the value of 0.70 calculated from v' for the methyl group. Then at least, in the case of the methyl group, eq 10 is approximately obeyed.

References and Notes

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(10) The v' values which we have calculated are of course related to the *A* values of Okamoto, Taft, and Hine (ref 2, 5, 6) as is shown by the correlation obtained between *A* and v' (set 1C, Table V). The v' values were defined in order to be on the same scale as and capable of comparison with the previously defined v values.

Singlet and Triplet Exciplexes in the Photoreaction of Phenanthrene with Dimethyl Fumarate

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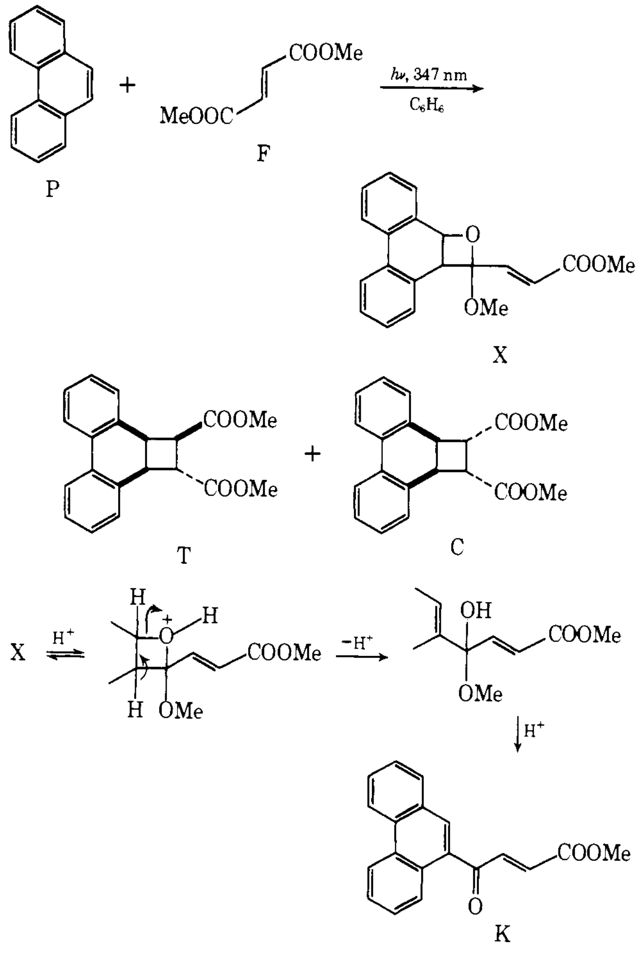
Abstract: The photoreaction of phenanthrene (P) with dimethyl fumarate (F) yields the oxetane (X) and the *trans*- and *cis*-cyclobutanes (T and C). The kinetics of the reaction and quenching experiments are consistent with a diffusion-controlled reaction of singlet excited phenanthrene (P^{*1}) with F to give a weakly emitting singlet exciplex (E^{*1}), which yields X (2.4%) and stereospecifically T (0.1%), intersystem crosses to a triplet exciplex (E^{*3}) (5.3%), and decays to P + F (92.2%). The triplet exciplex (E^{*3}) leads to T (3.2%) and C (1.7%), dissociates to P^{*3} + F (67.2%), and decays to P + F (27.9%, presumably via dissociation of the biradical preceding the formation of T and C).

The spectroscopic and chemical aspects of exciplexes (complexes in the electronically excited state) have attracted considerable interest in recent years.[1] The intermediacy of both singlet and triplet exciplexes has been proposed for several photochemical cycloaddition reactions.[2]

In a preliminary communication,[3] we reported about the involvement of a weakly emitting singlet and a triplet exciplex (which led to oxetane and cyclobutane formation) in the photoreaction of phenanthrene (P) and dimethyl fumarate (F). The intermediacy of a triplet exciplex in the sensitized reaction was also inferred by Caldwell[4] on the basis of rate constants. Recently, Caldwell[5] presented a powerful proof, based on an elegant quenching experiment, that the emitting singlet exciplex is a precursor to the addition products. In this paper, the details of this rather unusual reaction will be presented, together with further evidence for the intermediacy of both exciplexes.

Results and Discussion

From an irradiated benzene solution of phenanthrene (P) (0.05 *M*) and dimethyl fumarate (F) (0.05 *M*) using the filtered output of a Rayonet 3500 Å reactor (Figure 1), the *trans*- and *cis*-cyclobutane derivatives (T and C, respectively), together with the yellow-colored ketone (K), were isolated. The latter compound represents a 1:1 adduct of P and F with the loss of methanol. The formation of this compound could be rationalized if an oxetane (X) were formed as a primary photoproduct and underwent an acid-catalyzed cleavage to (K). To confirm this hypothesis, the reaction was carried out in the presence of traces of pyridine to keep the solution basic. The solution so treated remained colorless on irradiation and turned yellow on subsequent addition of hydrochloric acid. The formation of K on acidification was monitored by absorption spectroscopy. Gas chro-



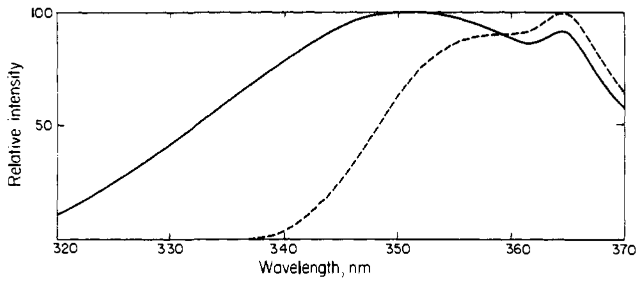


Figure 1. Wavelength distribution of the output of the 3500-Å lamps used in the Rayonet photoreactors (—), and the corresponding output after passing through a 1.9-cm thick filter solution, No. 9, described by Rappoldt[22] (- - -).

