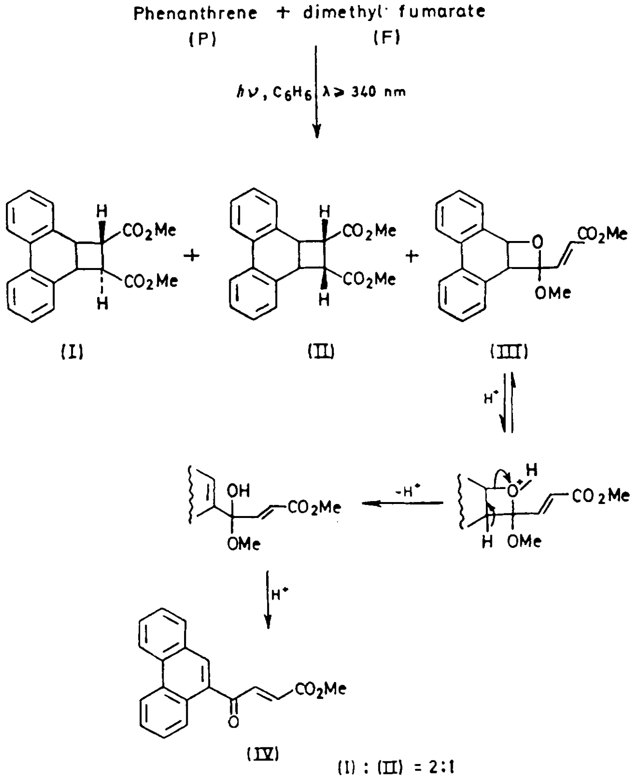
Reactions of the Exciplex from Singlet-excited Phenanthrene and Dimethyl Fumarate: Oxetan Formation, Intersystem Crossing, and Emission

By S. Farid,* J. C. Doty, and J. L. R. Williams
(Research Laboratories, Eastman Kodak Company, Rochester, New York 14650)

Summary An oxetan is formed *via* an exciplex from the reaction of singlet-excited phenanthrene with ground-state dimethyl fumarate; the formation of cyclobutane adducts is preceded by intersystem crossing in the exciplex as well as *via* triplet phenanthrene.



SCHEME

A NUMBER of examples is known of the formation of cyclobutane from the photoreaction of aromatic hydrocarbons with olefins.[1] The reaction of selectively excited phenanthrene (P) with dimethyl fumarate (F) yielded the cyclobutane derivatives (I), m.p. 112—113°, and (II), m.p. 114—115°, and, unexpectedly, the oxetan (III), m.p. 144—146°, which with traces of acid underwent degradation to the ketone (IV), m.p. 105—107°.

Evidence for exciplex formation in this reaction was obtained from fluorescence studies. Dimethyl fumarate quenched the fluorescence of phenanthrene at a nearly diffusion-controlled rate, and a new emission band (λ_{max} 450 nm in benzene) was observed in addition to the residual fluorescence of (P). The excitation spectrum for the exciplex emission and for the phenanthrene fluorescence were identical.

The quantum yield for the formation of (III) increased with [F], and the benzophenone-sensitized reaction gave the cyclobutanes (I) and (II) but no oxetan. These findings point to a reaction of the singlet-excited phenanthrene (P^1) to give (III).

The reported formation of oxetans, with very few exceptions,† proceeds from triplet or singlet-excited states of the carbonyl compounds.[2] In the present example, an

---

† *Cf.* C. DeBoer, *Tetrahedron Letters*, 1971, 4977, and references therein. In a personal communication C. DeBoer pointed out that for those reactions where it is proposed that triplet olefins (formed *via* energy transfer from triplet carbonyl compounds) react with ground-state carbonyl derivatives to give oxetans, there is an alternative mechanism which fulfils the kinetic requirements but does not involve excited olefin.

oxetan is formed *via* reaction of the directly excited singlet-state hydrocarbon with a ground-state carbonyl compound.

A linear relationship‡ was obtained for $\phi(\mathrm{I} + \mathrm{II})/\phi(\mathrm{III})$ *vs.* $1/[\mathrm{F}]$ with an intercept of 0·38. This indicates that (I) and (II) are formed from reactions of both singlet (P^1) and triplet (P^3) excited phenanthrene with (F). When *trans*-cinnamate esters§ (C) were used as quenchers for (P^3), a constant ratio for (I + II): (III) of 0·2 was reached at high cinnamate concentrations. This value differs from the product ratio of 0·38 at infinite concentration of (F) and in the absence of (C). There should be, therefore, two pathways for cyclobutane formation that proceed *via* the reaction of (P^1) with (F), one of them being interceptable by triplet quenching. The ratio (I): (II) was constant regardless of the concentration of (F) or presence of quencher or sensitizer.

