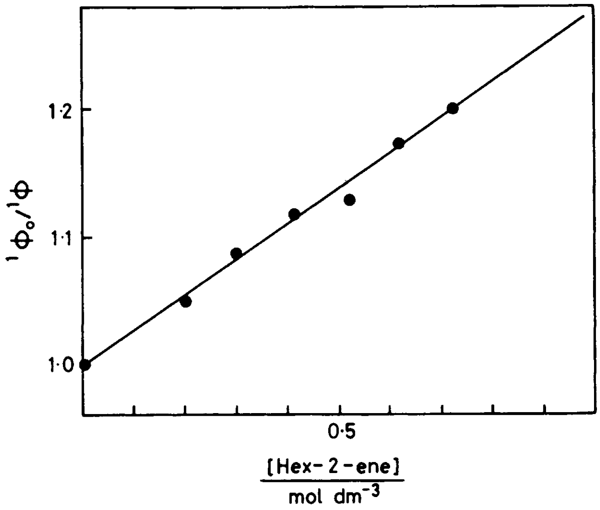


FIGURE 4 Effect of hex-2-ene on the photocycloaddition of 1-aminoanthraquinone (1) to *trans*-penta-1,3-diene in ethanol; [compound (1)] 1.00×10^{-4} mol dm^{-3}; [*trans*-penta-1,3-diene] 1.00×10^{-1} mol dm^{-3}; $\lambda = 470$ nm

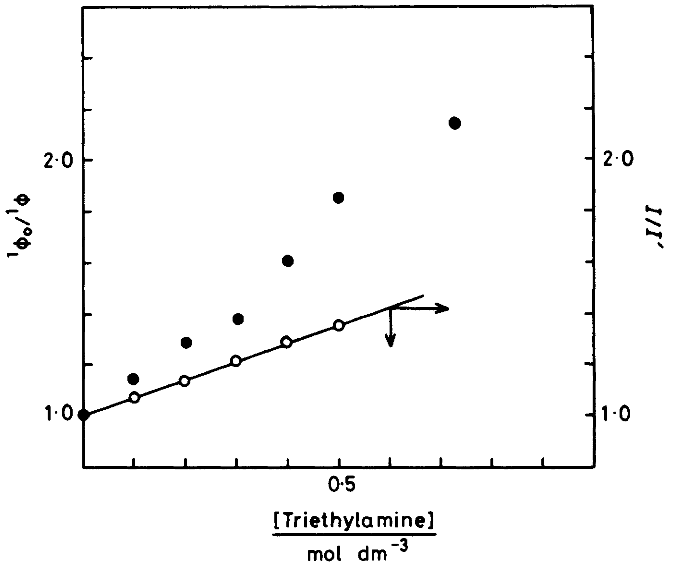


FIGURE 5 Effect of triethylamine on the photocycloaddition and the fluorescence intensity of 1-aminoanthraquinone (1) in ethanol; [compound (1)] 1.00×10^{-4} mol dm^{-3}; [*trans*-penta-1,3-diene] 1.00×10^{-1} mol dm^{-3}; $\lambda = 470$ nm; ●, effect on the photocycloaddition; ○, effect on the fluorescence intensity

Mechanism of the Photocycloaddition of 1-*Aminoanthraquinone* (1) *in Ethanol and Benzene*.—On the basis of the above experimental results the reaction scheme for the photocycloaddition of compound (1) can be depicted as shown in Figure 7.

The visible light irradiation (λ 470 nm) causes an exclusive excitation of compound (1) to its ^1CT state. It then reacts with the olefin (k_{rs}) to produce an exciplex, which leads to the oxetan (3) (k_{re}) by a process which competes

TABLE 3

Exciplex quenching by amines of the photocycloaddition of 1-aminoanthraquinone (1) to cyclohexa-1,3-diene in ethanol

	Triethylamine	Butylamine	Piperidine	Pyridine
Stern–Volmer constant for the exciplex quenching (dm^3 mol^{-1})	0.84	0.70	0.53	0.36

with the deactivation process (k_{de}). Amines and hex-2-ene can interact with the exciplex to quench the photocycloaddition (k_{qe}), and amines also quench the excited aminoanthraquinone (1) in its ^{1}CT state (k_{qs}). The quantum yield (${}^1\Phi_0$) for the production of the oxetan (3) without an exciplex quencher can be written as equation (1).