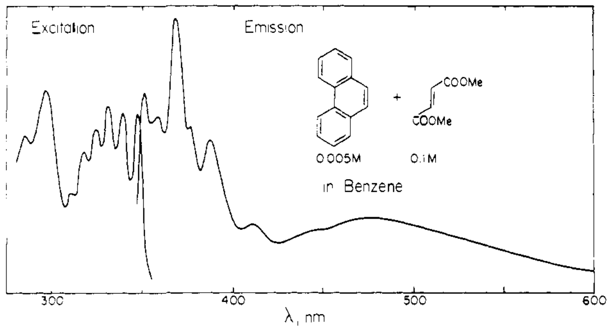


Figure 2. Emission spectrum from a benzene solution of phenanthrene (5×10^{-3} M) and dimethyl fumarate (0.1 M) excited with a N_2 laser at 337 nm. Excitation spectrum of the exciplex emission monitored at 475 nm. Identical excitation spectrum from the same sample was obtained at 370 nm (residual phenanthrene fluorescence).

matographic analysis of the sample prior to acid treatment did not show a peak for K, whereas the acid-treated one did. That no extra peak was detectable in the former sample is probably due to cleavage of the oxetane to the starting materials. By careful chromatographic separation on basic Al_2O_3, the oxetane (X) was isolated and its structure spectroscopically assured (cf. Experimental Section).

This oxetane formation represents an unusual reaction since, under the above-mentioned conditions, the carbonyl compound (F) was not the photoexcited reactant as in the case of the known photochemical oxetane formations.[2a-h,6] The fact that the same products were obtained on irradiating at 347 nm using a frequency-doubled ruby laser proves conclusively that the oxetane (X) results from a reaction of photoexcited phenanthrene.[7]

On using benzophenone as triplet sensitizer, we were unable to detect any X or K, whereas the cyclobutanes (T and C) were formed in practically the same ratio (T/C = 1.9) as in the unsensitized reaction. This suggests a singlet mechanism for the formation of X, which is supported by the fact that the fluorescence of P is quenched by F at a diffusion-controlled rate (see Kinetics section), and that the quantum yield for the formation of X parallels the fluorescence quenching of P.

With increasing amounts of F, a new emission band with a maximum at 470 nm could be detected besides the residual fluorescence of phenanthrene (Figure 2). This new emission has the features[8] of an exciplex emission, being broad, structureless, shifted to longer wavelength relative to the fluorescence of P, and upon addition of a polar solvent such as acetonitrile it diminishes in intensity and is further shifted to longer wavelength. This exciplex emission[9,10] was also observed in other nonpolar solvents such as tetrahydrofuran, but was absent in polar solvents such as methanol and acetonitrile.

The excitation spectra for the residual P fluorescence and this new band are identical (Figure 2). Extensive purification of F by several recrystallizations and distillation did not cause any change in the intensity of this band. We are confident that this emission is that of an exciplex from the reaction of P^{*1} with F.

The above-mentioned data would suggest the following simple mechanism (in which E^{*1} stands for a singlet exciplex) to account for the formation of X, T, and C.

$$\begin{aligned} P^{*1} &\longrightarrow P^{*3} \\ P^{*1} + F &\longrightarrow E^{*1} \\ E^{*1} &\longrightarrow X \\ P^{*3} + F &\longrightarrow T + C \end{aligned}$$

According to such a scheme, one would predict that ϕ_{T+C} will *increase* with *decreasing* [F] (keeping in mind that the lifetime of P^{*3} is much longer than that of P^{*1}), which was found to be the case. This scheme also requires a straight linear relationship for X/(T + C) vs. [F]. We obtained, however, a curved line for the plot of this function (Figure 3), which indicates that a constant X/(T + C) is approached at high [F]. This implies that T and C are formed from the reaction of both P^{*3} and P^{*1} with F; i.e., the following reaction has to be introduced into the scheme.

$$P^{*1} + F \longrightarrow \quad \longrightarrow T + C$$

Accordingly, a plot of (T + C)/X vs. 1/[F] should be a straight line with an intercept corresponding to the ratio of T + C from the singlet reaction to that of X. This was found to be the case (Figure 4), and an intercept of 0.38 was obtained.

The problem now was that the ratio T:C at [F] $\gtrsim$ 0.2, where practically all P^{*1} was trapped, was only slightly higher than that obtainable at low [F] or in the presence of a triplet sensitizer. One would expect such a reaction from the singlet state to be concerted and, if a singlet biradical were formed, it would not be expected to lose the stereospecificity completely.[7] We proposed, therefore, that intersystem crossing of the exciplex precedes the biradical formation, which leads to the cyclobutanes T and C. The intersystem crossing of exciplexes is a spectroscopically well-established phenomenon,[11] and it might be expected to take place in such a system. The following quenching experiments were carried out to support this view.

