Triplet Sensitization and Exciplex Quenching of the Photochemical Reaction between Phenanthrene and Dimethyl Fumarate

**David Creed,[1a] Richard A. Caldwell,*[1b] and (in part) Mary McKenney Ulrich**

Contribution from the Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, and the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received December 12, 1977

Abstract: The benzophenone-sensitized photochemical reaction of phenanthrene (P) with dimethyl fumarate (F) or dimethyl maleate (M) affords isomeric cyclobutanes C and T together with isomerized olefin. Sensitized reaction of P with maleic anhydride affords the cis-exo cyclobutane adduct, CA. In contrast, direct irradiation of P and F affords the oxetane, X, isolated as the keto ester, K, in addition to C, T, and M. The high rate of quenching (1.35×10^9 M^{-1} s^{-1}) of phenanthrene triplet, P^3, by F coupled with the low probability of M formation as a consequence of this process is consistent with formation of a triplet exciplex, E^3, as the dominant, if not exclusive, quenching mechanism. Collapse of E^3 to C or T most likely involves the intermediacy of a triplet biradical. A short-lived, weakly emissive singlet exciplex, E^1, is observed when P fluorescence is quenched by F. This emissive exciplex can be quenched by electron donors such as 2,3-dimethylbut-2-ene or triethylamine. Exciplex quenching efficiencies correlate with the electron-donating ability of the quencher suggesting a charge transfer quenching mechanism. Self-quenching of E^1 by P is also observed. The identical Stern–Volmer slopes obtained for E^1 fluorescence quenching and X and M formation quenching show unequivocally that E^1 is a true reaction intermediate. Stern–Volmer plots for quenching of T and C formation are nonlinear and can be quantitatively related to the formation of the two cyclobutanes by two routes: one directly through E^1, the other via intersystem crossing of P^1 to P^3. Involvement of significant intersystem crossing in encounter exciplexes is ruled out by detailed consideration of the quantitative results.

The intermediacy of both singlet and triplet complexes and excimers has been suggested for a wide variety of photochemical reactions.[2] Excited-state quenching rates which correlate with donor or acceptor properties of the quencher,[3] "trapping" experiments,[4] negative temperature dependence[5] of quantum yields, and deuterium isotope effects[6] have all been used as indirect criteria for the intermediacy of excited-state complexes in photochemical reactions. In only a few singlet state reactions[4b,5d,7,8] is product formation accompanied by exciplex or excimer emission so that the role of the excited-state complex in product formation can be directly explored. One such system is the photocycloaddition of phenanthrene, P, to dimethyl fumarate, F, first studied by Farid et al.[7] We now report[9] indirect kinetic evidence for a triplet exciplex and direct kinetic proof, via exciplex quenching, of a singlet exciplex, as intermediates in the photocycloaddition of P to F.

Results and Discussion

Photoproduct Studies. The benzophenone-sensitized reaction of P with either F or dimethyl maleate, M, in benzene gives rise to two cyclobutane photoadducts, the cis-exo adduct, C, and the trans adduct, T. A constant ratio of T/C = 1.85 ± 0.05 was obtained at low conversions (≲1%) whether F or M was the initial reactant. Material balance was maintained (±3%) throughout, by comparison of P + C + T with initial P, and F + M + C + T with initial M or F, run after prolonged irradiation (eight times the time necessary for 90% conversion). Benzophenone-sensitized reaction of P with maleic anhydride[10] leads to the single cis-exo adduct CA. Structural assignments were made on the basis of the following physical and chemical evidence. Elemental analysis indicated that only 1:1 adducts were formed. Short-wavelength irradiation of C or T gives rise to the starting materials P and M or F, respectively. The NMR spectra of C exhibits a symmetrical A$_2$B$_2$ splitting pattern for the cyclobutane protons whereas that of T is much more complex (Experimental Section). C can be converted to T using sodium methoxide in dry methanol and CA can be converted to C with acidic methanol. Ozonolysis[11] of C followed by esterification with diazomethane afforded the known[12] *cis,trans,cis*-cyclobutane-1,2,3,4-tetracarboxylic acid tetramethyl ester, CB. The NMR of reaction mixtures show that
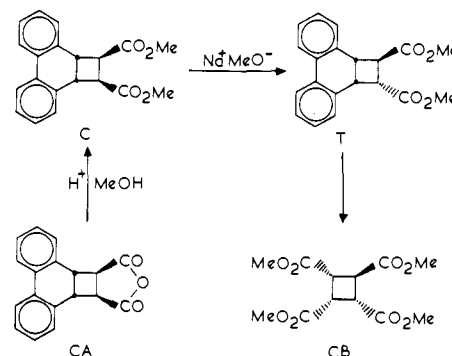
<5% of the cis-endo anhydride is formed in the reaction of P with MA. In the reaction with F or M the cis-endo isomer was absent (≲3%) by NMR and GLC analysis. The cis-endo isomer has been synthesized[13] for comparison purposes. Furthermore, the all-cis cyclobutane tetraester was absent (≲2%) in ozonized P + F or M reaction mixtures. Direct irradiation (λ >320 nm) of P + F in benzene followed by addition of methanol and acidification (HCl) afforded C, T, M, and the keto ester K. The latter had physical properties as previously described by Farid[7] and arises from acid-catalyzed rearrangement of the oxetane, X.
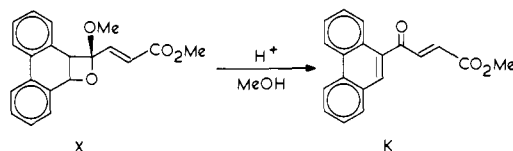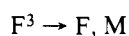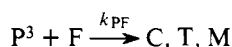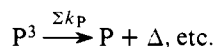

Mechanism of the Triplet-State Reaction between P and F. Quantum yield studies establish that the benzophenone-sensitized formation of C and T from P and F proceeds via the phenanthrene triplet, P^3, not the fumarate triplet, F^3, while M derives in part from each. We consider a partial kinetic scheme in which no assumptions need be made as to the precise mechanism of formation of C, T, or M from P^3 or F^3. Table I presents the quantum yields measured as a function of [P] and [F].

Table I. Concentration Dependence of ϕ_{C+T} and ϕ_M in the Benzophenone-Sensitized Reaction

ϕ_{C+T}	ϕ_M	[P]	[F]	$f_{P_3}{}^a$
	0.50	0	0.072, 0.111	0
0.0265	0.392	0.007 17	0.0857	0.218
0.0510	0.284	0.0265	0.113	0.438
0.0576	0.252	0.00717	0.0251	0.487
0.0700	0.256	0.0356	0.0936	0.559
0.072	0.25	0.0504	0.1003	0.626
0.081	0.22	0.1014	0.201	0.627
0.0851	0.166	0.0998	0.125	0.728
0.088	0.18	0.102	0.10	0.773
0.089	0.131	0.105	0.098	0.782
0.1035	0.145	0.2025	0.1037	0.867
0.104	0.091	0.2233	0.0310	0.960

^{a} Calculated as $f_{P_3} = [P]/([P] + 0.3[F])$ from rate constants given in text.

Scheme I

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO \; {}^1 \xrightarrow{\phi \, = \, 1.0} Ph_2CO^3$$

$$Ph_2CO^3 \xrightarrow{\Sigma k_B} Ph_2CO + \Delta, \text{ etc.}$$

$$Ph_2CO^3 + P \xrightarrow{k_{BP}} Ph_2CO + P^3$$

$$Ph_2CO^3 + F \xrightarrow{k_{BF}} Ph_2CO + F^3$$

$$P^3 \xrightarrow{\Sigma k_P} P + \Delta, \text{ etc.}$$

$$P^3 + F \xrightarrow{k_{PF}} C, T, M$$

$$F^3 \rightarrow F, M$$

$$P + F^3 \rightarrow C, T, M$$
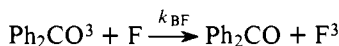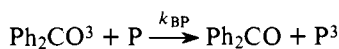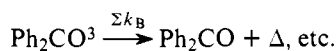
We assume that all Ph_2CO^3 are quenched by P or F, i.e., $\Sigma k_B \ll k_{BP}[P] + k_{BF}[F]$. The fractions of P^3 and F^3 formed, f_{P3} and f_{F3}, respectively, can be calculated knowing k_{BP}, k_{BF}, [P], and [F].

$$f_{P3} = \frac{k_{BP}[P]}{k_{BP}[P] + k_{BF}[F]} \quad (1)$$

$$f_{F3} = 1 - f_{P3}$$

Now $k_{BF} = 1.5 \times 10^9 \, M^{-1} \, s^{-1}$ [14] and we assume that quenching of Ph_2CO^3 ($E_T = 69 \, kcal \, mol^{-1}$) by P ($E_T = 62.0 \, kcal \, mol^{-1}$)[9a] is diffusion controlled, i.e., $k_{BP} \simeq 5 \times 10^9 \, M^{-1} \, s^{-1}$. Plots of total adduct quantum yields, ϕ_{C+T}, and M quantum yields, ϕ_M, vs. f_{P3} are linear (Figure 1), the intercepts giving ϕ_{C+T} and ϕ_M extrapolated to either 0% P^3 (100% F^3) or 100% P^3 (0% F^3). C + T formation occurs almost exclusively from P^3, since $\phi_{C+T}(P^3) = 0.111 \pm 0.013$, whereas $\phi_{C+T}(F^3) = 0.0067 \pm 0.0074$, i.e., essentially zero. M formation from F^3 has a quantum yield typical for a triplet excitation transfer mechanism, $\phi_M(F^3) = 0.483 \pm 0.022$, corresponding to F^3 formation via excitation energy transfer[15] from Ph_2CO^3. M formation from P^3 is much less quantum efficient, $\phi_M(P^3) = 0.076 \pm 0.008$, indicating that simple triplet excitation transfer from P^3 to F is not the dominant quenching mechanism. $\phi_M(F^3) = 0.50$ sets a lower limit for the decay fraction of $F^3 \rightarrow M$, and the upper limit for the fraction of F^3 formed from $P^3 + F$ must therefore be $\phi_M(P^3)/\phi_M(F^3) = 0.16$. We have determined the rate constant for quenching of P^3 by F using stilbene (S) as quencher of the benzophenone-sensitized formation of C and T from P and F.
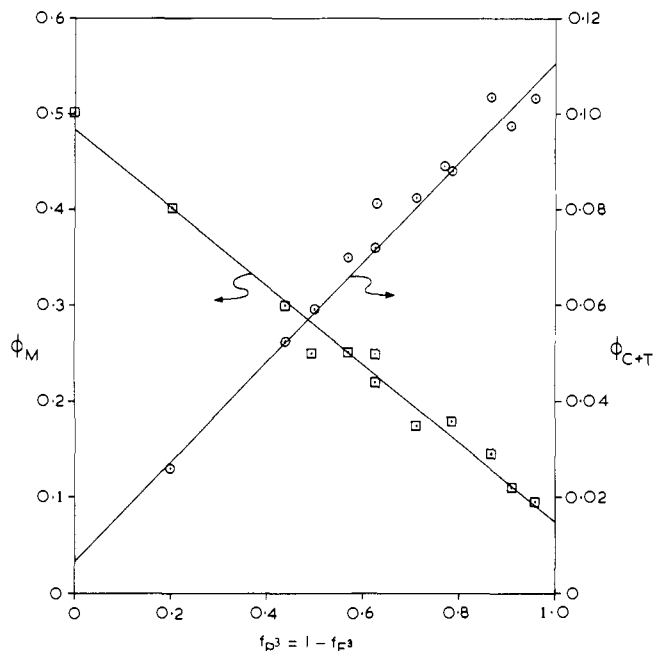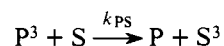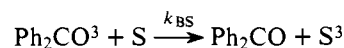

Figure 1. Quantum yields of C + T formation (⊙) and M formation (□) vs. fraction of phenanthrene triplet formed (f_{P3}) in the benzophenone-sensitized reaction of P and F in outgassed benzene.