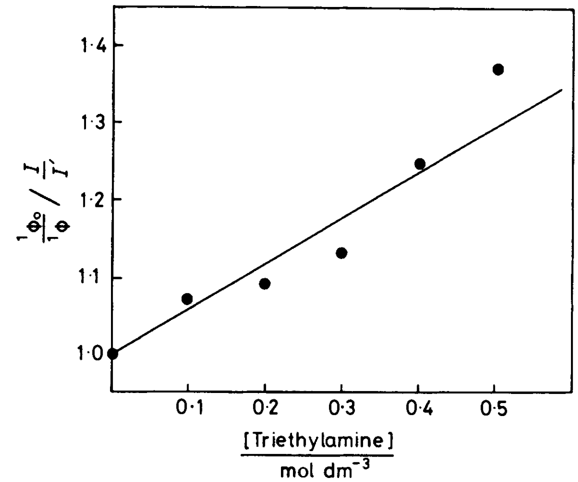


FIGURE 6 Exciplex quenching of the photocycloaddition of 1-aminoanthraquinone (1) to *trans*-penta-1,3-diene by triethylamine; [compound (1)] 1.00 × 10^{-4} mol dm^{-3}; [*trans*-penta-1,3-diene] 1.00 × 10^{-1} mol dm^{-3}; λ = 470 nm

$$ {}^1\Phi_0 = \left(\frac{k_{rs}[\text{Olefin}]}{k_{ds} + k_{rs}[\text{Olefin}]}\right)\cdot\left(\frac{k_{re}}{k_{de} + k_{re}}\right) \quad (1) $$

The reciprocal of the quantum yield is given by equation (2).

$$ ({}^1\Phi_0)^{-1} = \left(1 + \frac{k_{ds}}{k_{rs}[\text{Olefin}]}\right)\cdot\left(1 + \frac{k_{de}}{k_{re}}\right) \quad (2) $$

The Stern–Volmer equation for the fluorescence quenching is shown in equation (3) where I and I_0 denote the

$$ \frac{I_0}{I} = 1 + \frac{k_{rs}[\text{Olefin}]}{k_{ds}} \quad (3) $$

fluorescence intensity with and without olefins, respectively. Equations (2) and (3) indicate that the good agreement between the ratio of the intercept to the slope in the plot of Figure 2 and the slope of Figure 1 strongly supports the reaction scheme in Figure 7.

In the presence of an appropriate exciplex quencher, the Stern–Volmer relation becomes equation (4).

$$ \frac{{}^1\Phi_0}{{}^1\Phi} = \left(1 + \frac{k_{qs}[Q]}{k_{ds} + k_{rs}[\text{Olefin}]}\right)\cdot\left(1 + \frac{k_{qe}[Q]}{k_{de} + k_{re}}\right) \quad (4) $$

${}^1\Phi$ and ${}^1\Phi_0$ denote the overall quantum yield with and without an exciplex quencher Q. The fluorescence quenching by the exciplex quencher in the presence of olefins is also expressed by equation (5).

$$ \frac{I}{I'} = 1 + \frac{k_{qs}[Q]}{k_{ds} + k_{rs}[\text{Olefin}]} \quad (5) $$

I' and I denote the fluorescence intensity of the aminoanthraquinone (1) with and without the exciplex quencher in the presence of olefins. Thus the ratio of Equations (4) to (5), as plotted in Figure 6, gives equation (6).

$$ \frac{{}^1\Phi_0}{{}^1\Phi}\cdot\frac{I'}{I} = 1 + \frac{k_{qe}[Q]}{k_{de} + k_{re}} \quad (6) $$

When hex-2-ene is used as an exciplex quencher, k_{qs} is taken to be zero and I/I' equals unity. The exciplex quenching constant listed in Table 3 corresponds to $k_{qe}/(k_{de} + k_{re})$. If the rate constant k_{qe} of the exciplex quenching is taken to be a diffusion-controlled one (0.92 × 10^9 dm^3 mol^{-1} s^{-1}), the value of $k_{de} + k_{re}$ in each case is of the order of 10^{10} s^{-1}, *i.e.* the lifetime of the exciplex is estimated to be several tens of a picosecond.