2,3-Dimethylbutadiene appears to be an appropriate triplet quencher for the present system. It has a triplet energy (60 kcal/mol)[12] lower than that of P (62 kcal/mol)[13] and, at low concentrations (<0.2 M), it does not interact with the singlet excited phenanthrene or with the singlet exciplex. This was evident from the emission spectra of these species which were not affected in intensity or distribution on addition of the diene.

As expected for a singlet reaction, the quantum yield for the formation of X is not affected by low concentrations ($\leq$0.2 M) of the diene. On the other hand, the quantum yield for the formation of T and C decreased with increasing quencher concentration. With [F] = 0.01 M, the ratio of (T + C)/X decreased from 1.4 in the absence of quencher to $\leq$0.2 at a quencher concentration of ~0.1 M. Further increase of the quencher concentration to 0.2 or 0.3 M did not correspondingly decrease the (T + C)/X ratio. This ratio of less than 0.2 is lower than the product ratio of 0.38 at infinite concentration of F and in the absence of a quencher. These data indicate that a large fraction of the cyclobutanes formed via the reaction of P^{*1} with F is quite susceptible to triplet quenching, which confirms the proposed intersystem crossing (isc) of the singlet exciplex.

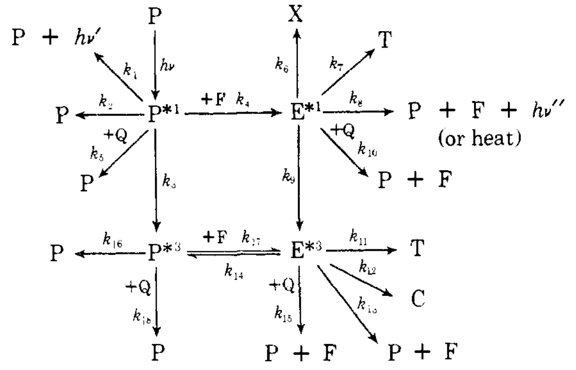
At [F] = 0.01 M and a diene concentration of 0.1 M, which is sufficient to strongly suppress the reactions of P^{*3}, the ratio of T/C is 3.2, compared with the ratio of 1.9 measured in the absence of a quencher or in the presence of a triplet sensitizer. As shown below, this increase in the T/C ratio is *not* due to the formation of a more stereospecific singlet biradical.

If we accept the idea of isc of E^{*1}, for which strong evidence was obtained, then a triplet exciplex or at least an encounter complex of P^{*3}/F will be formed, which can dissociate to $P^{*3} + F$ or react directly to give the biradical preceding the cyclobutane formation. The ease of quenching of the cyclobutane fraction formed in this latter process will depend on the lifetime of the triplet exciplex or encounter complex (E^{*3}). This will certainly be shorter than the lifetime of P^{*3} and would be appreciably quenched only at much higher diene concentrations. Indeed, further decrease of the cyclobutane-to-oxetane ratio[14] was achieved, although at a lower efficiency, at diene concentrations from 0.1 to 1.0 *M*. Interestingly, the T/C ratio also increased. This can be best rationalized in terms of a minor, stereospecific (most probably concerted) reaction of the singlet exciplex leading to T. In perfect agreement with this view is the fact that the ratio[15] (T − 1.9C)/X was constant at ~0.05, independently of the quencher concentration; i.e., the singlet exciplex yields T and X directly in the ratio 0.05:1. Further support for this stereospecific reaction was obtained from the reaction in neat 2,3-dimethylbutadiene, which led to X and T. Compound C in this reaction, if formed, was below the detection point. The ratio T/X was 0.09. This higher ratio is probably due to the difference in solvents between benzene and the diene.

Kinetics

The reactions discussed in the previous section together with the decay processes of the different intermediates are presented in Scheme I. On the basis of this scheme, the kinetic expressions for the quantum yields and product distributions were derived.

Scheme I



In the absence of a quencher, the cyclobutane/oxetane ratio, (T + C)/X, is given by eq 1, based on the approximation that k_{16} is negligible as compared with $k_{17}[F]$, which is fully justified under the concentrations of F chosen. From

$$\frac{T + C}{X} = \frac{k_7}{k_6} + \frac{k_9}{k_6}\alpha + \frac{k_3}{k_4}\left(\frac{k_6 + k_7 + k_8 + k_9}{k_6}\right)\alpha\frac{1}{[F]} \quad (1)$$

where

$$\alpha = (k_{11} + k_{12})/(k_{11} + k_{12} + k_{13})$$

the plot of (T + C)/X vs. 1/[F] (Figure 4), a slope of 0.011 and an intercept of 0.38 were obtained.

The fraction α can be determined from the quantum yield of cyclobutane formation in a triplet-sensitized reaction. Using benzophenone as a sensitizer for an equimolar solution of P and F (0.05 or 0.1 *M*), a ϕ_{T+C} of 0.1 was measured. Because of its long lifetime, triplet phenanthrene is completely trapped by F at the given concentrations. The fraction of triplet benzophenone consumed in energy transfer to F is wasted, because this process does not lead to adduct formation.[4] Correcting for this fraction[16] gave a quantum efficiency, which corresponds to α, of 0.15 for adduct formation via P^{*3}.