Consider Scheme I with the addition of the following quenching steps:

$$Ph_2CO^3 + S \xrightarrow{k_{BS}} Ph_2CO + S^3$$

$$P^3 + S \xrightarrow{k_{PS}} P + S^3$$

In the absence of S:

$$\phi^{S=0}{}_{C+T} = \frac{k_{BP}[P]}{k_{BP}[P] + k_{BF}[F] + \Sigma k_B} \frac{k_{PF}[F]}{k_{PF}[F] + \Sigma k_p} \phi^0{}_{C+T} \quad (2)$$

where $\phi^0{}_{C+T}$ is the quantum yield of C + T formation extrapolated to 100% Ph_2CO^3 quenching by P (vide supra). We assume that unimolecular decay of Ph_2CO^3 and P^3 is negligible compared with quenching by P and F and F, respectively, i.e., $\Sigma k_B \ll k_{BP}[P] + k_{BF}[F]$ and $\Sigma k_p \ll k_{PF}[F]$. Equation 2 then reduces to

$$\phi^{S+0}{}_{C+T} = \phi^0{}_{P_3}\phi^0{}_{C+T} \quad (3)$$

where $\phi^0{}_{P_3}$ is the yield of P^3 from Ph_2CO^3. In the presence of S:

$$\phi^S{}_{C+T} = \frac{k_{BP}[P]}{k_{BP}[P] + k_{BF}[F] + k_{BS}[S]}$$
$$\times \frac{k_{PF}[F]}{k_{PF}[F] + k_{PS}[S]} \phi^0{}_{C+T} \quad (4)$$

$$= \phi_{P3} \frac{k_{PF}[F]}{k_{PF}[F] + k_{PS}[S]} \phi^0{}_{C+T} \quad (5)$$

and

$$\frac{\phi^{S=0}{}_{T+C}}{\phi^S{}_{T+C}} = \frac{\phi^0{}_{P3}}{\phi_{P3}}\left(1 + \frac{k_{PS}[S]}{k_{PF}[F]}\right) \quad (6)$$

We have determined $\phi^{S=0}{}_{T+C}/\phi^S{}_{T+C}$ as a function of [S]/[F] (Table II). Corresponding values of $\phi^0{}_{P3}/\phi_{P3}$ can be calculated from $k_{BF} = 1.5 \times 10^9 \, M^{-1} \, s^{-1}$ and assuming $k_{BP} = k_{BS} = 5 \times 10^9 \, M^{-1} \, s^{-1}$. A plot of $(\phi^{S=0}{}_{T+C}/\phi^S{}_{T+C})/(\phi^0{}_{P3}/\phi_{P3})$ vs. [S]/[F] is linear (Figure 2) with a slope $k_{PS}/k_{PF} = 3.7$. Thus

Table II. Dependence of ϕ_{T+C} and ϕ_M on *trans*-Stilbene [S] in the Benzophenone-Sensitized Reaction[a]

[S]	ϕ_{T+C}	ϕ_M	f_{P_3}[b]
0	0.095	0.111	0.902
0.0106	0.0356	0.0576	0.814
0.0215	0.0206	0.043	0.740
0.0424	0.0106	0.033	0.629

[a] Benzophenone = 0.059 M, [P] = 0.088 M, [F] = 0.0311 M, 365 nm in benzene. [b] f_{P_3} = [P]/([P] + [S] + 0.030[F]). See text.
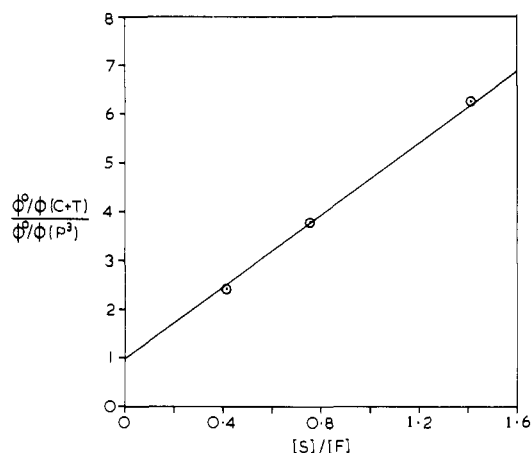

**Figure 2.** Quenching of C + T formation by *trans*-stilbene. See text for full explanation.

$k_{PF} = 1.35 \times 10^9$ M^{-1} s^{-1} follows from the assumption that $k_{PS} = 5 \times 10^9$ M^{-1} s^{-1}. We have recently measured[16] k_{PF} directly. P^3 was generated in benzene by pulse radiolysis[17] in the presence of varying [F]. From the pseudo-first-order decay of the 490-nm absorption of P^3 a value of $k_{PF} = 1.6 \pm 0.2 \times 10^9$ M^{-1} s^{-1} was obtained. This high quenching rate seems to indicate a "classical" triplet excitation transfer mechanism. However, the low value of $\phi_M(P^3)$, vide supra, excludes this possibility. Simple radical-like addition of P^3 to F is precluded by the magnitude of k_{PF}. We are forced to the conclusion that "nonclassical" quenching of P^3 + F, leading to a triplet exciplex, E^3, is the predominant, if not exclusive, quenching mechanism. We note that P^3 (E_T = 62 kcal mol^{-1})[9a] and F^3 (E_T = 61–67 kcal mol^{-1})[15a] are almost isoenergetic, P is a good electron donor, and F is a good electron acceptor.[18] Excitation resonance and charge-transfer interactions both may contribute to exciplex stabilization and both are expected to operate in this specific case. There is evidence for triplet exciplex formation in a number of quite different systems[5a,6,21] and emission from triplet excimers of aromatic hydrocarbons in fluid solution has been recently reported.[22]

Triplet State Reaction between P and M. The benzophenone-sensitized reaction of P and M leads within experimental error to the same T/C ratio as does the reaction of P and F. The interpretation of quantum yield data obtained with M is hampered, however, by lack of reproducibility. The relative yeilds of T, C, and F are constant for a constant P/M ratio but the absolute quantum yields vary. We have estimated the rate constant for the reaction of P^3 with M by an isoprene quenching experiment. At I/M = 0.12, the yield of C + T is diminished eightfold. We estimate, assuming that the rate constant for ^{3}P quenching by I is 5×10^9 M^{-1} s^{-1}, that the rate constant for ^{3}P quenching by M is about 8×10^7 M^{-1}s^{-1}, i.e., some 20-fold lower than quenching of ^{3}P by F, and well within the range where trace amounts of adventitious triplet quencher(s) can cause irreproducibility. The highest quantum yields obtained from M in a benzophenone-sensitized experi-

ment were ϕ_F = 0.36 and ϕ_{T+C} = 0.053 at [P] = 0.053 and [M] = 0.076. Under these conditions <5% of the ^{3}B should have been quenched by M. This experiment corresponds closely to the f_{P3} = 1.0 condition attained by extrapolation of the P + F data. The quantum yield of ^{3}P + M → C + T is, however, much lower than that of ^{3}P + F → C + T. This effect could be due to adventitious quencher that is not separated from M on preparative gas chromatography, or to a component of ^{3}P + M → P + M + heat, or a combination of both effects. We favor the first possibility in view of the lack of reproducibility of absolute quantum yields.

Relative Rates of Quenching of ^{3}P by F and M. That the rate constant for quenching of ^{3}P by F is much greater than that for quenching of ^{3}P by M may be due to one of two factors. First, the triplet excitation energy of F (61–67 kcal/mol) is much lower than that of M (72–77 kcal/mol) and is thus a much better match for that of P. Second, the cis ester groups presumably make planarity of M difficult or impossible; should a "sandwich" triplet exciplex intervene, approach of the π system of M to ^{3}P will be sterically hindered. An alternative argument, that the exciplex is largely stabilized by charge transfer from P to F (or M), does not explain the relative rates since[23] M is apparently reduced at a potential slightly less cathodic than is F. We conclude that, if CT is important in stabilizing these exciplexes, there is probably a significant and counterbalancing effect of steric hindrance in the case of M to approach of the π systems. Effects of increased crowding on the properties of exciplexes have also been previously noted.[8a,24] The dilemma of whether CT or ER dominates stabilization of these exciplexes thus still is not resolved.

Role of a Triplet Biradical in the Formation of T and C. The constant ratio of T to C (1.85 ± 0.05) at low conversion ($\simeq 1\%$) in all our experiments, independent of whether F or M was initially the reactant, indicates a triplet 1,4-biradical, formed via a triplet exciplex, as the immediate precursor of C and T. Analogous biradicals have been suggested in other triplet-state photocycloadditions.[25] Two stereoisomeric biradicals, SR and SS, are possible (in the original communication[9a] SS was incorrectly assigned the SR structure and vice versa). Both C and

SS   SR
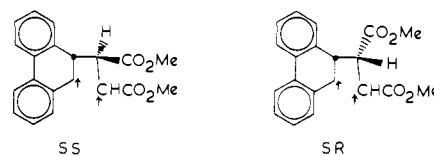
T can be formed from SS but SR would give both T and the isomeric cis-endo diester. Since the latter is never observed, either SR is formed and reverts to P + F via β-scission, or both M and F give the same ratio of SS to SR (with SR collapsing *only* to T or starting materials) or, most economically, the triplet exciplex affords SS exclusively and is the sole biradical precursor of C and T.

The ratio of F to T + C from P^3 + M is 0.36/0.053 = 6.8 (vide supra). If we assume that this ratio is due only to SS decay and that SS decays only to F, M, T, and C then ϕ_{C+T} = 0.111 from P^3 + F implies ϕ_F = 0.754. Experimentally ϕ_M = 0.076 $\pm$ 0.008 from P^3 + F. We therefore believe that the fraction of SS formed from P^3 + F by decay of the triplet exciplex is at least 0.111 + 0.754 + 0.076 = 0.94. The value of ϕ_{C+T} = 0.053 from P^3 + M may truly reflect a lower efficiency ($\simeq 48\%$) of SS formation but, as we have discussed earlier, it seems more likely to be due to experimental difficulties in obtaining absolute quantum yields in experiments utilizing M.

Mechanism of the Direct Reaction. Farid and his co-workers[7] have carried out a detailed and very elegant study of the mechanism of the direct photocycloaddition of P + F. Their key conclusions, based mainly on [F] dependence and triplet
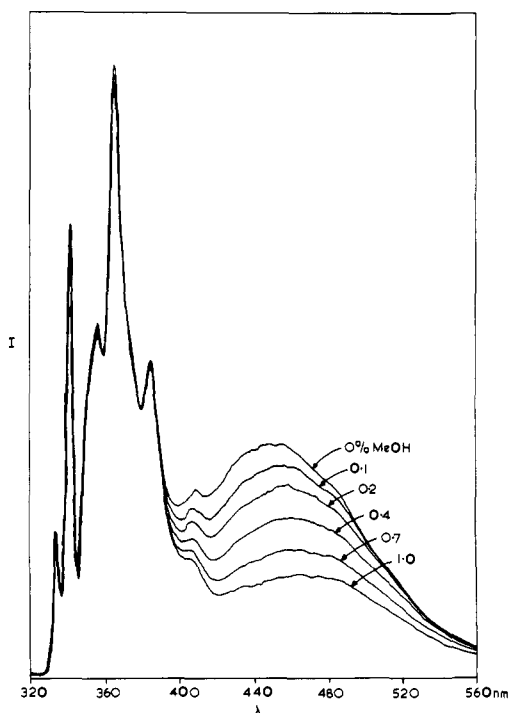
Figure 3. E^1 and residual P^1 fluorescence at $[P] = 10^{-2}$ M, $[F] = 0.2$ M in air-saturated benzene and benzene-methanol mixtures (% by volume of methanol indicated).