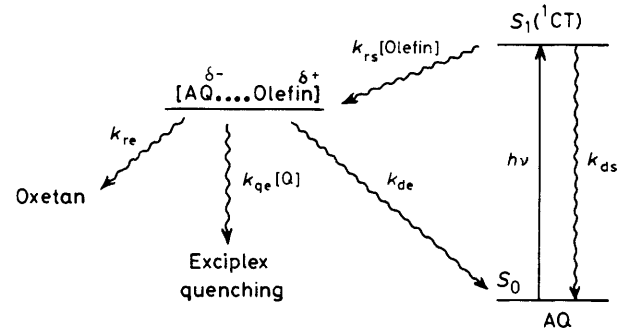


FIGURE 7 Reaction scheme for the photocycloaddition of 1-aminoanthraquinone (1) to olefins

This rather short lifetime may cause the non-emissivity of the exciplexes. Dimethyl acetylenedicarboxylate, an effective quencher in other systems,[7] did not affect the reaction at all. This suggests that in the quenching process amines and electron-rich olefins such as hex-2-ene act as electron donors towards the exciplexes. The intercept in the plot of Φ^{-1} *versus* $[\text{olefin}]^{-1}$ corresponds to $1 + k_{de}/k_{re}$ [equation (2)]. 2,5-Dimethylhexa-2,4-diene had larger intercepts than other olefins (Tables 1 and 2). This may reflect the differences in steric factors of the olefins in the exciplexes. Although the molecular configurations in the exciplex remain equivocal, the stereoselective production of the oxetan, as reported in the case of styrene,[5] suggests the sandwich-type configuration shown in Figure 8 as possibly leading to the oxetan compound.

Effect of a Triplet Sensitizer.—Although the photocycloaddition of compound (1) to the olefin by direct irradiation was clearly shown to proceed through the lowest excited singlet state (^{1}CT), the possibility of the reaction occurring *via* the lowest excited triplet state was further examined. When the aminoanthraquinone (1) (1.00 × 10^{-4} mol dm^{-3}) and *trans*-penta-1,3-diene in benzene were irradiated by light of wavelength $340 < \lambda < 390$ nm in the presence of fluorenone (1.00 × 10^{-2} mol dm^{-3}) (as a triplet sensitizer),* the photocycloaddition was accelerated considerably, by a factor of 13.4, compared with the photoreaction without fluorenone. Since the triplet level of fluorenone (*ca.* 226 kJ mol^{-1}) is lower than the T_2(${}^3n\pi^*$) (*ca.* 260 kJ mol^{-1})[3] and higher than the T_1(^{3}CT) level of compound (1) (176—197 kJ mol^{-1}),[9] the photocycloaddition induced by the selective excitation of fluorenone may proceed through the lowest excited triplet state (^{3}CT) of the aminoanthraquinone (1). The result strongly suggests that this lowest excited triplet state is also reactive towards photocycloaddition when it can be populated. The fact that only the reaction *via* the ^{1}CT level is observed on direct irradiation also indicates that the triplet yield of compound (1) is negligible both in benzene and in ethanol.[6]