The quantum yield of oxetane formation as a function of [F] is given by eq 2.

$$\phi_X = \frac{k_4[F]}{k_1 + k_2 + k_3 + k_4[F]}\,\frac{k_6}{(k_6 + k_7 + k_8 + k_9)} \quad (2)$$

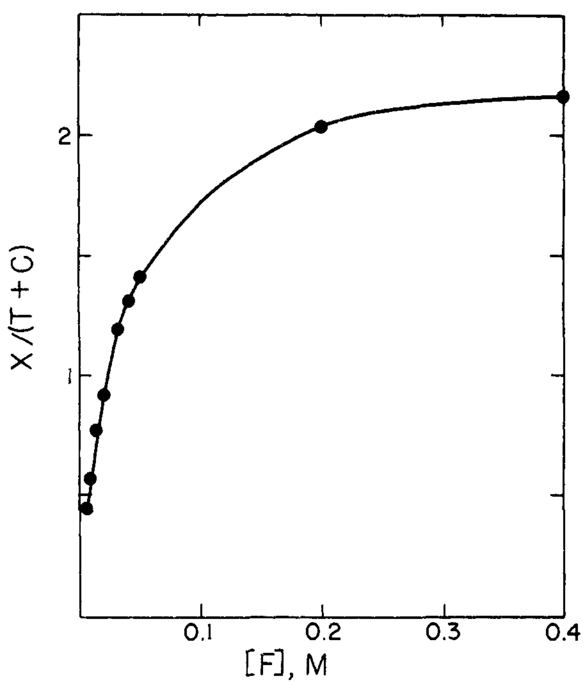


Figure 3. Plot of the ratio of oxetane (X) to cyclobutanes (T + C) vs. [F] from the reaction of P (0.05 *M*) with F in benzene.

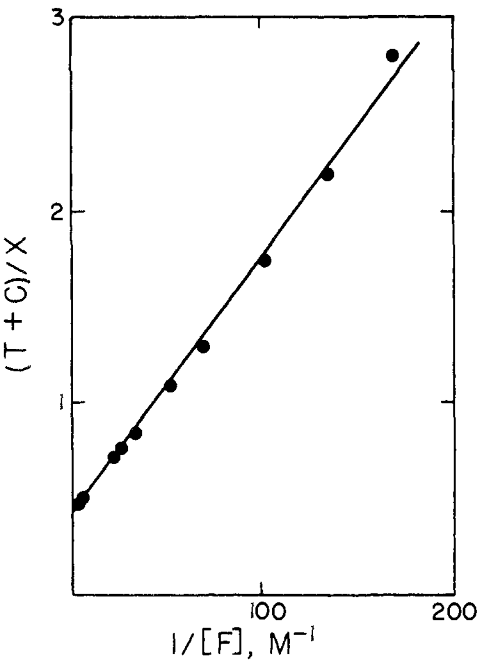


Figure 4. Plot of the ratio of cyclobutanes (T + C) to oxetane (X) vs. 1/[F] from the reaction of P (0.05 *M*) with F in benzene.

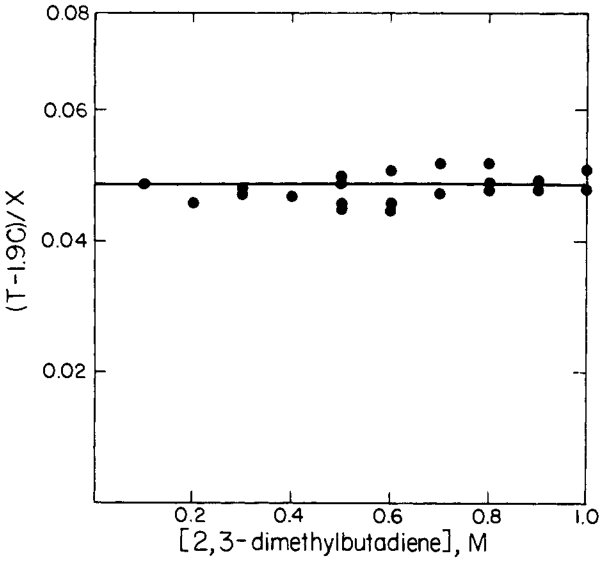


Figure 5. Plot of the ratio (T − 1.9 C)/X vs. the concentration of 2,3-dimethylbutadiene from the reaction of P (0.004 *M*) and F (0.01 *M*) in benzene.

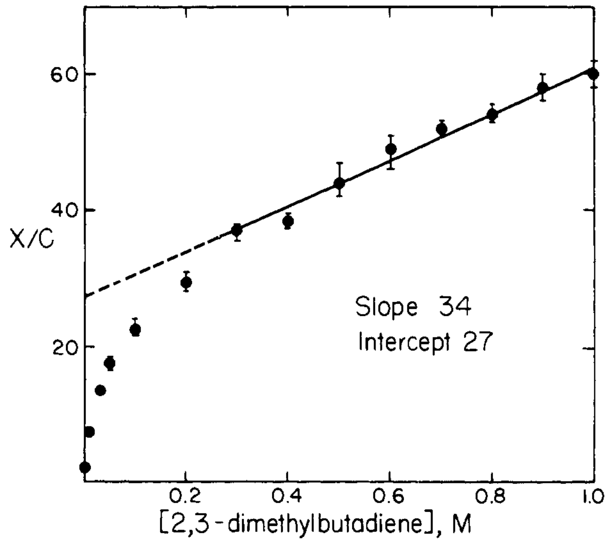


Figure 6. Plot of the product ratio X/C vs. 2,3-dimethylbutadiene from the reaction of P (0.004 *M*) and F (0.01 *M*) in benzene.