Figure 4. Quenching of E^1 by 2,3-dimethylbut-2-ene in air-saturated benzene at $[P] = 8 \times 10^{-3}$ M, $[F] = 0.1$ M. Inset: Stern-Volmer quenching plot.

quenching studies, were that (1) X and a fraction of T arise directly from an emissive singlet exciplex, E^1, observed when P fluorescence is quenched by F; (2) C and the major fraction of T arise from a triplet exciplex, E^3, formed either via isc from E^1 or via F quenching of P^3. The origin of M was not discussed. Our data for C + T formation via triplet sensitization are entirely consistent with Farid's and provide complementary evidence for the role of E^3. Our data further indicate that M derives at least in part from E^3. Kaupp[26] has, however, questioned the intermediacy of E^1 in the reaction and suggested an alternative singlet biradical pathway. The data of both Farid[7] and Kaupp[26] leave no doubt that quenching of P^1 is of crucial importance in the P + F reaction. The mere observation[7] of an emissive exciplex does not prove its intermediacy in the formation of the observed photoproducts. The exciplex could be located on a path *parallel* to the paths leading to any or all of C, T, X, or M, especially when one considers that the major process resulting from P^1 quenching by F is radiationless deactivation to P + F ($\phi_D = 0.922$).[7]

We find that P fluorescence in benzene is quenched by F ($k_{E1M}\tau_{P1} = 430$ M^{-1}). The lifetime of P^1 is 60 ns, and consequently $k_{E1M} = 7.2 \times 10^9$ M^{-1} s^{-1}, i.e., essentially diffusion controlled. A weakly emissive exciplex (λ_{max} 480 ± 5 nm, $\phi^{E1}_F \simeq 3 \times 10^{-3}$) can be observed (Figure 3) at high $[F]$. The exciplex fluorescence in benzene is slightly quenched by air saturation. At $[F] = 0.25$ M and $[P] = 10^{-3}$ M in benzene $\phi_F{}^{argon}/\phi_F{}^{air} = 1 + k^{O_2}{}_Q\tau_{E1}[O_2] = 1.049 \pm 0.010$. We have carried out several argon-saturated vs. air-saturated exciplex fluorescence quenching experiments on exciplexes whose lifetimes are sufficiently long ($\tau \gtrsim 5$ ns) for direct measurement by nanosecond flash spectroscopy. From these data a reasonably constant value of $k^{O_2}{}_Q[O_2] = 4.2 \times 10^7$ s^{-1} is obtained for O_2 quenching of exciplexes in air-saturated benzene,[27] and, when inserted into the Stern-Volmer expression above, leads to an estimated lifetime of E^1, τ_{E1}, of 1.2 ns. The exciplex λ_{max} shifts to the red and is diminished in intensity[28] on addition of up to 1% by volume of methanol (Figure 3). The exciplex is thus at least partly stabilized by charge-transfer (CT) interaction and we reasoned that it ought to be suscep-
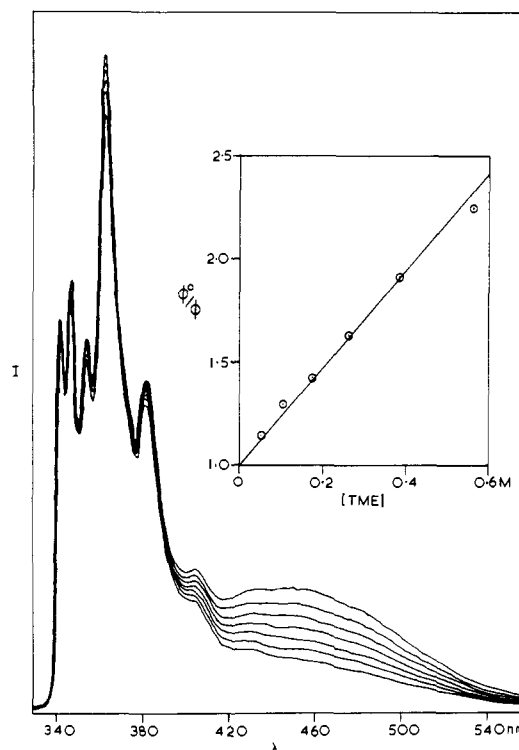
tible to further CT perturbation. We find that electron donors which are inefficient quenchers of P fluorescence are capable of quenching the exciplex. For example, 2,3-dimethylbut-2-ene (tetramethylethylene, TME) quenches ($k_{QT} = 2.5$ M^{-1}) E^1 fluorescence (Figure 4) but not P^1 fluorescence ($k_{QT} \lesssim 0.10$ M^{-1}). The small effect of the quencher on residual P^1 fluorescence in the P + F system (Figure 4) is almost certainly due to incident light absorption by a weak ground-state complex between F and TME. The complex was studied only in the wavelength range 310–350 nm, i.e., the range of exciting light used, and under these conditions the absorbance is proportional within experimental error to $[F][TME]$, as expected if K_{eq} is small. Benesi–Hildebrand plots[29] lead to an estimate of $K_{eq} \lesssim 0.05$ M^{-1} for the formation of the F···TME ground-state complex. Thus at the maximum [TME] used (0.39 M) in the E^1 + TME experiment (Figure 4) the [F···TME] $\lesssim 0.002$ M, $\lesssim 2$% of the F, and $\lesssim 0.5$% of the TME are bound in the ground-state complex. We note that P^1 fluorescence is quenched at the diffusion-controlled rate (9.2×10^9 M^{-1} s^{-1}) by fumaronitrile in benzene[30] *despite* the fact[31] that a large fraction (~50% at $[FN] = 0.01$ M) of the nitrile is present as a weak ground-state CT complex ($K_{eq} = 0.16$ M^{-1}) with the solvent (benzene). The perturbation of the electronic structure of the components in "weak" ground-state complexes may be insufficient to affect their interaction with a much better reducing (such as P^1) or oxidizing agent. In any event it seems clear that in these systems ground-state complexation is irrelevant to exciplex quenching.

A referee has suggested that we consider the role of a P–F ground state complex as an intermediate in the cycloaddition. While it is difficult to eliminate the possibility that a small amount of the reaction occurs via a ground-state complex, we believe that diffusive quenching surely dominates. Dr. W. S. Burnham in these laboratories has measured the association constant of P with the excellent electron acceptor dichloromaleic anhydride, by the customary Benesi–Hildebrand technique, as 0.3 M^{-1}. We believe that this is the maximum

Table III. Stern–Volmer Slopes for Quenching of ^1E Fluorescence by Tetramethylethylene in Aerated Benzene

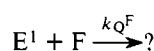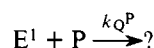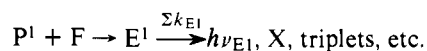| [P]	[F]	$k_Q\tau$(fluorescence), M^{-1}
4.02×10^{-3}	0.051	2.44
4.02×10^{-3}	0.204	2.35
8.0×10^{-3}	0.10	2.36
2.01×10^{-2}	0.051	2.4
4.02×10^{-2}	0.051	2.0
4.0×10^{-2}	0.10	2.06
4.02×10^{-2}	0.204	1.9
4.02×10^{-2}	0.408	1.9
8.0×10^{-2}		1.8
1.2×10^{-1}	0.10	1.5

Table IV. Stern–Volmer Slopes for Quenching of Exciplex Fluorescence, X and M Formation,[a,b] and Phenanthrene Fluorescence by Electron Donors

quencher	IP,[c]eV	$k_{ET}{}^Q\tau_{E1}$, M^{-1} [b,g]	$k_{P1}{}^Q\tau_{P1}$, M^{-1} [k]
2-methylbut-2-ene	8.89	<0.1	<0.04
ethyl vinyl ether	8.49[d]	0.7	≈0.04
2,3-dimethylbut-2-ene	8.30	2.5[h] (2.3)[i]	≈0.10
dihydropyran	8.34	3.9 (4.2)	<0.04
phenanthrene	7.86[e]	5.4[h,j]	
trans-anethole	7.68[f]	9.8	0.10
triethylamine	7.50	9.7[i] (9.3)[i]	0.35

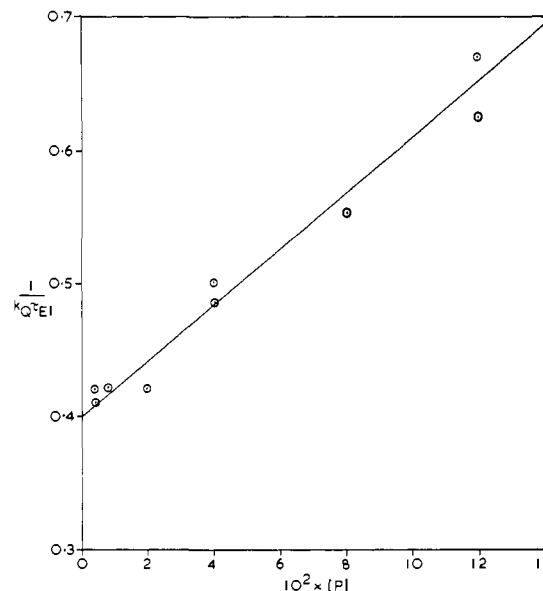[a] [P] = 8×10^{-3} M, [F] = 0.10 M, in benzene. [b] Numbers in parentheses are for quenching of X, M formation. [c] Vertical IPs from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Fraxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969). [d] M. P. Niemczyk, N. E. Schore, and N. J. Turro, *Mol. Photochem.*, **5**, 69 (1973). [e] Reference 19. [f] R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, **96**, 2994 (1974). [g] ±5%, air-saturated benzene. [h] Extrapolated to [P] = 0. [i] Outgassed benzene. Air-saturated values are the same within experimental error. [j] ±10%. [k] Air-saturated benzene; for outgassed values multiply by τ_{P1}/τ_{P1}(air) = 3.20.

value that could be expected for a P–F complex; at the highest concentrations we have studied, a complex with an 0.3 M^{-1} formation constant would comprise only some 5% of the total phenanthrene. There is no spectroscopic evidence to support a P–F complex in any case; the near-UV spectrum of phenanthrene ($\lambda > 320$ nm) is not affected by F up to 0.07 M or M up to 0.14 M. The concentration of such a complex would be proportional to the product of [P] and [F]; for the results in Table I and Figure 1, the product varies about two orders of magnitude, with no data anomalous vis-a-vis our diffusive treatment.