These results can be rationalized in terms of formation of an exciplex (E^1) from the reaction of (P^1) with (F). In addition to other reactions (*cf.* Scheme), this singlet exciplex can undergo intersystem crossing to a triplet intermediate (E^3), which can react to give (I) and (II) and dissociate to (P^3) + (F). Triplet phenanthrene formed *via* this pathway, like that accessible through intersystem crossing from (P^1), can react with (F) to give (I + II) and would be quenchable.

$$\begin{array}{lll}
\mathrm{P} & \xrightarrow{h\nu} \mathrm{P}^1 & \\
\mathrm{P}^1 & \longrightarrow \mathrm{P} + h\nu' & (1)\\
\mathrm{P}^1 & \longrightarrow \mathrm{P} & (2)\\
\mathrm{P}^1 & \longrightarrow \mathrm{P}^3 & (3)\\
\mathrm{P}^1 + \mathrm{F} & \longrightarrow \mathrm{E}^1 & (4)\\
\mathrm{P}^1 + \mathrm{C} & \longrightarrow \text{products§} & (5)\\
\mathrm{E}^1 & \longrightarrow (\mathrm{III}) & (6)\\
\mathrm{E}^1 & \longrightarrow \mathrm{P} + \mathrm{F} + (h\nu'' \text{ or heat}) & (7)\\
\mathrm{E}^1 & \longrightarrow \mathrm{E}^3 & (8)\\
\mathrm{E}^3 & \longrightarrow (\mathrm{I}) + (\mathrm{II}) & (9)\\
\mathrm{E}^3 & \longrightarrow \mathrm{P} + \mathrm{F} & (10)\\
\mathrm{E}^3 & \longrightarrow \mathrm{P}^3 + \mathrm{F} & (11)\\
\mathrm{P}^3 & \longrightarrow \mathrm{P} & (12)\\
\mathrm{P}^3 + \mathrm{F} & \longrightarrow (\mathrm{I}) + (\mathrm{II}) & (13)\\
\mathrm{P}^3 + \mathrm{F} & \longrightarrow \mathrm{P} + \mathrm{F} & (14)\\
\mathrm{P}^3 + \mathrm{C} & \longrightarrow \mathrm{P} + \mathrm{C}^3 & (15)
\end{array}$$

Equations (16) and (17) were derived from the above Scheme for $[\mathrm{C}] = 0$ and for $(k_{13} + k_{14})\,[\mathrm{F}] \gg k_{12}$, which is well fulfilled for $[\mathrm{F}] \geqslant 5 \times 10^{-3}\,\mathrm{M}$ because of the long lifetime of (P^3).

$$\frac{\phi(\mathrm{I} + \mathrm{II})}{\phi(\mathrm{III})} = \underbrace{\frac{k_3}{k_4}\,\frac{(k_6 + k_7 + k_8)}{k_6}\,\frac{k_{13}}{(k_{13} + k_{14})}}_{s}\,\frac{1}{[\mathrm{F}]} +$$

$$\underbrace{\frac{k_8}{k_6}\,\frac{k_{11}}{(k_9 + k_{10} + k_{11})}\,\frac{k_{13}}{(k_{13} + k_{14})}}_{p} + \underbrace{\frac{k_8}{k_6}\,\frac{k_9}{(k_9 + k_{10} + k_{11})}}_{q} \qquad (16)$$

$$\phi(\mathrm{III}) = \frac{k_4[\mathrm{F}]}{k_1 + k_2 + k_3 + k_4\,[\mathrm{F}]}\,\frac{(k_6)}{(k_6 + k_7 + k_8)} \qquad (17)$$

for $k_4\,[\mathrm{F}] \gg (k_1 + k_2 + k_3)$, $\phi(\mathrm{III}) = ca. \dfrac{k_6}{k_6 + k_7 + k_8} = r$

It can be shown that the constant ratio of $\phi(\mathrm{I} + \mathrm{II})/\phi(\mathrm{III})$ which is reached at high [C] is equal to q. Experimentally determined values were: $s = 0{\cdot}011$, $p = 0{\cdot}18$, $q = 0{\cdot}2$, and $r = 0{\cdot}024$. From reported data[3] $(k_1 + k_2 + k_3) = 1{\cdot}74 \times 10^7\,\mathrm{s}^{-1}$ and $k_3 = 1{\cdot}32 \times 10^7\,\mathrm{s}^{-1}$. From the kinetics of the fluorescence quenching $k_4/k_1 + k_2 + k_3 = 595$, *i.e.* $k_4 = 10^{10}\,\mathrm{l\,mol^{-1}\,s^{-1}}$. It can be shown from the above data that the ratio $k_{13}/k_{13} + k_{14}$ is 0·2 and that the percentage of the reactions of (E^1) and (E^3) are: formation of (III) 2·4, of (I) and (II) 0·5, of (P^3) 2·2 and decay to (P) + (F) 94·9%. The radiative fraction of the latter process is very low.

(*Received*, 24*th March* 1972; *Com.* 498.)

---

‡ (I) and (III) undergo benzophenone- and phenanthrene-photosensitized decomposition. All kinetics were, therefore, studied under less than 1% fumarate conversion for the least diluted solution. The reactions were carried out under degassed conditions.

§ *trans*-Cinnamate esters have $E_{\mathrm{T}} = ca.$ 57 kcal/mol. We used in this study $\alpha\omega$-alkane dicinnamates to simplify the g.l.c. analysis.

[1] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 46; R. M. Bowman and J. J. McGullough, *Chem. Comm.*, 1970, 948; T. Miyamoto, T. Mori, and Y. Odaira, *ibid.*, p. 1598.

[2] D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301; N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, 1967, **89**, 5465; N. J. Turro and P. A. Wriede, *ibid.*, 1970, **92**, 320; and references therein.

[3] I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1965; $\phi_{\mathrm{isc}} = 0{\cdot}76$ (A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1965, **43**, 2129).