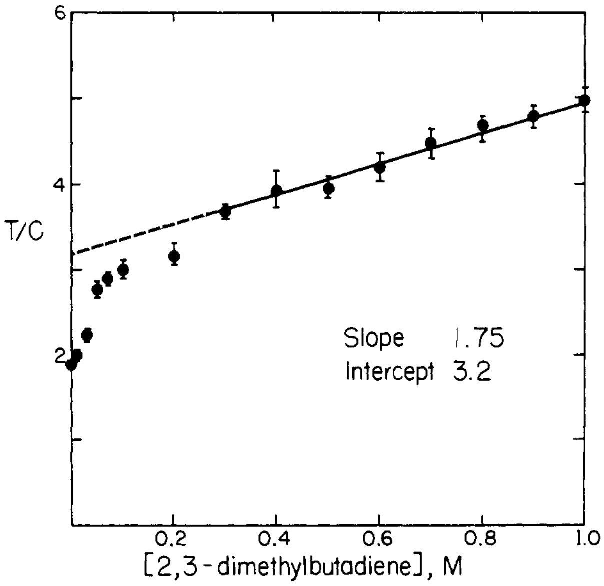


Figure 7. Plot of the product ratio T/C vs. 2,3-dimethylbutadiene from the reaction of P (0.004 *M*) and F (0.01 *M*) in benzene.

Table I. Relative Distributions of the Reactions of E^{*1} and E^{*3}

Reactions of E^{*1}		Reactions of E^{*3}	
Formation of X	2.4%	Formation of T	3.2%
Formation of T	0.1	Formation of C	1.7
isc	5.3	Dissociation to P^{*3} + F	67.2
Decay	92.2	Decay	27.9

For $k_4[\mathrm{F}] \gg k_1 + k_2 + k_3$, then

$$\phi_{\mathrm{X}} \approx k_6/(k_6 + k_7 + k_8 + k_9) \tag{3}$$

Since k_4 is about[17] 8×10^9 l. mol^{-1} sec^{-1} and $(k_1 + k_2 + k_3)$[18] = 1.8×10^7 sec^{-1}, then ϕ_{X} should be practically constant at [F] $\gtrsim 5 \times 10^{-2}$. This was found to be the case, and a limiting quantum yield for ϕ_{X} of 0.024 was measured, which corresponds to the ratio $k_6/(k_6 + k_7 + k_8 + k_9)$. According to eq 1, this ratio can be calculated independently from the slope of Figure 4 (0.011), the ratio α (0.15), and the reaction constants k_3 (1.37×10^7 sec^{-1})[18] and k_4 (8×10^9 l. mol^{-1} sec^{-1}). The ratio of $k_6/(k_6 + k_7 + k_8 + k_9)$ so calculated is 0.023, which is in good agreement with the value of 0.024 determined from the quantum yield of X as mentioned above.

The first term in eq 1, k_7/k_6, is given by the ratio of the fraction of T, formed directly from E^{*1}, to X. This ratio is obtained from (T − 1.9C)/X[15] (Figure 5), which is equal to 0.05. Since the sum of the first two terms in eq 1 (the intercept of plot 4) is 0.38, $k_9\alpha/k_6 = 0.38 - 0.05 = 0.33$; i.e., $k_9/k_6 = 0.33/0.15 = 2.2$. From these ratios, the percentages of the different reactions of E^{*1} can be determined (Table I).

At quencher concentrations >0.2 *M*, practically all P^{*3} is quenched; i.e., the cyclobutane C is formed only via $E^{*1} \rightarrow E^{*3} \rightarrow$ C. Under these conditions of high quencher concentrations, the ratio X/C is given by eq 4 and T/C by eq 5. The plot of X/C vs. [Q] is shown in Figure 6 and that of

$$(\mathrm{X/C})_{\mathrm{high[Q]}} \approx \frac{k_6(k_{11} + k_{12} + k_{13} + k_{14})}{k_9k_{12}} + \frac{k_6k_{15}}{k_9k_{12}}[\mathrm{Q}] \tag{4}$$

$$(\mathrm{T/C})_{\mathrm{high[Q]}} \approx \frac{k_{11}}{k_{12}} + \frac{k_7(k_{11} + k_{12} + k_{13} + k_{14})}{k_9k_{12}} + \frac{k_7k_{15}}{k_9k_{12}}[\mathrm{Q}] \tag{5}$$

T/C vs. [Q] in Figure 7. These gave intercepts of 27 and 3.2, respectively. On substitution in eq 4 and 5 by the above-determined ratios of k_6/k_9 and k_7/k_9, respectively, values of 59.4 and 58 for the ratio $(k_{11} + k_{12} + k_{13} + k_{14})/k_{12}$ were obtained, which shows that the proposed mechanism is consistent. From this ratio and those reported above, the relative weight of the reactions of E^{*3} was determined (see Table I).