The Stern–Volmer slope ($k_Q{}^{TME}\tau_{E1}$) for E^1 quenching by TME is sensitive to [P] but relatively insensitive to [F] (Table III). The [P] dependence is attributed to quenching[32] of E^1 by P. The ionization potential (IP) of P falls[19] within the same range as IPs of good quenchers of E^1 (Table IV). Assuming essentially irreversible exciplex formation and quenching we have the following partial kinetic scheme for exciplex quenching:

$$P^1 + F \xrightarrow{\Sigma k_{E1}} E^1 \longrightarrow h\nu_{E1}, X, \text{ triplets, etc.}$$

$$E^1 + TME \xrightarrow{k_Q{}^{TME}} ?$$

$$E^1 + P \xrightarrow{k_Q{}^P} ?$$

$$E^1 + F \xrightarrow{k_Q{}^F} ?$$

from which at a fixed [P], [F] but variable [TME]

Figure 5. Reciprocal Stern–Volmer slopes ($1/k_Q\tau$) for E^1 quenching by 2,3-dimethylbut-2-ene vs. [P] in air-saturated benzene.

$$k_Q{}^{TME}\tau_{E1} = \frac{k_Q{}^{TME}}{\Sigma k_{E1} + k_Q{}^P[P] + k_Q{}^F[F]} \quad (7)$$

whence for a fixed [F]

$$\frac{1}{k_Q{}^{TME}\tau_{E1}} = \frac{1}{k_Q{}^{TME}\tau^0_{E1}} + \frac{k_Q{}^P[P]}{k_Q{}^{TME}} \quad (8)$$

where τ^0_{E1} is the lifetime of E^1 at [P] = 0 at a fixed [F]. A plot of $1/k_Q\tau_{E1}$ for E^1 quenching by TME vs. [P] at [F] = 0.1 M is linear, as expected (Figure 5), with a slope of 2.15. Thus

Table V. Relative Direct Irradiation Quantum Yields at 347 nm for T, C, and X Formation, as a Function of Triethylamine Concentration, Corrected[a] for Absorption by the Triethylamine-Dimethyl Fumarate Ground-State Complex

[Et$_3$N], M	factor[a]	$\phi_T{}^0/\phi_T$	$\phi_C{}^0/\phi_C$	$\phi_X{}^0/\phi_X$
0	1.00	1.00	1.00	1.00
0.0239	1.01	1.24	1.09	1.23
0.0479	1.02	1.39	1.50	1.40
0.0958	1.04	1.64	1.46	1.74
0.1676	1.07	2.03	1.83	2.53
0.359	1.15	3.30	3.27	4.32
0.599	1.25	4.22	3.29	5.84
0.958	1.41	4.66	3.78	8.12

[a] Factor = OD(P)/[OD(P) + OD(complex)], where OD(complex) was determined from absorption spectra of benzene solutions containing appropriate concentrations of F and Et$_3$N. Reported ϕ^0/ϕ values were obtained from raw data by division of ϕ^0/ϕ (raw) by the factor.

Table VI. Corrected[a] Relative Direct Irradiation Quantum Yields at 347 nm for M formation as a Function of Triethylamine

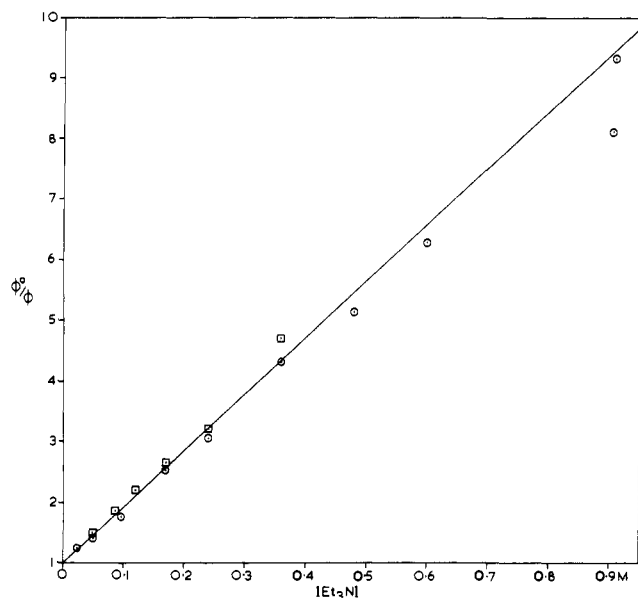| [Et$_3$N], M	factor[a]	$\phi_M{}^0/\phi_M$
0	1.00	1.00
0.0239	1.01	1.24
0.0479	1.03	1.52
0.0838	1.055	1.86
0.1197	1.08	2.22
0.1676	1.13	2.67
0.2394	1.16	3.22
0.3591	1.24	4.71

[a] See note to Table V.

Figure 6. Stern–Volmer plot for quenching of X (K) formation (○) and M formation (□) by triethylamine in outgassed benzene. ([P] = 8 × 10⁻³ M, [F] = 0.1 M).

Figure 7. Stern–Volmer plot for quenching of T (○) and C (□) formation by triethylamine in outgassed benzene. ([P] = 8 × 10⁻³ M, [F] = 0.1 M). Straight line is plot for E^1 fluorescence quenching. Calculated curves for T and C quenching are indicated.

$k_Q^P \tau_{E1} = 2.15 k_Q^{TME} \tau_{E1} = 5.4$ M⁻¹. Quenching slopes for E^1 + TME are insensitive to [F] over the range [F] = 0.05–0.20 M leading to an estimation of $k_0^F \tau_{E1} \lesssim 0.05$ M⁻¹. This observation also supports our contention that ground-state F···Q complexes are irrelevant in these systems to quenching of E^1 by Q. Quenching of E^1 with dimethyl acetylenedicarboxylate was similarly inefficient ($k_Q \tau \lesssim 0.1$ M⁻¹). Data for quenching of both E^1 and P^1 by several electron donors are summarized in Table I. Using absorption spectroscopy we estimate[29] K_{eq} < 0.05 for the ground-state CT complexes between F and TME (IP = 8.30 eV), dihydropyran (IP = 8.34 eV), and triethylamine (IP = 7.50 eV). The dependence of donor quenching rates on IPs of the quenchers suggests that exciplex quenching occurs by a charge-transfer process.[34] Experiments with several other emissive complexes and the pyrene excimer confirm this conclusion and a frontier molecular orbital approach can be used for order of magnitude predictions of rates of donor quenching of any exciplex.[35] A more detailed discussion of exciplex quenching will be presented in a separate full paper.

Our observation of E^1 but insignificant P^1 quenching by electron donors enables the role of E^1 in the observed reactions to be explored in detail. Quenching of E^1 fluorescence is accompanied by quenching of *all* of the observed photoproducts (Tables V and VI). Stern–Volmer plots for quenching of E^1 fluorescence, and X and M formation by triethylamine, for example, are linear (Figure 6) and within experimental error have the same slopes. The Stern–Volmer slope for quenching of P^1 by Et₃N ($k_Q \tau = 1.05$) is about 400 times less than for quenching of P^1 by F. Thus at [F] = 0.1 M and [Et₃N] = 1.0 M, only 2.5% of P^1 is quenched by Et₃N. Using our estimate of $K_{eq} \lesssim 0.05$ for the Et₃N···F ground-state CT complex, ≲4.5% of F and ≲0.45% of the Et₃N are present as the complex at [F] = 0.1 M, [Et₃N] = 1.0 M.

The linearity of the Stern–Volmer plots leaves no doubt that X and M derive from E^1. However, plots for quenching of T and C formation deviate markedly from linearity (Figure 7) at high quencher (Q) concentrations. This observation is consistent with multiple pathways to T and C. The fraction of T and C formed via E^1, either stereospecifically in the case of a small fraction of T, or via $E^1 \rightarrow E^3$ for a fraction of T and all of C, is quenchable by quenchers of E^1. The fraction of T and C which derives from
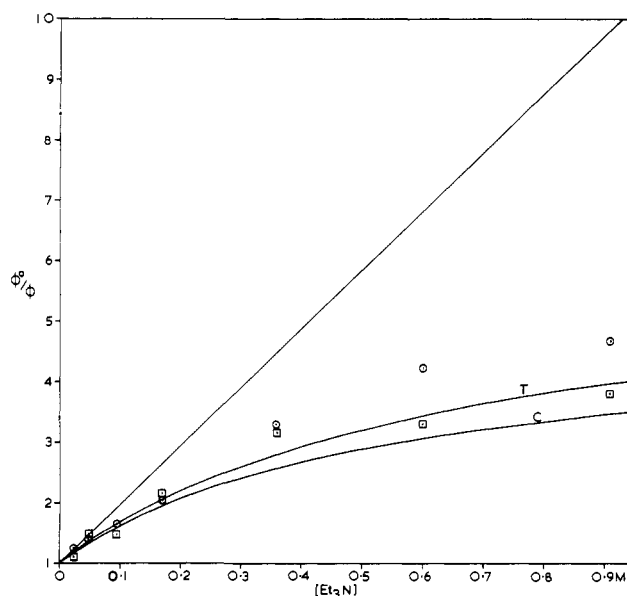
$$P^1 \rightarrow P^3 \xrightarrow{F} E^3$$
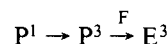
is not quenchable by quenchers of E^1 and accounts for the curvature of Stern–Volmer plots for T and C quenching.

The formation and quenching of all four photoproducts X, T, C, and M, can be dealt with more quantitatively. As a starting point let us consider Farid's kinetic analysis[7] (Scheme

Scheme II
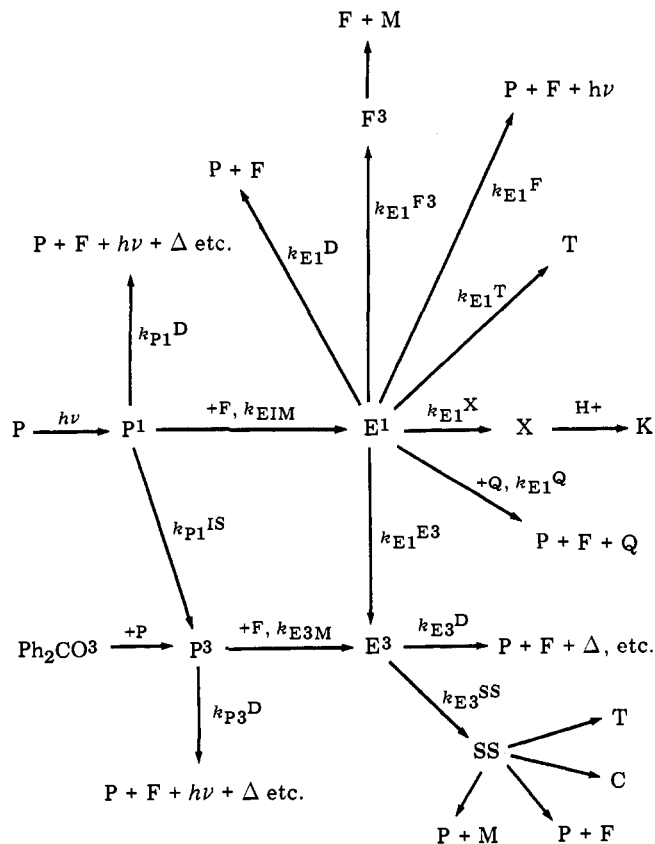
II) with the addition of pathways for M formation from E^1 and E^3, decay of the biradical SS to C with probability β and T with probability 1.85β, and exciplex quenching by Q. We assume irreversible E^1 formation,[33] irreversible E^1 quenching, and negligible quenching of P^3 and E^3 by Q. Steady-state expressions for the quantum yields of X, T, C, and M formation, ϕ^X, ϕ^T, ϕ^C, and ϕ^M, respectively, can be derived in the usual manner. For X formation in the absence of Q:

$$\phi^{0X} = \frac{k_{E1M}}{\Sigma k_{P1} + k_{E1M}[F]} \frac{k_{E1}{}^X}{\Sigma k_{E1}} = f_{E1}\frac{k_{E1}{}^X}{\Sigma k_{E1}} \qquad (9)$$

where f_{E1} is the fraction of P^1 quenched by F to give E^1. We assume that every fluorescence quenching event produces a singlet exciplex. Σk_{P1} and Σk_{E1} are summations of all the unimolecular decay rate constants for P^1 and E^1, respectively. For X formation in the presence of Q:

$$\phi^X = f_{E1}\frac{k_{E1}{}^X}{\Sigma k_{E1} + k_{E1}{}^Q[Q]} \qquad (10)$$

$$\frac{\phi^{0X}}{\phi^X} = 1 + \frac{k_{E1}{}^Q}{\Sigma k_{E1}}[Q] = 1 + k_{E1}{}^Q\tau_{E1}[Q] \qquad (11)$$

Equation 11 is the usual Stern–Volmer expression for a single quenchable intermediate, in this case E^1.