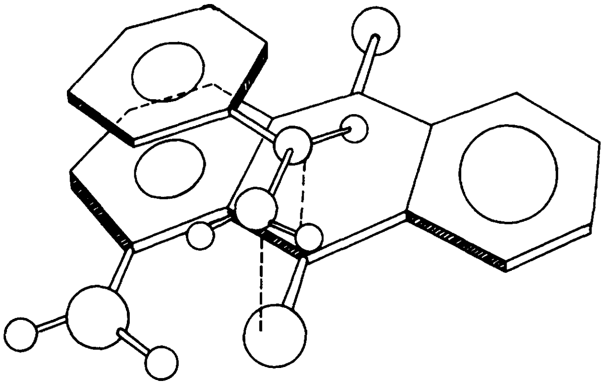
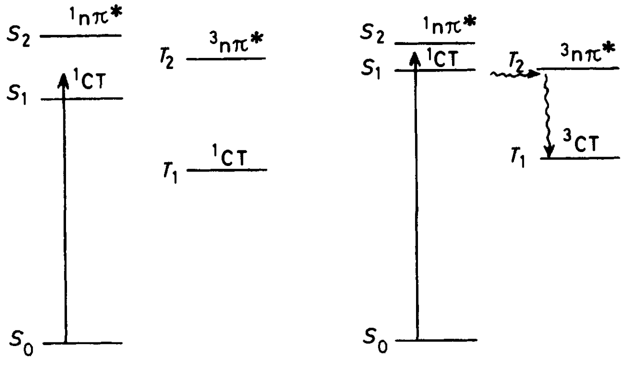


FIGURE 8 Possible configuration of the exciplex formed with styrene

Photocycloaddition of 1-*Amino*-2,4-*dibromoanthraquinone* (2) *in Benzene and in Ethanol*.—The excited state of 1-amino-2,4-dibromoanthraquinone (2) is known to show a considerable solvent effect.[10] The energy diagrams for the excited state of compound (2) in ethanol and benzene are indicated in Figure 9.[10] In benzene the T_1(^{3}CT) level is predominantly populated because of the proximity of, or inversion in, the relative positions of the S_1(^{1}CT) and T_2(${}^3n\pi^*$) states in contrast to the situation in ethanol.

When the dibromoanthraquinone (2) (1.00 × 10^{-4} mol dm^{-3}) and *trans*-penta-1,3-diene (1.00 × 10^{-1} mol dm^{-3}) in benzene were irradiated with light of $\lambda > 420$ nm under nitrogen, an oxetan, similar to that from the photocycloaddition of compound (1), was produced with rather a low quantum yield of 3.7 × 10^{-4}. A plot of the reciprocal of the quantum yield under nitrogen *versus* the reciprocal of the concentration of the olefin gave a good straight line; the ratio of the slope to the intercept was 1.03 mol dm^{-3} (Figure 10). In air the reaction was retarded in contrast to that of compound (1) and the plot gave a larger slope with the same intercept, as indicated in Figure 10. These results clearly indicate that the olefin reacts with the excited state of compound (2), which can be quenched by oxygen. The Stern–Volmer plot of the effect of quenching by oxygen gave a good straight line; a Stern–Volmer constant of 493 mol dm^{-3} was obtained when the concentration of *trans*-penta-1,3-diene used was 0.1 mol dm^{-3} (Figure 11). Thus it was concluded that the photocycloaddition of compound (2) in benzene proceeded through its lowest excited triplet state (^{3}CT) as depicted in Figure 12. The reciprocal of the quantum yield (${}^3\Phi_0$) under nitrogen and the Stern–Volmer equation can be written as equations (7) and (8), respectively.



(a) In ethanol (b) In benzene

FIGURE 9 Energy state diagram for the dibromo-compound (2) in ethanol and benzene

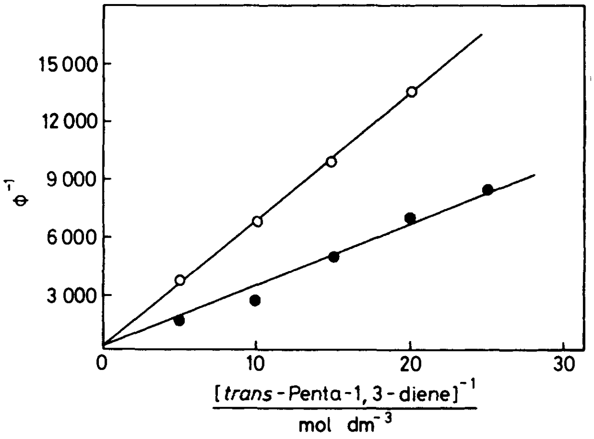


FIGURE 10 Effect of the concentration of *trans*-penta-1,3-diene on the photocycloaddition of the dibromo-compound (2) in benzene; [compound (2)] 1.00 × 10^{-4} mol dm^{-3}; λ = 470 nm; ●, under nitrogen; ○, in air

$$({}^3\Phi_0)^{-1} = \frac{1}{\Phi_{\text{isc}}}\cdot\left(1 + \frac{k_{dT}}{k_{rT}[\text{Olefin}]}\right) \tag{7}$$