According to eq 4 and 5, the slope/intercept ratio of Figure 6 and the slope/(intercept − 1.9) of Figure 7 are equal $k_{15}/(k_{11} + k_{12} + k_{13} + k_{14})$. The measured values are 1.26 and 1.35, respectively. Turro[19] has shown that the upper limit for the reaction constant of exothermic triplet-triplet energy transfer is about half that of k_{dif}.[20] Taking an upper limit of 4×10^9 l. mol^{-1} sec^{-1} for k_{15} and using the data in Table I, we get

$$k_{14} \le \frac{4 \times 10^9 \times 0.67}{1.3} \le 2 \times 10^9 \text{ sec}^{-1}$$

In the absence of any interaction in an encounter complex, the reaction constant for dissociation to its components is expected[21] to be $\geq 8 \times 10^9$ sec^{-1} for benzene solutions. Since the upper limit for the rate of dissociation of E^{*3} to $P^{*3} + F$ is about one-fourth of this value, it can be concluded that, in this complex, there is a certain binding energy, although it may be small. That is, E^{*3} represents a triplet exciplex rather than an encounter pair (P^{*3}/F).

Experimental Section

The irradiations for the kinetic studies were carried out in a small merry-go-round rotating inside a 1.9 cm thick cocylindrical container filled with a filter solution No. 9 described by Rappoldt,[22] using a Rayonet photoreactor equipped with 3500-Å lamps. The output of these lamps so modified is given in Figure 1. At different concentrations of the reactants, the product distribution of such irradiations could be duplicated on irradiating at 347 nm using a frequency-doubled ruby laser as a light source.

All chemicals were purified before use. Phenanthrene, Eastman fluorescent grade, was zone refined. Dimethyl fumarate was recrystallized from benzene and fractionally sublimed; the middle fraction was used. In control experiments to the emission and product distribution studies, no detectable difference was observed on using the purified chemicals compared with those commercially available. All irradiations were carried out in freshly distilled spectro grade solvents. The samples were degassed in three freeze-pump-thaw cycles. The adducts T and X were found to undergo benzophenone- and phenanthrene-photosensitized decomposition. All kinetics were, therefore, studied under less than 1% fumarate conversion.

Since oxetane X is very sensitive to acids, the irradiations were carried out in the presence of 0.1% pyridine to keep the solution basic. The irradiated samples (3 ml each) were transferred to flasks, 3 drops of concentrated hydrochloric acid was added, and the mixture was rotated at 40° for 10 min. Sodium bicarbonate and sodium sulfate were then added, and the samples were quantitatively filtered, distilled, and redissolved in 0.5 ml of benzene and subjected to analysis. With a 6 ft × ⅛ in. column packed with 1.5% Dexsil on Chromosorb W at 240°, the peaks appeared at 6 (T), 7 (C), and 11.5 (X) min.

***trans*-Dimethyl 1,2,2a,10b-Tetrahydrocyclobuta[*l*]phenanthrene-1,2-dicarboxylate.** A 100-ml equimolar (0.1 *M*) benzene solution of benzophenone, phenanthrene, and dimethyl fumarate was irradiated for 6 hr in an immersion apparatus equipped with a Philips HPK 125-W lamp and a glass filter (GWCa) to cut off light of $\lambda < 366$ nm. The solvent was distilled and the residue freed from benzophenone by repeated digestion and extraction with pentane at −20°. Recrystallization of the insoluble fraction from cyclohexane gave 0.35 g of the *trans*-cyclobutane adduct (T): mp 112–113° (after a second recrystallization from the same solvent); NMR ($CDCl_3$) δ 3.50 (s, OCH_3), 3.71 (s, OCH_3), 3.5–4.4 (m, 4 H of the cyclobutane ring), 6.9–7.4 (m, 6 H), 7.6–8.0 (m, 2 H at positions 4 and 5 of the phenanthrene moiety); mass spectrum *m/e* (% rel intensity) 322 (M^+) (0.6), 262 (0.8), 231 (2.2), 203 (3.1), 202 (3), 178 (100).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.7; H, 5.5.

***cis*-Dimethyl 1,2,2a,10b-Tetrahydrocyclobuta[*l*]phenanthrene-1,2-dicarboxylate.** A similar solution of benzophenone, phenanthrene, and dimethyl fumarate was irradiated as mentioned above for 90 hr. According to analysis, this solution contained the adducts C and T in the ratio 3.3:1. Extraction of the benzophenone with pentane followed by recrystallization from cyclohexane gave 0.63 g of practically pure *cis*-cyclobutane adduct (C): mp 114–115°; NMR ($CDCl_3$) δ 3.74 (s, $2(OCH_3)$), 3.44 and 4.16 (AA′BB′, $J_{AA'} \approx J_{BB'} \approx 9.6$, $J_{AB} = 6.3$, $J'_{AB} = -1.2$ Hz),[23] 7.0–7.4 (m, 6 H), 7.6–8.0 (m, 2 H at positions 4 and 5 of the phenanthrene moiety); mass spectrum *m/e* (% rel intensity) 322 (M^+) (1.4), 262 (1.7), 231 (4), 203 (4), 202 (4), 178 (100).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.6; H, 5.5.