A much more complex relationship holds for ϕ^T since T arises via three pathways: stereospecific collapse of E^1, via isc of the singlet exciplex ($E^1 \rightarrow E^3 \rightarrow SS \rightarrow T$), and via isc of phenanthrene singlet ($P^1 \rightarrow P^3 \rightarrow E^3 \rightarrow SS \rightarrow T$). Thus

$$\phi^{0T} = f_{E1}\frac{k_{E1}{}^T}{\Sigma k_{E1}} + \frac{k_{E1}{}^{E3}}{\Sigma k_{E1}}\frac{k_{E3}{}^{SS}}{\Sigma k_{E3}}1.85\beta$$
$$+ \frac{k_{P1}{}^{1S}}{\Sigma k_{P1} + k_{E1M}[F]} \frac{k_{E3M}}{\Sigma k_{P3} + k_{E3M}[F]} \frac{k_{E3}{}^{SS}}{\Sigma k_{E3}}1.85\beta \qquad (12)$$

$$\phi^{0T} = \frac{f_{E1}}{\Sigma k_{E1}}(k_{E1}{}^T + k_{E1}{}^{E3}\phi_{E3}{}^T) + f_{P3}f_{E3}\phi_{E3}{}^T \qquad (13)$$

where f_{P3} is the probability of intersystem crossing (isc) of P^1 to P^3 and f_{E3} is the probability of E^3 formation from P^3. Under our experimental conditions (Figures 6, 7), [F] = 0.10 M and $k_{E3M}[F] = 1.35 \times 10^8$ s^{-1}. Since $\Sigma k_{P3} < 1.4 \times 10^5$ s^{-1} in benzene,[36] negligible in comparison with $k_{E3M}[F]$, then $f_{E3} \simeq 1.0$. $\phi_{E3}{}^T = (k_{E3}/^{SS}\Sigma k_{E3})1.85\beta$ is the probability of E^3 giving T which is equated with the quantum yield of T formation, $\phi_{E3}{}^T$, in the Ph$_2$CO sensitized experiments. As with P^1 quenching each P^3 quenched by F is assumed to give an E^3. For T formation in the presence of Q

$$\phi^T = \frac{f_{E1}}{\Sigma k_{E1} + k_{E1}{}^Q[Q]}(k_{E1} + k_{E1}\phi_{E3}{}^T) + f_{P3}\phi_{E3}{}^T \qquad (14)$$

leads to the "complex" Stern–Volmer relationship:

$$\frac{\phi^{0T}}{\phi^T} =$$
$$\frac{\{f_{E1}(k_{E1}{}^T + k_{E1}{}^{E3}\phi_{E3}{}^T) + f_{P3}\phi_{E3}{}^T\Sigma k_{E1}\}\{\Sigma k_{E1} + k_{E1}{}^Q[Q]\}}{\Sigma k_{E1}\{f_{E1}(k_{E1}{}^T + k_{E1}{}^{E3}\phi_{E3}) + f_{P3}\phi_{E3}{}^T(\Sigma k_{E1} + k_{E1}{}^Q[Q])\}}$$
$$(15)$$

An expression for quenching of C formation by Q can be obtained in a like manner:

$$\phi^{0C} = \frac{f_{E1}}{\Sigma k_{E1}}k_{E1}{}^{E3}\phi_{E3}{}^C + f_{P3}\phi_{E3}{}^C \qquad (16)$$

in the presence of Q:

$$\phi^C = \frac{f_{E1}}{\Sigma k_{E1} + k_{E1}{}^Q[Q]}k_{E1}{}^{E3}\phi_{E3}{}^C + f_{P3}\phi_{E3}{}^C \qquad (17)$$

$$\frac{\phi^{0C}}{\phi^C} = \frac{\{f_{E1}{}^{E3}k_{E1}{}^C\phi_{E3} + \Sigma k_{E1}f_{P3}\phi_{E3}{}^C\}\{\Sigma k_{E1}{}^Q + k_{E1}{}^Q[Q]\}}{\Sigma k_{E1}\{f_{E1}k^{E3}\phi_{E3}{}^C + f_{P3}\phi_{E3}{}^C(\Sigma k_{E1} + k_{E1}{}^Q[Q])\}}$$
$$(18)$$

where $\phi_{E3}{}^C$ is the probability of E^3 collapsing to C, or the quantum yield of C formation from P^3 in the Ph$_2$CO-sensitized experiments.

Formation of M from E^1 is assumed to occur via isc to F^3 which has a 50% probability[15] of collapsing to M. $\phi_{E3}{}^M$ is the probability of M formation from E^3, either via F^3 or the biradical SS. It is the quantum yield of M formation from P^3 in the Ph$_2$CO-sensitized experiments. These assumptions lead to:

$$\phi^{0M} = \frac{f_{E1}}{\Sigma k_{E1}}(k_{E1}{}^{F3} \times 0.5 + k_{E1}{}^{E3}\phi_{E3}{}^M) + f_{P3}\phi_{E3}{}^M \qquad (19)$$

in the presence of Q:

$$\phi^M = \frac{f_{E1}}{\Sigma k_{E1} + k_{E1}{}^Q[Q]}(k_{E1}{}^{F3} \times 0.5$$
$$+ k_{E1}{}^{E3}\phi_{E3}{}^M + f_{P3}\phi_{E3}{}^M \qquad (20)$$

$$\frac{\phi^{0M}}{\phi^M} =$$
$$\frac{\{f_{E1}(k_{E1}{}^{F3} \times 0.5 + k_{E1}{}^{E3}\phi_{E3}{}^M + \Sigma k_{E1}f_{P3}\phi_{E3}{}^M\}}{\Sigma k_{E1}\{f_{E1}(k_{E1}{}^{F3} \times 0.5} \quad \genfrac{}{}{0pt}{}{\times \{\Sigma k_{E1} + k_{E1}{}^Q[Q]\}}{}$$
$$\frac{}{+ k_{E1}{}^{F3}\phi_{E3}{}^M) + f_{P3}\phi_{E3}{}^M(\Sigma k_{E1} + k_{E1}{}^Q[Q])\}}$$
$$(21)$$

In order to test the suggested mechanism we have fitted the experimental quenching data for T, C, and M quenching to expressions 15, 18, 21. It was first necessary to obtain all the unknown parameters. The E^1 fluorescence quenching experiments afford $k_{E1}{}^Q = 8.1 \times 10^9$ M^{-1} s^{-1} for quenching by Et$_3$N. The air quenching experiment gives $\tau_{E1} = 1/\Sigma k_{E1} = 1.2 \times 10^{-9}$ s^{-1}. Probabilities of E^3 decay to T, C, and M have been equated with quantum yields of the Ph$_2$CO-sensitized reaction: $\phi_{E3}{}^T = 0.0721 \pm 0.008$, $\phi_{E3}{}^C = 0.0389 \pm 0.005$, and $\phi_{E3}{}^M = 0.0760 \pm 0.008$. The probability f_{P3} of isc of P^1 to P^3 at any [F] is obtained[7,9] from $k_{P1}{}^{1S} = 1.32 \times 10^7$ s^{-1}, $\Sigma k_{P1} = 1.75 \times 10^7$ s^{-1}, and $k_{E1M} = 7.5 \times 10^9$ M^{-1} s^{-1}. Quantum yields of X (K), T, C, and M formation have been measured, in the direct reaction, as a function of [F] at [F] > 0.05 M and are plotted (Figure 8) against $f_{P1} = 1 - f_{E1} = \phi^F/\phi^{0F}$, the fraction of P^1 fluorescence not quenched by F. At $f_{P1} = 0$, the "pure exciplex" condition, $\phi_S{}^X = 0.0274 \pm 0.0010$, $\phi_S{}^T = 0.006\,20 \pm 0.0003$, $\phi_S{}^C = 0.002\,57 \pm 0.0001$, and $\phi_S{}^M = 0.0472 \pm 0.00012$. At $f_{P1} = 0$ T derives both stereospecifically from E^1, with $\phi_{E1}{}^T$, and via isc of $E^1 \rightarrow E^3$, with $\phi^T_{E1\rightarrow E3}$, i.e., $\phi_S{}^T = \phi_{E1}{}^T + \phi^T_{E1\rightarrow E3}$. However, C derives only via isc of $E^1 \rightarrow E^3$, $\phi_S{}^C = \phi^C_{E1\rightarrow E3}$, but from the Ph$_2$CO-sensitized experiments decay of E^3 affords T/C = 1.85 ± 0.05. Hence $1.85\phi^C_{E1\rightarrow E3} = \phi^T_{E1\rightarrow E3} = 0.004\,75 \pm 0.0004$ and $\phi_{E1}{}^T = \phi_S{}^T - \phi^T_{E1\rightarrow E3} = 0.001\,45 \pm 0.0005$. For 100% E^3 formation by Ph$_2$CO sensitization, $\phi_{E3}{}^T + \phi_{E3}{}^C = 0.111 \pm 0.011$. Hence $\phi^T_{E1\rightarrow E3} + \phi^C_{E1\rightarrow E3} = 0.007\,32 \pm 0.0004$ implies that the quantum yield of isc of E^1 to E^3, $\phi_{E1}{}^{E3} = (\phi^T_{E1\rightarrow E3} + \phi^C_{E1\rightarrow E3})/0.111 = 0.0654 \pm 0.013$. In the direct reaction of $f_{P1} = 0$ ($f_{E1} = 1.0$), $\phi_S{}^M = 0.0472 \pm 0.0012$. We have assumed that maleate formation can occur via isc of $E^1 \rightarrow F^3$, with a quantum yield of $0.5\phi_{E1}{}^{E3}$, or via isc of $E^1 \rightarrow E^3$, with a quantum yield of $\phi^M_{E1\rightarrow E3}$. Now $\phi_{E1}{}^{E3} = 0.0659 \pm 0.013$ and from the Ph$_2$CO-sensitized experiments the quantum yield of M formation from E^3 is $\phi_{E3}{}^M = 0.076 \pm 0.008$. Hence $\phi^M_{E1\rightarrow E3} = \phi_{E1}{}^{E3}\phi_{E3}{}^M = 0.0050 \pm 0.0011$ and $0.5\phi_{E1}{}^{F3} = \phi_S{}^M - \phi^M_{E1\rightarrow E3} = 0.0422 \pm 0.0016$, i.e., $\phi_{E1}{}^{F3} = 0.0844 \pm 0.0032$. Quantum yields of X formation, $\phi_S{}^X$, and E^1 fluorescence, $\phi_{E1}{}^F$, are equated with $\phi_{E1}{}^X$ and $\phi_{E1}{}^F$ since X and flu-

Table VII. Dependence of ϕ_C, ϕ_T, ϕ_X, and ϕ_M on [F] on Direct Irradiation in Benzene[a]

[F], M	ϕ_C	ϕ_T	ϕ_X	ϕ_M	f_{P_1}[b]
0.254	0.002 82[c]	0.006 57[c]	0.027	0.0477	0.0091
0.151	0.002 99	0.007 21	0.027	0.0474	0.0151
0.098	0.003 30[c]	0.007 60[c]	0.0263	0.0488	0.0231
0.053	0.003 71	0.00848	0.0258	0.0489	0.0420

[a] [P] = 8.0×10^{-3} M, 347 ± 10 nm, unless otherwise noted. [b] $f_{P_1} = 1/(1 + 430[F])$; see text. [c] Measured at 334 nm, where P absorbs all the exciting light. Values at 347 nm are relative to these. P absorbs only ca. 85% of the exciting light at 347 ± 10 nm.
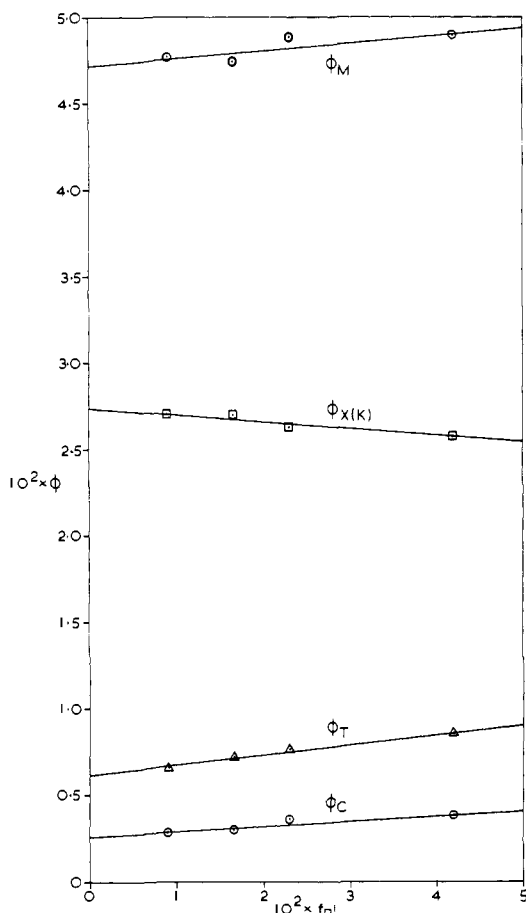

Figure 8. Quantum yields of photoproduct formation in outgassed benzene vs. the fraction of phenanthrene fluorescence (f_{P_1}) not quenched by F. ([P] = 10^{-2} M).