---

* Under these conditions, fluorenone molecules absorb more than 97% of the incident light.

$$^3\Phi_o/^3\Phi = 1 + \frac{k_{qT}[O_2]}{k_{dT} + k_{rT}[\text{Olefin}]} \quad (8)$$

Φ_{isc} denotes the intersystem crossing efficiency and k_{dT}, k_{rT}, and k_{qT} are the rate constants indicated in Figure 12.

From equations (7) and (8) and Figures 10 and 11 the following relations are obtained: $k_{dT}/k_{rT} = 1.03$ mol dm^{-3}. $k_{qT}/(k_{dT} + k_{rT}[\text{Olefin}]) = 493$ mol dm^{-3}, where [Olefin] = 0.1 mol dm^{-3}.

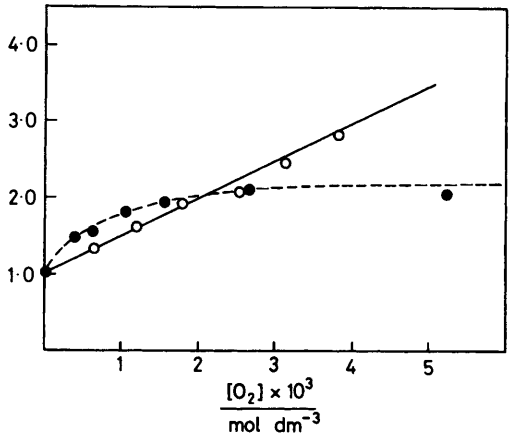


FIGURE 11 Effect of the concentration of oxygen on the photocycloaddition of the dibromo-compound (2) to *trans*-penta-1,3-diene; [compound (2)] 1.00 × 10^{-4} mol dm^{-3}; [*trans*-penta-1,3-diene] 1.00 × 10^{-1} mol dm^{-3}; ●, in ethanol; ○, in benzene; ––––, simulated curve using equation (10) with $^3\Phi_o/^1\Phi = 1.43$ and $k_{qT}\cdot\tau = 3.03 \times 10^3$ dm^3 mol^{-1}

If the rate constant k_{qT} for the quenching by oxygen is taken to be a diffusion-controlled one (1.6 × 10^{10} dm^{-3} mol^{-1} s^{-1}), the rate constants were obtained as k_{rT} = 2.9 × 10^7 dm^3 mol^{-1} s^{-1} and k_{dT} = 3.0 × 10^7 s^{-1}. The last value coincides well with the k_{dT} (2.8 × 10^7 s^{-1}) reported for the photoamination of compound (2).[10]

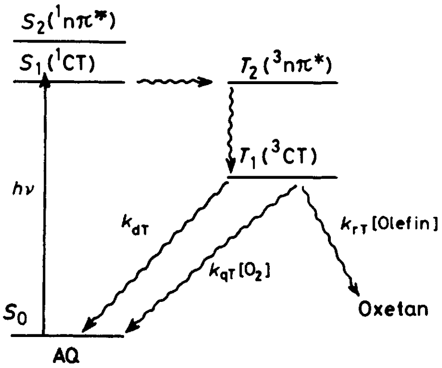


FIGURE 12 Reaction scheme for the photocycloaddition of the dibromo-compound (2) to olefins in benzene

