by factors of 2 and 3, respectively, than did host compound **1** without the two methyl groups. Apparently although more sterically hindering, the methyl group's inductive effect makes the aryl oxygens of **2** more basic than those of **1**, and **2** is therefore a better binder. Host **2** carried the faster moving enantiomers of the three racemic salts through chloroform at rates that varied with structure as follows: **5** ~ **4** > **6**. Without host present, the orders of relative rates of transport also were **5** ~ **4** > **6**. These orders probably reflect both the hydrophilicity–lipophilicity of the organic salts and the binding capacity of the salts for the hosts.

Although these results describe passive transport, active transport experiments involving chiral recognition by charged and noncharged hosts have been designed and are in progress.

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(6) In a "∪-tube" of 14 mm internal diameter was placed 10 ml of spectral grade chloroform that was 0.027 M in optically pure host compound. Water, 0.80 M in LiPF$_6$ and 0.08 M in HCl (5.0 ml) containing the guest amine salt, was placed in the α-arm. The β-arm contained 5.0 ml of 0.10 M HCl solution in water. The α- and β-interfaces were about 1.5 cm^2 each, and the average chloroform path length was about 6.5 cm. A small magnetic stirrer in the chloroform mixed (constant rate) that phase, and less well the aqueous phases. Transport rates of the guest salts were followed with the absorbence of the β-phases in the uv spectrum at 256 nm for **4**, 265 or 272 nm for **5**, and 291 nm for **6**. Host compound was undetectable (uv) in the aqueous phases. In method one individual transport rates for each optically pure guest salt (ref 5) were measured in separate runs under identical conditions through ~10% transport. Essentially linear plots of ten or more points of absorbance *vs.* time for the β-phase extrapolated to zero time gave zero-order rate constants for transport of each enantiomer. Method two involved racemic guest salt. After ~10% transport, amine in the β-phase was isolated. From the signs and magnitudes of rotations, and the established maximum rotations and configurations of the amines, k_A and k_B values (one point first-order rate constants) were estimated. Control runs on the isolation procedures with known starting solutions were made and established the validity of the procedure.

(7) M. Newcomb and D. J. Cram, to be submitted for publication.

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Role of a Singlet Exciplex in the Photocycloaddition of Phenanthrene to Dimethyl Fumarate

Sir:

Many 2 + 2 photocycloadditions are thought[1] to proceed *via* the intermediacy of exciplexes,[2] but direct evidence for this mechanistic pathway is sparse.[3] Both singlet[4] and triplet[4,5] exciplexes have been suggested as intermediates in the photoaddition of phenanthrene (P) to dimethyl fumarate (F) and maleate (M), and there is strong evidence[3,6] that photoadditions of 9-cyanophenanthrene to "electron-rich" olefins proceed *via* singlet exciplexes. Kaupp[7] has recently questioned the intermediacy of an exciplex in the P + F and M photocycloadditions and has suggested an alternative singlet biradical pathway. We now report the quenching of

the P + F singlet exciplex by electron donors. The results confirm the mechanism originally suggested by Farid[4] for the P + F photocycloaddition and indicate that charge transfer is an important factor in the quenching of singlet exciplexes.

Irradiation (347 nm) of P in the presence of F in outgassed benzene afforded[4] the isomeric cyclobutanes C and T and the oxetane X (isolated as the ketoester K following acid treatment). The ratio T/C was 2.2 and X/(C + T) was 2.3 at [F] = 0.26 M. The fluorescence of P in benzene was quenched by F (k_F = 7.5 × 10^9 l. mol^{-1} sec^{-1}) and a broad, weak, emission (λ_{max} = 452 nm) was observed at increasing [F]. This new emission is red shifted (λ_{max} = 467 nm) and diminished in intensity[8] on addition of methanol (5% by volume). These results confirm Farid's observation[4] of a singlet exciplex.[2,8] The weakness of the exciplex fluorescence may explain Kaupp's failure[7] to observe it.