Table VIII. Quantum Yields (ϕ) and Rate Constants (k) for Decay of E^1 in Outgassed Benzene

product	ϕ_{E1}[a]	$10^7 k_{E1}$,[a] s^{-1}
X	0.0274 ± 0.0010	2.3 ± 0.8
T	$0.001\ 45 \pm 0.0007$	1.2 ± 0.7
E^3	0.0659 ± 0.0130	5.4 ± 2.1
F^3	0.0844 ± 0.0032	7.0 ± 1.2
$P + F + h\nu$	0.003 ± 0.001	0.25 ± 0.12
$P + F + \Delta$	0.820 ± 0.014	68.3 ± 22.8

[a] $\pm 2\sigma$.

orescence derive only from E^1. The quantum yield of radiationless deactivation, $\phi_{E1}{}^D = 1.0 - (\phi_{E1}{}^T + \phi_{E1}{}^{E3} + \phi_{E1}{}^X + \phi_{E1}{}^{F3} + \phi_{E1}{}^F)$. From these known quantum yields the rate constants for E^1 decay, $k_{E1}{}^T$, $k_{E1}{}^{E3}$, $k_{E1}{}^X$, $k_{E1}{}^{F3}$, $k_{E1}{}^F$, and $k_{E1}{}^D$, can all be obtained[37] (Table VIII) using the relationship $\phi_{E1} = k_{E1}\tau_{E1}$ where, from the air-quenching experiments, $\phi_{E1} = 1.2 \times 10^{-9}$ s.

Stern-Volmer plots for quenching of T, C, and M formation by quenchers of E^1 fluorescence can now be calculated using expressions 7, 10, and 13 and the parameters obtained above. Good agreement is obtained between the calculated and experimental data for quenching of T formation of Et$_3$N at [F] = 0.1 M (Figure 7). There is considerable scatter in the experimental data for quenching of C formation (see Experimental Section) but the Stern-Volmer plot is clearly nonlinear as predicted by Scheme II. As Et$_3$N $\rightarrow \infty$ the Stern-Volmer plots should plateau since $\phi^T \rightarrow f_{P3}\phi_{E3}{}^T$ and $\phi^C \rightarrow f_{P3}\phi_{E3}{}^C$. Thus at [Et$_3$N] $\rightarrow \infty$, $\phi^{0T}/\phi_T \rightarrow 0.0076/0.001\ 25 = 6.08$ and $\phi^{0C}/\phi^C \rightarrow 0.0033/0.000\ 675 = 4.89$. The fact that the experimental ϕ^0/ϕ points lie above the calculated curve (Figure 7) may be significant. Farid's data[7] imply a lifetime of a few

tenths of a nanosecond for E^3, and quenching of E^3 (or P^3) by Et$_3$N, if it were to occur, would give rise to a deviation in this direction. A priori we believe that triplet exciplexes ought to be susceptible to charge-transfer quenching[38] but further experiments are required. Our data indicate the absence of isc from an "encounter complex"[39] formed prior to E^1. Such isc has been suggested[40] and questioned[41] in other systems. Since $\phi_{E3}{}^T$ is an order of magnitude greater than $\phi_S{}^T$ the Stern-Volmer plots are very sensitive to isc of P^1 to P^3 whatever the mechanism. At [F] = 0.1 M a value of $f_{P3} = 0.017$ (1.7% isc of P^1 to P^3) is sufficient to produce the marked curvature of the calculated Stern-Volmer plot for T quenching (Figure 7). It seems inconceivable that we would not observe the effect of even a few tenths of a percent of additional enhanced isc from an encounter complex.

In contrast to the data for T and C quenching both calculated and experimental plots for M quenching (Figure 6) do not significantly deviate from linearity over the (practical) range of [Et$_3$N] used. This is a consequence of the small difference between the direct and sensitized quantum yields of M formation. At [F] = 0.1 M only a small fraction ($\simeq 3.5\%$) of M arises from isc of P^1 to P^3, i.e., $f_{P3}\phi_{E3}{}^M \ll f_{E1}$ ($0.5k_{E1}{}^{F3} + k_{E1}{}^{F3}\phi_{E3}{}^M/\Sigma k_{E1}$ in eq 21, and the Stern-Volmer plot is not expected to plateau till $\phi^0/\phi \simeq 30$.

Since Stern-Volmer plots for quenching of E^1 fluorescence, X formation, and M formation are essentially identical, there is no doubt that E^1 is a precursor of X and M. The good agreement between the experimental and calculated nonlinear Stern-Volmer plots for quenching of T and C formation provides strong support for Farid's suggestion[7] that T and C derive from both E^1 and E^3 in the direct reaction. We have presented evidence that both a triplet exciplex, E^3, and a triplet biradical, SS, are involved in the triplet-sensitized reaction. Farid's suggestion of isc of E^1 to E^3 and hence to SS is the most economical way of explaining the formation of both T and C in both the direct and sensitized reactions. In a subsequent paper[42] we will present evidence from oxygen quenching experiments that E^1 behaves analogously to P^1 with respect to physical decay processes such as intersystem crossing. We have already presented evidence indicating that the triplet biradical, SS, can be intercepted by paramagnetic molecules such as oxygen or di-*tert*-butyl nitroxide.[43]

A singlet biradical, if formed, must be derived from E^1. However it does not readily explain the loss of stereochemistry in formation of C in the direct reaction, particularly when compared to other photochemically generated biradicals.[44] The

question of whether nonvertical E^1 decay involves formation of a singlet biradical or "biradicaloid" at a so-called pericyclic minimum in the lowest excited singlet surface[45] must await more detailed exploration of the "unimolecular" $E^{1 \rightarrow T}$, $E^1 \rightarrow X$, and $E^1 \rightarrow P + F$ pathways.

Experimental Section

Benzene (Fisher, ACS Certified) was extracted with H_2SO_4 until no further coloration of the acid occurred, washed (dilute KOH, H_2O), dried (Na_2SO_4), and distilled off sodium–lead alloy. It was stored over Na/Pb alloy or 4A molecular sieves. Hexane (Fisher, AR mixed) was used without further purification. Methanol (Fisher, ACS) was distilled once. Phenanthrene (Aldrich) was refluxed with maleic anhydride in xylene, extracted with base to remove anhydrides, and recrystallized from ethanol. No UV absorption due to anthracene was detected. Dimethyl fumarate (Eastman) was recrystallized twice from benzene; it contained <0.03% of maleate (GLC analysis). Dimethyl maleate (Eastman) was distilled under reduced pressure through a Nester-Faust Teflon spinning band distillation apparatus. A fraction was used containing 0.16% of fumarate (GLC analysis). Maleic anhydride (Aldrich) was recrystallized from benzene–hexane after filtration of insoluble maleic acid. Benzophenone (Eastman) was recrystallized from aqueous ethanol. *trans*-Stilbene (K+K) was recrystallized once from ethanol, mp 122–123.4 °C. Potassium ferrioxalate (Oxford Chemicals) was used as received. The exciplex quenchers 2-methylbut-2-ene, ethyl vinyl ether, 2,3-dimethylbut-2-ene, dihydropyran, and triethylamine (all from Aldrich) were freshly distilled at atmospheric pressure prior to use. *trans*-Anethole (Aldrich) was distilled under reduced pressure, it contained <0.1% of *cis*-anethole and 0.5% of anisaldehyde (GLC). Ultraviolet spectra were run on either a Bausch and Lomb 505 or a Beckman Model 25 spectrophotometer. Nuclear magnetic resonance spectra were run in $CDCl_3$ on a Varian A-60A or a Jeolco C-60HL spectrometer with Me_4Si as internal standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected.

Preparative photolyses were performed using Hanovia 450-W medium-pressure mercury lamps in a water-cooled immersion well apparatus of standard design (Ace Glass Co.). Uranium (Corning 3320) and Pyrex glass filters were used for the sensitized and direct photolyses, respectively.

Isolation of T and C from the Benzophenone-Sensitized Reaction. Use was made of the high T/C ratio in the initial stages of the reaction and the low T/C ratio over long-term irradiation in order to isolate T and C.

Trans Diester, T. Phenanthrene (10.0 g), dimethyl fumarate (8.1 g), and benzophenone (5 g) in hexane (1000 mL) were irradiated under nitrogen for 8 h. A crystalline product (3.6 g) was obtained by filtration of the reaction mixture. Recrystallization from ethanol (175 mL) and glacial acetic acid (1 mL) afforded white prisms (1.0 g), mp 111.5–113.2 °C, containing (NMR) ≃6% of the cis diester. This material from three runs (2.8 g) was combined and recrystallized from methanol (87 mL) and acetic acid (1 mL), affording *trans*-dimethyl 1,2,2a,10b-tetrahydrocyclobuta[1]phenanthrene-1,2-dicarboxylate (1 g): mp 111.8–113 °C; δ ($CDCl_3$) 3.43 (s, endo-CO_2 Me), 3.67 (s, exo-CO_2Me), 3.6–4.3 (m, cyclobutane 4-H), 6.9–7.4 (m, 6 aromatic H), 7.6–8.0 (4- and 5-H of aromatic rings). The product contained <0.25% (by GLC) of the cis diester.

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.72; H, 5.55.

Cis Diester, C. Phenanthrene (5.4 g), dimethyl fumarate (4.3 g), and benzophenone (5.1 g) in benzene (1080 mL) were irradiated under nitrogen for 3 days. GLC analysis indicated a T/C ratio of 0.37 at this time, almost identical with that obtained by irradiation of P (5.4 g), dimethyl maleate (4.3 g), and benzophenone (5.0 g) in benzene (1080 mL) for 26 h. The two mixtures were combined, the benzene was evaporated (water pump), and the residue was recrystallized once from methanol (400 mL) affording white crystals (5.4 g) of *cis*-dimethyl 1,2,2a,10b-tetrahydrocyclobuta[1]phenanthrenecarboxylate: mp 113–114.2 °C (lit.[10] mp 112 °C); δ ($CDCl_3$) 3.25–3.45 and 4.0–4.20 (two m, 4 H, centrosymmetric A_2B_2 pattern of cyclobutane H), 3.67 (s, 6 H, 2 OMe), 7.1–7.3 (m, 6 aromatic H), 7.65–8.0 (m, 2 H, 4- and 5-H of aromatic rings). The product contained <0.2% of the trans diester (GLC analysis).

Cis-Exo Anhydride, CA. Phenanthrene (3.0 g), maleic anhydride

(1.5 g), and benzophenone (2.0 g) in hexane (1100 mL) were irradiated under nitrogen for 5.5 h. The solid residue was dissolved in acetone (75 mL), hexane (100 mL) was added, and the mixture was evaporated to about 50 mL total volume. White crystals (0.4 g) of 1,2,2a,10b-tetrahydrocyclobuta[1]phenanthrene-*cis*-1,2-dicarboxylic acid anhydride were obtained upon cooling to 0 °C, mp 217.5–219 °C (lit.[10] mp 222 °C).