Methyl 3-(2a,10b-Dihydro-2-methoxy-2*H*-phenanthro[9,10-*b*]oxet-2-yl)-2-propenoate. A 50-ml solution of phenanthrene (0.1 *M*) and dimethyl fumarate (0.1 *M*) in benzene containing 0.5% pyridine was irradiated with the filtered 3500 Å Rayonet photoreactor for 60 hr. The residue after distillation of the solvent was column chromatographed on basic Al_2O_3 deactivated by 5% water. After elution of the unreacted phenanthrene with cyclohexane, the oxetane X was eluted with a 1:4 mixture of benzene and cyclohexane. Recrystallization of the oxetane from cyclohexane gave 80 mg of colorless crystals: mp 144–146°; NMR ($CDCl_3$) δ 3.47 (s, OCH_3), 3.58 (s, OCH_3), 4.52 and 5.96 (AB, $J = 8$ Hz, β- and α-H of the oxetane ring, respectively), 5.77 and 6.42 (AB, $J = 15.4$ Hz, *trans*-CO_2—CH=CH); ir (KBr) 1720, 1300, 1280, 1165, 1150, 930, 905 cm^{-1}; the mass spectrum shows a weak molecular ion *m/e* 322 with the main cleavage to *m/e* 178 (phenanthrene$^+$).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.4; H, 5.4.

(*E*)-Methyl 4-Oxo-4-(9-phenanthryl)-2-butenoate. A similar solution of phenanthrene and dimethyl fumarate was irradiated as mentioned in the preceding experiment, 0.5 ml of concentrated hydrochloric acid was added, and the mixture was heated at 50° for 1 hr, neutralized with $NaHCO_3$, filtered, distilled, and the residue was chromatographed on silica gel. With 40% benzene–cyclohexane, the yellow zone of the ketone (K) was eluted. Recrystallization from cyclohexane gave 0.1 g of yellow needles: mp 105–107°; uv (cyclohexane) λ_{max} 334 nm (ϵ 7500) tailing to >400 nm (ϵ_{400} 200); ir (KBr) 1730, 1660, 1300, 1270 cm^{-1}; NMR ($CDCl_3$) δ 3.85 (s, OCH_3), 6.85 and 7.80 (AB, $J = 15.3$ Hz, *trans*-CO—CH=CH—COO), 8.11 (s, H at position 10 of the phenanthrene moiety); mass spectrum *m/e* (% rel intensity) 290 (M^+) (38), 275 (7.3), 273 (3.6), 231 (100), 205 (55), 203 (15), 202 (20), 177 (61), 176 (38), 151 (13), 150 (8), 129.5 (7), 129 (5), 115.5 (6), 102.5 (14), 101 (10), 88.5 (20), 88 (39).

Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.8; H, 4.7.

Irradiation of 15 mg of the *E* isomer of the ketone K in 1 ml of $CDCl_3$ for 5 min at 405 nm led to 70% isomerization to the *Z* isomer: NMR δ 3.45 (s, OMe), 6.37 and 7.17 (AB, $J = 11.2$ Hz, *cis*-CO—CH=CH—COO), 8.16 (s, H at position 10 of the phenanthrene moiety). Addition of 1 drop of 20% DCl in D_2O to the irradiated mixture led, within 1 hr, to $Z \rightarrow E$ reisomerization. In the gas chromatograph, the peak of the *Z* isomer appears at a lower retention time than that of the *E* isomer.

References and Notes

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(7) In a recent report [G. Kaupp, *Angew. Chem.*, **85**, 766 (1973)], it was implied that, in the photoreaction of phenanthrene and dimethyl fumarate, no acid-sensitive product (oxetane) was formed if direct excitation of the fumarate was avoided, and that the exciplex emission is due to impurities in the chemicals. This author proposed a mechanism involving nonstereospecific singlet biradicals to account for the cyclobutane formation rather than the exciplex mechanism proposed[3] earlier. We feel that the data given in the present paper and in that of Caldwell[5b] answer these points adequately and do not require further comment.

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(9) We observed similar exciplex emissions with λ_{max} at 500 and 530 nm