In ethanol the photoreaction of the aminoanthraquinone (1) (1.00 × 10^{-4} mol dm^{-3}) and *trans*-penta-1,3-diene (1.00 × 10^{-1} mol dm^{-3}) under nitrogen afforded the same oxetan, but the reactivity was greater (Φ = 1.4 × 10^{-2}) than in benzene. The quenching by oxygen contrasted with that in benzene. The Stern–Volmer plot in Figure 11 exhibited saturation at a higher concentration of dissolved oxygen, indicating that the photocycloaddition was only being partially quenched by oxygen. This strongly suggests that the photocycloaddition of compound (2) in ethanol has a dual mode: (i) the reaction *via* the singlet state (^{1}CT) which is not affected by oxygen, and (ii) that *via* the triplet state (^{3}CT) which can be quenched by oxygen. Thus the reaction scheme for this photocycloaddition may be depicted as shown in Figure 13. The overall quantum yield (Φ) can be expressed as the sum of that of the singlet mode ($^1\Phi$) and that of the triplet mode ($^3\Phi$), as shown in equation (9).

$$\Phi = {}^1\Phi + {}^3\Phi \quad (9)$$

Since the Stern–Volmer equation for the effect of quenching by oxygen on $^3\Phi$ must be the same as equation (8), the overall Stern–Volmer equation can be written as equation (10).

$$\frac{\Phi_o}{\Phi} = \frac{1 + {}^3\Phi_o/^1\Phi}{1 + {}^3\Phi_o/^1\Phi\,(1 + k_{qT}\cdot\tau[O_2])} \quad (10)$$

$\tau = (k_{dt} + k_{rT}[\text{Olefin}])^{-1}$. When the concentration of oxygen is very large, Φ_o/Φ approaches 1 + ($^3\Phi_o/^1\Phi$), the limiting value. Taking [1 + ($^3\Phi_o/^1\Phi$)] as 2.43 and $k_{qT}\cdot\tau$ as 3.03 × 10^3 dm^3 mol^{-1}, the Stern–Volmer plot is best simulated as indicated by the broken line in Figure 11. The correlation factor in the simulation was 0.993. Thus the ratio of the quantum yield of the singlet mode to that of the triplet mode is found to be $^3\Phi_o/^1\Phi$ = 1.43 when the concentration of *trans*-penta-1,3-diene is 0.1 mol dm^{-3}. While the quantum yield of the singlet mode ($^1\Phi$) must be a similar expression to equation (1), that of the triplet mode ($^3\Phi_o$) under nitrogen can be written as equation (11.)

$$^3\Phi_o = \left(\frac{k_{isc}}{k_{ds} + k_{rs}[\text{Olefin}]}\right)\cdot\left(\frac{k_{rT}[\text{Olefin}]}{k_{dT} + k_{rT}[\text{Olefin}]}\right) \quad (11)$$

The ratio of $^1\Phi$ to $^3\Phi_o$ is therefore equation (12).

$$\frac{^1\Phi}{^3\Phi_o} = \left(\frac{k_{re}}{k_{isc}(k_{de} + k_{re})}\right)\cdot\left(\frac{k_{rs}}{k_{rT}}\right)\cdot(k_{dT} + k_{rT}[\text{Olefin}] \quad (12)$$

A plot of $^1\Phi/^3\Phi_o$ against the concentration of *trans*-penta-1,3-diene indeed gave a straight line, with the ratio of the slope to the intercept k_{rT}/k_{dT} being 8.52 dm^3 mol^{-1}. If the quenching rate constant k_{qT} is taken to be a diffusion-controlled one (0.92 × 10^9 dm^3 mol^{-1} s^{-1}) in ethanol, k_{rT} and k_{dT} are calculated as 1.4 × 10^7 dm^3 mol^{-1} s^{-1} and 1.6 × 10^6 s^{-1} respectively, using the values of $k_{qT}\cdot\tau$ obtained in the simulation in Figure 11 and k_{rT}/k_{dT}. The value of k_{dT} also coincides well with the k_{dT} (2.0 × 10^6 s^{-1}) obtained for the photoamination of compound (2).[11]

For the singlet mode reaction, the double reciprocal plot of $^1\Phi$ *versus* the concentration of *trans*-penta-1,3-diene also gave a straight line with the value of k_{ds}/k_{rs} being 10.7 dm^3 mol^{-1}. Since the lifetime of the $S_1(^1CT)$ state of compound (2) in ethanol was determined to be 150 ps by a measurement of the picosecond fluorescence