Conversion of CA to C. A suspension of the anhydride, CA (2.0 g), was refluxed in methanol (50 mL) containing concentrated H_2SO_4 (1 mL) for several hours until it had all dissolved. Most of the methanol was distilled off and the residue was cooled (0 °C), filtered, and washed with 5% $NaHCO_3$ and distilled water. Recrystallization from methanol afforded C, mp 112–112.5 °C, identical (mmp 113–114.5 °C, NMR spectrum) with C isolated from the irradiation of P + F (vide supra).

Epimerization of C to T. Metallic sodium (~0.2 g) and cis ester C (4.0 g) were added to magnesium-dried methanol (100 mL). The mixture was refluxed for 3 h, cooled, and acidified (acetic acid). Upon leaving overnight a crystalline product was obtained (1.6 g) which upon recrystallization from methanol afford trans diester T (mp 110–111 °C) identical (NMR) with material obtained in the sensitized irradiation of P and F.

Ozonolysis of the Trans Diester, T. Ozone was passed through a solution of T (50 mg) in 80% aqueous acetic acid (40 mL) at room temperature for 48 h. Following removal of solvents under reduced pressure (water pump) at 30–40 °C the residue was dissolved in methanol and treated with diazomethane. GLC analysis (8 ft × 1/4 in. 5% Carbowax 20M, 210 °C) showed a single peak with retention time (8.5 min) longer than 2 min. Preparative GLC (8 ft × 1/4 in. Carbowax 20M, 210 °C) yielded *cis,cis,trans*-1,2,3,4-tetracarbomethoxycyclobutane, CB (11 mg), which upon recrystallization from acetone had mp 71–73 °C (lit.[12] mp 73–74 °C).

Isolation of Keto Ester, K. An authentic sample of K required for the kinetic work was isolated from the direct irradiation by a slight modification of the method of Farid et al.[7b] P (0.76 g) and F (0.90 g) in benzene (60 mL) were irradiated in a square Pyrex cell (total volume ≃ 100 mL) under nitrogen for 17 h. Following evaporation of benzene (water pump) the residue was dissolved in methanol (10 mL), concentrated HCl (≃0.2 mL) was added, and the mixture was stirred for 1 h at room temperature. Benzene (10 mL) was then added and the solvents were evaporated under reduced pressure (water pump) at 70–80 °C. The yellow residue was dissolved in acetone and chromatographed on six Brinkmann 2-mm thick silica gel F-254 preparative TLC plates using benzene as eluent. A bright yellow band (R_f ≃ 0.5) when eluted with ether and recrystallized from benzene–hexane afforded yellow crystals of (E)-methyl 4-oxo-4-(9-phenanthryl)-2-butenoate, K (22 mg), mp 105–106 °C (lit.[7] 105–107 °C); GLC analysis of a slower moving, colorless band (dark under UV illumination) showed that it contained T and C in the approximate ratio of 2:1.

Fluorescence spectra were recorded on a Farrand MK1 ratio recording spectrofluorimeter using a Houston Instruments Omnigraphic X-Y recorder. Spectra in air-saturated benzene were run in standard 10-mm path length quartz cuvettes. Spectra in outgassed benzene were run in 13-mm o.d. Pyrex tubes prepared as described below.

Quantum yield of E^1 fluorescence was measured using residual P fluorescence as an internal standard for E^1 fluorescence in the corrected spectra. The ϕ for residual P fluorescence, $\phi_P{}^F$, can be calculated from $\phi_P{}^F = 0.13^{46}$ at [F] = 0, the [F], and the Stern–Volmer slope (430 M^{-1}) for P fluorescence quenched by F. Thus at [F] = 0.2 M, 98.8% of P^1 is quenched by F and $\phi_P{}^F = 1.5 \times 10^{-3}$. We assume no E^1 fluorescence at the 0–0 band (348 nm) of P^1 fluorescence and subtract out the P^1 contribution to the total corrected spectrum. The relative areas of the P^1 and E^1 spectra give $\phi_P{}^F/\phi_{E1}{}^F$ and hence $\phi_{E1}{}^F$.

Light Sources for Kinetic Measurements. In some of the sensitized photolyses standard glass and chemical filters were used to isolate the 366-nm line of the Hanovia medium-pressure mercury lamps. However, for most ϕ measurements a Bausch and Lomb SP200 superpressure mercury lamp and UV monochromator was used. Standard slit combinations afforded band-passes of ±2.5, ±5, or ±10 nm at the wavelengths of irradiation, either 334, 347, or 366 nm.

Actinometry. Light intensities were measured using ferrioxalate actinometry.

Sample Preparation. Samples (3–4 mL) contained in 13-mm o.d. Pyrex tubes were outgassed to <10^{-3} mmHg by the freeze-pump-

thaw method and sealed off under vacuum. For some absolute ϕ measurements cells made from $\simeq 10$ mm i.d. square Pyrex tubing were used to obviate effects[47] due to the refractive index difference between benzene and the (aqueous) actinometer.

Sample irradiations were carried out with the samples rotated in a merry-go-round apparatus of standard design. Conversions were always to <1%. The Ph$_2$CO-sensitized photolyses were carried out at 366 ± 10 nm with [Ph$_2$CO] $\simeq 0.06$ M to ensure complete absorption of incident light. For absolute ϕ measurements in the direct reactions irradiations were carried out at 334 ± 2.5 nm with [P] = 10^{-2} M. A small correction is made for the fraction of light (3.2%) not absorbed by P under these conditions. Absorption spectra indicate no significant direct excitation of F (up to saturation $\simeq 0.3$ M) at 334 ± 2.5 nm. A small effect ($\lesssim 5\%$) of self-quenching by P is expected at [P] = 10^{-2} M (Results and Discussion). This effect has been ignored in ϕ measurements. In the exciplex quenching experiments irradiations were carried out at 347 ± 10 nm, the longest practical wavelength, to minimize light absorption by the CT complexes formed between F and the exciplex quenchers, Q. A correction has been made to the Stern-Volmer plots for the fraction of light absorbed by the CT complexes. The fraction of light absorbed by P was assumed to be OD$^P_{347}$/OD$^P_{347}$ + OD$^{CT}_{347}$.

Photoproduct analyses were performed by GLC using either an F and M Model 700 with a thermal conductivity detector or a Hewlett-Packard 5710A with a flame ionization detector. **T, C,** and **K (X)** analysis (vide infra) was carried out on silicone oil columns (either UCW98 on HP Chromosorb W or 5-8% Apiezon J on Chromosorb P or W) at 250-290 °C. They elute in the order T, C, and finally K. An additional small peak, most probably due to the Z isomer of K, interferes with C analysis in the direct irradiations. M analysis was carried out on a Carbowax column (5% Carbowax 20M on HP Chromosorb W) at 140 °C. M elutes after F; all other components elute at very long times. Since conversions were <1%, P was used as an internal standard in analysis of T, C, and K. The relative molar sensitivities, in parentheses, using the FID GLC were P (1.0), T and C (1.18), and K (1.03).

Analysis of X (K). Under the GLC conditions X reverts to P + F. Therefore analysis for X in the direct photolyses were carried out by converting X into the keto ester K. The sample (3-4 mL) was evaporated at reduced pressure (water pump) and low temperature ($\lesssim 50$ °C). Methanol (3 mL) and concentrated HCl (10 drops) were added, and the mixture was warmed to dissolve the residue and left at room temperature for 20 min. Benzene (5 mL) was added and the sample analyzed for P, T, C, and K as described above. More prolonged acid treatment does not increase the amount of K observed.

References and Notes

(1) (a) Fellow of the Robert A. Welch Foundation. (b) Address correspondence to this author at the University of Texas at Dallas.
(2) (a) A. Lablache-Combier, *Bull. Soc. Chim. Fr.*, **4791** (1972); (b) R. S. Davidson in "Molecular Association" Vol. 1, R. Foster, Ed., Academic Press, New York, N.Y., 1975; (c) B. Stevens, *Annu. Rep. Prog. Chem., Sect. A*, **29** (1974); (d) B. Stevens, *Adv. Photochem.*, **6**, 161 (1971).
(3) (a) A. Weller in "Fast Reactions and Primary Processes in Chemical Kinetics. Proceedings of the Fifth Nobel Symposium", S. Claesson, Ed., Interscience, New York, N.Y., 1967, p 413; (b) T. R. Evans, *J. Am. Chem. Soc.*, **93**, 2081 (1971), and references cited therein; (c) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *ibid.*, **94**, 3679 (1972); (d) I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970); (e) N. E. Schore and N. J. Turro, *ibid.*, **97**, 2482 (1975); (f) F. D. Lewis and R. H. Hirsch, *ibid.*, **98**, 5914 (1976).
(4) (a) R. M. Bowman, T. R. Chamberlain, C-W. Huang, and J. J. McCullough, *J. Am. Chem. Soc.*, **96**, 642 (1974); (b) K. Mizuno, C. Pac, and H. Sakurai, *ibid.*, **96**, 2993 (1974).
(5) (a) R. O. Loutfy, P. de Mayo, and M. F. Tchir, *J. Am. Chem. Soc.*, **91**, 3984 (1969); (b) O. L. Chapman and R. D. Lura, *ibid.*, **92**, 6352 (1970); (c) J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, *ibid.*, **93**, 2804 (1971); (d) T. Sugioka, C. Pac, and H. Sakurai, *Chem. Lett.*, 667 (1972).
(6) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973).