from chrysene (5×10^{-4} *M*) and pyrene (5×10^{-5} *M*) with dimethyl fumarate (0.1 *M*) in benzene. In other related studies of reactions of aromatic hydrocarbons with olefins, no new emission band was observed in the phenanthrene–*trans*-methyl cinnamate system even at high enough concentrations of the cinnamate to drastically suppress the phenanthrene fluorescence. An exciplex emission was observed, however, in the pyrene–*trans*-cinnamonitrile system in benzene.
(10) Exciplex emissions from the reaction of a number of aromatic hydrocarbons with fumaronitrile were recently reported [Y. Shirota, I. Tsushi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **47**, 991 (1974)].
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(12) For a discussion of the triplet energies of dienes, cf. R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).
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(14) At high diene concentrations, quenching of the singlet exciplex[5] is detectable. The decrease of the cyclobutane–oxetane ratio is, however, a measure for the triplet quenching as shown in eq 4 in the Kinetics section.
(15) The ratio of *T/C* from the triplet reaction[3,4] is 1.9. The amount of ($T - 1.9C$) will, therefore, give the amount of [T] formed via the stereospecific singlet pathway.
(16) On using F as a quencher for the benzophenone sensitized trans → cis isomerization of stilbene, it was found that the reaction constant for quenching benzophenone triplet (B^{*3}) by *F* is 0.45 times the reaction constant for energy transfer from B^{*3} to stilbene. The latter reaction constant is assumed to be equal to that of energy transfer from B^{*3} to P.
(17) The Stern–Volmer slope for the fluorescence quenching of phenanthrene with dimethyl fumarate in degassed benzene was 595 *l.* mol^{-1} and in aerated benzene was 144. From the reported lifetime of P^{*1} in degassed and aerated solutions,[18] values of 10^{10} and 8.5×10^{9} mol^{-1} sec^{-1} were obtained for k_4. Caldwell[4] reported a value of 7.5×10^{9} for this reaction constant.
(18) The reported lifetime of P^{*1} at room temperature in degassed cyclohexane and benzene ranges between 55 and 57 nsec [C. D. Amata, M. Burton, W. P. Helman, P. K. Ludwig, and S. A. Rodemeyer, *J. Chem. Phys.*, **48**, 2374 (1966); F. D. Lewis and J. C. Dalton, *J. Am. Chem. Soc.*, **91**, 5260 (1969); I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N.Y., 1965]. In aerated cyclohexane, a value of 17 nsec is reported (F. Wilkinson, "Fluorescence", G. G. Guilbault, Ed., Arnold Ltd., London, 1967). The reported quantum yield of Isc of P^{*1} is 0.76 [A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965)]; i.e. $(k_1 + k_2 + k_3) = 1.8 \times 10^{7}\ sec^{-1}$, and $k_3 = 1.37 \times 10^{7}\ sec^{-1}$.
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(20) Furthermore, in the present case, the quencher used (2,3-dimethylbutadiene) has a triplet energy only 2 kcal/mol lower than that of P and, if there is any interaction in the complex E^{*3} between P^{*3} and F, the difference in triplet energy between the quencher and the complex will be even smaller, which will result in a quenching rate below that of the upper limit. The quenching of a complex might also be slower than that of a molecular species owing to steric interaction.
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(23) The AA′BB′ spectrum indicates that the two carbomethoxy groups have cis configuration. The negative value of the 1,3-coupling constant (^4J) is consistent with the anti (or exo) structure [R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98**, 3854 (1965); C. H. Kranch, S. Farid, and G. O. Schenck, *ibid.*, **99**, 625 (1966); R. Mondelli and A. Gamba, *Org. Magn. Reson.*, **5**, 101 (1973)]. Caldwell[4] came to the same conclusion on the basis of ozonolysis experiments.

The SRN1 Mechanism in Heteroaromatic Nucleophilic Substitution. An Investigation of the Generality of Photostimulated Reactions of Ketone Enolates with 2-Chloroquinoline[1]

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Abstract: Secondary and tertiary lithium enolates, derived from a series of representative ketones, fail to react with 2-chloroquinoline (**1**) in liquid ammonia by the expected SRN1 mechanism when irradiated at 3500 Å. However, the corresponding potassium enolates react smoothly with **1** via this mechanism when subjected to photostimulation. With mixtures of primary and tertiary potassium enolates, quinolyl radicals, unlike phenyl radicals generated under similar conditions, show appreciable preference for combination with tertiary enolates. When **1** and iodobenzene are present in the same reaction mixture, potassioacetone reacts preferentially with the former under photostimulation. Potassio salts derived from β-dicarbonyl compounds do not undergo photostimulated SRN1 reaction with **1**, even when the potassium enolate of 2,4-dimethyl-3-pentanone is added to the reaction mixture as a potential entraining agent.

Recently, we presented evidence that the lithium salts of acetone and acetophenone react with 2-chloroquinoline (**1**) in liquid ammonia under near-ultraviolet irradiation to produce the appropriate α-(2-quinolyl) ketones via the radical-chain mechanism shown in Scheme I.[2] Photostimulation[3] apparently causes enhancement of the electron-transferring ability of the enolate ion, thereby permitting it to initiate the chain process by donating an electron to the heterocyclic substrate (step 1); steps 2–4 are propagating reactions. Similar reactions, designated by Bunnett[4] as SRN1, have been verified for reactions of carbanionic nucleophiles with aliphatic[5] and carboaromatic[4,6] systems containing appropriate nucleofugic groups. However, reports of related radical-chain pathways in heteroaromatic nucleophilic substitution are rare,[2,7] and photostimulation has not been generally recognized as a method for promoting such reactions.

Scheme I[a]

$$\mathrm{ClQ + RCOCH_2^- \longrightarrow ClQ\cdot^- + RCOCH_2\cdot} \qquad (1)$$

$$\mathrm{ClQ\cdot^- \longrightarrow Q\cdot + Cl^-} \qquad (2)$$

$$\mathrm{Q\cdot + RCOCH_2^- \longrightarrow QCH_2COR\cdot^-} \qquad (3)$$

$$\mathrm{QCH_2COR\cdot^- + ClQ \longrightarrow QCH_2COR + ClQ\cdot^-} \qquad (4)$$

[a] ClQ = 2-chloroquinoline

We now describe the results of a study undertaken to test the generality of photostimulated SRN1 reactions of **1** with secondary and tertiary ketone enolates, as well as with enolates derived from β-dicarbonyl compounds.