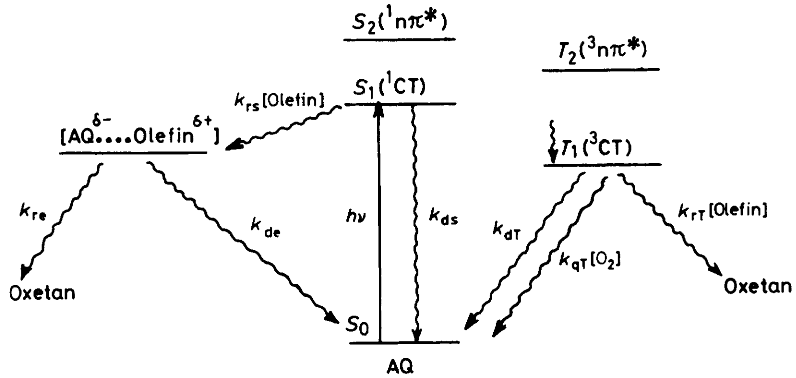


FIGURE 13 Reaction scheme for the photocycloaddition of the dibromo-compound (2) to olefins in ethanol

lifetime,[12] k_{rs} was calculated to be 6.2×10^8 dm^3 mol^{-1} s^{-1}. All the rate constants obtained for the photocycloaddition of compound (2) to *trans*-penta-1,2-diene are tabulated in Table 4. The exciplex quenching experiments with amines were not carried out for the triplet mode reaction because the amines could easily cause photoamination of the dibromo-compound (2).[10] Although it remains equivocal whether or not an exciplex is also formed on the reaction pathway of the triplet mode, the same stereoselective product in the triplet mode reaction as that from the singlet mode implies the formation of some intermediate such as a triplet exciplex which leads to the oxetan product.

TABLE 4

Rate constants for the photocycloaddition of the dibromo-compound (2) to olefins

Solvent	k_{rs}/dm^3 mol^{-1} s^{-1}	k_{dT}[a]/s^{-1}	k_{dT}[b]/s^{-1}	k_{rT}/dm^3 mol^{-1} s^{-1}
Ethanol	6.2×10^8	1.6×10^6	2.0×10^6	1.4×10^7
Benzene		3.0×10^7	2.8×10^7	2.9×10^7

[a] Obtained from the photocycloaddition. [b] Obtained from the photoamination.[11,12]

[1/1397 *Received, 7th September*, 1981]

REFERENCES

[1] D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *Tetrahedron Lett.*, 1968, 2863.

[2] J. M. Bruce, ' The Chemistry of the Quinonoid Compounds, ed. S. Patai, Wiley, London, 1974, p. 465.

[3] H. Inoue and M. Hida, *Yuki Gosei Kagaku Kyokai Shi*, 1974, **32**, 348.

[4] H. Inoue, A. Ezaki, H. Tomono, and M. Hida, *J. Chem. Soc., Chem. Commun.*, 1979, 860.

[5] H. Inoue, A. Ezaki, D. Nakajima, H. Tomono, and M. Hida, *J. Chem. Soc., Perkin Trans. 1*, in the press.

[6] H. Inoue, M. Hida, N. Nakashima, and K. Yoshihara, *J. Phys. Chem.*, in the press.

[7] R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, 1974, **96**, 2994; R. A. Caldwell, *ibid.*, 1974, **96**, 7369; R. A. Caldwell, D. Creed, and H. Ohta, *ibid.*, 1975, **97**, 3246; H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *ibid.*, **1976**, **98**, 2002; D. Creed, R. A. Caldwell, H. Ohta, and D. C. DeMareo, *ibid.*, 1977, **99**, 277; R. A. Caldwell, N. I. Ghali, C. K. Chien, D. DeMareo, and L. Smith, *ibid.*, 1978, **100**, 2857.

[8] T. Majima, C. Pac, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1811.

[9] B. E. Hulme, E. J. Land, and G. O. Phillips, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 2003.

[10] H. Inoue and M. Hida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1793.

[11] H. Inoue, T. Shinoda, and M. Hida, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 154.

[12] H. Inoue, M. Hida, N. Nakashima, and K. Yoshihara, unpublished results.