(7) (a) S. Farid, J. C. Doty, and J. L. R. Williams, *J. Chem. Soc., Chem. Commun.*, 711 (1972); (b) S. Farid, S. E. Hartman, J. C. Doty, and J. L. R. Williams, *J. Am. Chem. Soc.*, **97**, 3697 (1975).
(8) (a) R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, **96**, 2994 (1974); (b) J. Ferguson, A. W. H. Mau, and M. Puza, *Mol. Phys.*, **27**, 377 (1974); **28**, 1457, 1467 (1974); (c) F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, **99**, 3779 (1977); (d) S. Farid and K. A. Brown, *J. Chem. Soc., Chem. Commun.*, 564 (1976); (e) N. C. Yang, D. M. Shold, and J. K. McVey, *J. Am. Chem. Soc.*, **97**, 5004 (1975); (f) N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *ibid.*, **97**, 5006 (1975); (g) C. Pac and H. Sakurai, *Chem. Lett.*, 1067 (1976).
(9) Preliminary accounts of part of this work have already been published: (a) R. A. Caldwell, *J. Am. Chem. Soc.*, **95**, 1690 (1973); (b) D. Creed and R. A. Caldwell, *ibid.*, **96**, 7369 (1974).
(10) D. Bryce-Smith and B. Vickery, *Chem. Ind. (London)*, 429 (1961).
(11) We thank Dr. J. W. Young for carrying out the ozonolysis experiment.
(12) J. Meinwald and J. W. Young, *J. Am. Chem. Soc.*, **93**, 725 (1971).
(13) The cis-exo cyclobutane photoadduct from phenanthrene and dichloromaleic anhydride was refluxed with acidic methanol to give the corresponding diester. Dehalogenation (zinc-acetic acid) of the diester afforded a cyclobutane diester which upon hydrogenation give the cis-endo phenanthrene-dimethyl maleate adduct. W. S. Burnham and R. A. Caldwell, unpublished results.
(14) By isoprene quenching of F → M isomerization sensitized by benzophenone, assuming that isoprene quenches ^{3}B with $k = 5 \times 10^9$ M^{-1} s^{-1}.
(15) (a) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and J. C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964); (b) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).
(16) D. Creed, R. A. Caldwell, and M. A. J. Rodgers, unpublished work carried out at the Center for Fast Kinetics Research, University of Texas at Austin.
(17) (a) J. P. Keene, T. J. Kemp, G. A. Salmon, *Proc. R. Soc. London, Ser. A*, **287**, 494 (1965); (b) F. S. Dainton, T. J. Kemp, G. A. Salmon, and J. P. Keene, *Nature (London)*, **203**, 1050 (1964).
(18) P has[19] IP = 7.86 eV and E_S (singlet energy) = 3.57 eV. Its electron affinity is assumed to be IP − E_S = 4.29 eV. F has[20] IP(n) = 10.47 eV, E_S = 4.00 eV, and electron affinity IP − E_S = 6.47 eV.
(19) R. Boschi, E. Clar, and W. Schmidt, *J. Chem. Phys.*, **60**, 4406 (1974).
(20) R. Sustmann and H. Trill, *Tetrahedron Lett.*, 4271 (1972).
(21) See, for example, (a) J. K. Roy, F. A. Carroll, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 6349 (1974); (b) I. P. Bell and M. A. J. Rodgers, *Chem. Phys. Lett.*, **44**, 249 (1976); (c) R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, **99**, 3559 (1977); (d) M. W. Wolf, R. E. Brown, and L. A. Singer, *ibid.*, **99**, 526 (1977); (e) D. I. Schuster and T. M. Weil, *Mol. Photochem.*, **6**, 69 (1974).
(22) (a) T. Takemura, H. Baba, and Y. Shindo, *Chem. Lett.*, 1091 (1974); (b) T. Takemura, M. Aikawa, H. Baba, and Y. Shindo, *J. Am. Chem. Soc.*, **98**, 2205 (1976); (c) M. Aikawa, T. Takemura, and H. Baba, *Bull. Chem. Soc. Jpn.*, **49**, 437 (1976).
(23) (a) J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, **116**, 743 (1969); (b) R. Takahashi and P. J. Elving, *Electrochim. Acta*, **12**, 213 (1967).
(24) (a) D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **98**, 621 (1976); (b) G. N. Taylor, E. A. Chandross, and A. H. Scheibel, *ibid.*, **96**, 2693 (1974).
(25) (a) P. de Mayo, *Acc. Chem. Res.*, **4**, 41 (1971); (b) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968), and references cited therein.
(26) G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **12**, 765 (1973).
(27) The technique has also been used by others, who also find a value of 4.2 × 10^7 s^{-1} for k_{O2}[O$_2$] in aerated benzene. See J. L. Charlton, D. E. Townsend, B. D. Watson, P. Shannon, J. Kowalewska, and J. Saltiel, *J. Am. Chem. Soc.*, **99**, 5992 (1977).
(28) (a) H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967); (b) H. Knibbe, K. Rollig, F. P. Schafer, and A. Weller, *ibid.*, **47**, 1184 (1967); (c) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 397 (1971); (d) G. S. Beddard, S. E. Carlin, and C. Lewis, *J. Chem. Soc., Faraday Trans. 2*, 1894 (1975).
(29) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
(30) Y. Shirota, I. Tsushi, and H. Mikawa, *Bull. Chem. Soc., Jpn.*, **47**, 991 (1974).
(31) P. Schuler and H. Heusinger, *Photochem. Photobiol.*, **24**, 307 (1976).
(32) There are several other examples known of self-quenching of exciplexes. (a) H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968); (b) J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, *J. Am. Chem. Soc.*, **97**, 5688 (1975); (c) N. C. Yang, D. M. Shold, and B. Kim, *ibid.*, **98**, 6587 (1976); (d) J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, *ibid.*, **99**, 884 (1977).
(33) K_{eq} = 660 for the closely related P-fumaronitrile exciplex.[27]
(34) See also (a) R. A. Caldwell, D. Creed, and H. Ohta, *J. Am. Chem. Soc.*, **97**, 3246 (1975); (b) H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *ibid.*, **98**, 2002 (1976).
(35) D. Creed, R. A. Caldwell, H. Ohta, and D. C. DeMarco, *J. Am. Chem. Soc.*, **99**, 277 (1977).
(36) Upper limit by pulse radiolysis of P in benzene.[16]
(37) Our data for quantum yields of E^1 decay to X, T, and E^3 are in excellent agreement with those of Farid.[7b] Quantum yields for fluorescence and F^3 formation from E^1 were not determined by Farid.
(38) Evidence for quenching by piperylene of an acetophenone-*trans*-3,4-dimethyl-2-pentene triplet exciplex has been recently presented: A. Gupta and G. S. Hammond, *J. Am. Chem. Soc.*, **98**, 1218 (1976).
(39) An emissive "encounter exciplex" has been directly observed in the system 9,10-difluoroanthracene + 2,5-dimethyl-2,4-hexadiene. N. C. Yang, D. M. Shold, J. K. McVey, and B. Kim, *J. Chem. Phys.*, **62**, 4559 (1975).
(40) (a) N. Orbach, R. Potashnik, and M. Ottolenghi, *J. Phys. Chem.*, **76**, 1133 (1972); (b) C. R. Goldschmidt, R. Potashnik, and M. Ottolenghi, *Acc. Chem. Res.*, **6**, 153 (1973).

(41) (a) K. H. Grellmann and U. Suckow, *Chem. Phys. Lett.*, **32**, 250 (1975); (b) T. Nishimura, N. Nakashima, and N. Mataga, *Chem. Phys. Lett.*, **46**, 334 (1977).
(42) D. Creed and R. A. Caldwell, *J. Am. Chem. Soc.*, submitted for publication.
(43) R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **99**, 8360 (1977).
(44) L. M. Stephenson and J. I. Brauman, *J. Am. Chem. Soc.*, **93**, 1988 (1971),

and references cited therein.
(45) (a) W. Gerhartz, R. D. Poshusta, and J. Michl, *J. Am. Chem. Soc.*, **98**, 6427 (1976); (b) J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977), and references cited therein; (c) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975), and references cited therein.
(46) B. R. Henry and M. Kasha, *J. Mol. Spectrosc.*, **26**, 536 (1968).
(47) M. D. Shetlar, *Mol. Photochem.*, **5**, 287 (1973).

Laser-Induced Photoconversion of *trans*-Stilbene Dianions into *cis*-Stilbene Radical Anions

G. Levin, B. E. Holloway, C. R. Mao, and M. Szwarc*

Contribution from the Department of Chemistry, State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210. Received February 24, 1978

Abstract: Laser-pulse photolysis of the sodium salt of *trans*-stilbene dianions induced by tunable dye laser leads to electron ejection. The ejected electron is captured by biphenyl present in a large excess and a transient absorbance at 400 nm (λ_{max} of the formed biphenylide) monitors the electron ejection process. The formation of *trans*-stilbene radical anions, resulting from the electron photoejection, should be revealed by a transient absorbance at 480 nm, but at high light intensity this transient is weaker than needed for the 1:1 stoichiometric ratio biphenylide:*trans*-stilbenide. Moreover, under these conditions the 480-nm transient grows for a period of 8–10 μs, the growth obeying a first-order law with the first-order rate constant proportional to the concentration of the dianions present in large excess in the solution. We conclude that *cis*-stilbenide is formed in the photolysis and the reaction *cis*-stilbenide + trans dianion → cis dianion + *trans*-stilbenide, followed by the extremely fast conversion, cis dianion → trans dianion, is responsible for the observed growth of the 480-nm transient, because at this wavelength the molar absorbance of *trans*-stilbenide is higher than that of *cis*-stilbenide. The electron transfer biphenylide + *trans*-stilbenide → biphenyl + trans dianion eventually restores the system to its initial state. The fraction of trans dianions converted into *cis*-stilbenide instead of *trans*-stilbenide increases with light intensity. The cause of this effect is discussed.

Radical anions and even the dianions of the stilbenes exist in two distinct forms referred to as the cis, $C^-\cdot$ and C^{-2}, and trans, $T^-\cdot$ and T^{2-}. This designation does not necessarily imply the conventional difference in geometry of these isomers. Rather it is used in operational meaning. The cis radical anion of stilbene is the one that is formed on attachment of an electron to *cis*-stilbene, C, and is converted back into *cis*-stilbene when the electron is removed. Similar definition applies to the term *trans*-stilbene radical anion, i.e.,

$$C + e^- \rightleftarrows C^-\cdot \text{ and } T + e^- \rightleftarrows T^-\cdot$$
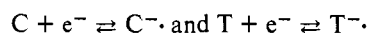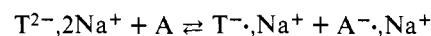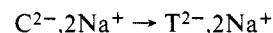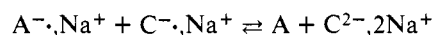
A radical anion may be formed from the respective dianion by electron photodetachment. One would anticipate the electron photodetachment from *trans*-stilbene dianions to yield *trans*-stilbene radical anions but, as will be shown later, laser pulse photolysis of $T^{2-},2Na^+$ yields, at least partially, the *cis*-stilbene radical anions.

In this paper we wish to present the experimental results leading to this conclusion and discuss their significance. It is advisable, however, first to review briefly the evidence for the existence of the distinct *cis*- and *trans*-stilbene radical anions and dianions and to describe their optical spectra.

Radical Anions and Dianions of the Stilbenes. The results reported in the past by various workers[1–3] led to the belief that radical anions of the stilbenes exist in one form only or, if there are two isomers, the one derived from *cis*-stilbene converts extremely rapidly into the known and stable species derived from *trans*-stilbene. The work carried out in our laboratory[4–6] showed this not to be the case. Kinetic studies of electron transfer induced isomerization of *cis*-stilbene into the trans isomer conclusively demonstrated the presence of *cis*-stilbene

radical anions, $C^-\cdot$, that only slowly isomerize into *trans*-stilbene radical anions. In fact, for the free radical anions not associated with cations the direct isomerization, $C^-\cdot \rightarrow T^-\cdot$, proceeds very slowly with a rate constant of about 5×10^{-3} s^{-1}. Such a reaction was studied in hexamethylphosphoric triamide.[6] In tetrahydrofuran the radical anions are associated with counterions into pairs, e.g., $C^-\cdot,Na^+$ and $T^-\cdot,Na^+$. The direct isomerization, $C^-\cdot,Na^+ \rightarrow T^-\cdot,Na^+$, cannot be observed under these conditions because an alternative faster route leads to the transformation of $C^-\cdot,Na^+$ into $T^-\cdot,Na^+$. In the presence of a suitable electron donor, say $A^-\cdot,Na^+$, the $C^-\cdot,Na^+$ radical anions are reduced to the $C^{2-},2Na^+$ dianions and the latter isomerize with a rate constant of about 10^6–10^7 s^{-1} into $T^{2-},2Na^+$. Thus the following sequence of reactions takes place,[4]

$$A^-\cdot,Na^+ + C^-\cdot,Na^+ \rightleftarrows A + C^{2-},2Na^+$$

$$C^{2-},2Na^+ \rightarrow T^{2-},2Na^+$$

$$T^{2-},2Na^+ + A \rightleftarrows T^-\cdot,Na^+ + A^-\cdot,Na^+$$

the isomerization $C^{2-},2Na^+$ into $T^{2-},2Na^+$ being the rate-determining step. This work proved the existence not only of two different radical anions of the stilbenes but also of two different dianions, provided that the latter are associated with cations. The absorption spectra of $C^-\cdot,Na^+$ and $T^-\cdot,Na^+$ in tetrahydrofuran were eventually recorded by application of flash photolysis.[6] The absorption maxima are close to each other, namely, at 498 nm for $C^-\cdot,Na^+$ and 490 nm for $T^-\cdot,Na^+$; however, the molar absorbances are different, viz., 3.3×10^4 and 5.2×10^4, respectively. These results have been confirmed recently by pulse-radiolytic studies of Levanon and