R = CO$_2$Me
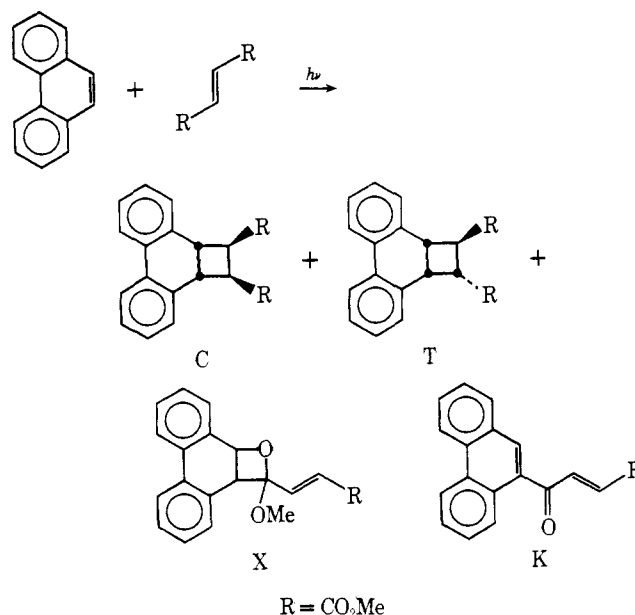
An exciplex can be simply regarded as an excited donor: acceptor pair, *e.g.*, (P$^{\delta+}$- - -$^{\delta-}$F)*, and ought to be susceptible to further charge-transfer perturbation. Thus the P + F exciplex fluorescence intensity is dramatically attenuated by electron donors (see Figure 1) with no concomitant effect on the residual P fluorescence. The quenching efficiencies ($k_Q^F\tau_x$) parallel[9] the ionization potentials (Ip) of the donors (Table I). P itself quenches the exciplex fluorescence (see Table I) but F does not. Formation of ground state

Table I. Quenching of Exciplex Fluorescence and Photoproduct Formation by Electron Donors^a

Quencher, Q	$Ip,^b$ eV	$k_Q^F\tau_x,$ $M^{-1\ d}$	$k_Q^R\tau_x,$ $M^{-1\ f}$
2-Methylbut-2-ene	8.89	<0.1	
Ethyl vinyl ether	8.49^c	0.7	
2,3-Dimethylbut-2-ene	8.30	2.4	2.3^e
Dihydropyran	8.34	3.9	4.2
Phenanthrene	8.10	5.0^g	
Triethylamine	7.50	9.4^e	8.7^e

^{a} [P] = 8 × 10^{-3} M, [F] = 0.1 M. ^{b} Adiabatic Ip's from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Fraxl, and F. H. Field, *Nat. Stand. Ref. Data. Ser., Nat. Bur. Stand.* No. 26 (1969). ^{c} M. P. Niemczyk, N. E. Schore, and N. J. Turro, *Mol. Photochem.*, **5**, 69 (1973). ^{d} Precision ±5% air saturated benzene. ^{e} Outgassed benzene. Air saturated values are the same within experimental error. ^{f} Precision ±10%. ^{g} From [P] dependence of $k_Q\tau$ values for quenching by 2,3-dimethyl-2-butene.
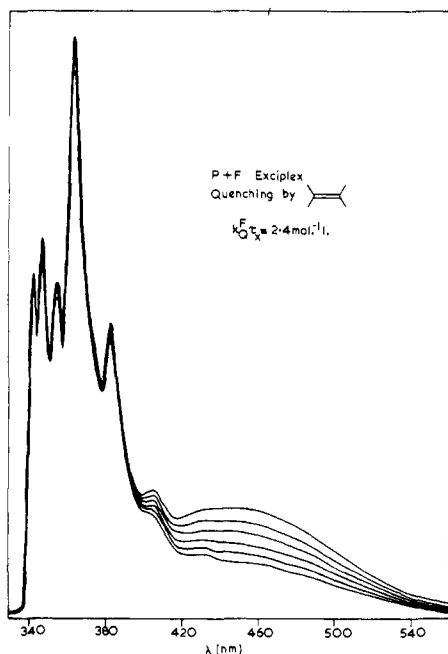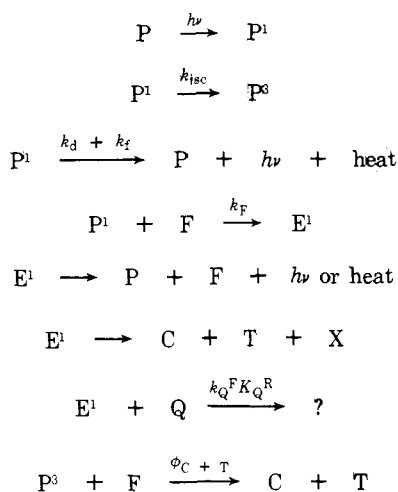
Figure 1.

Figure 2.

charge-transfer complexes between F and the donors does not affect the exciplex quenching rates within experimental error. The equilibrium constants for complex formation, although finite, are very low. An exciplex lifetime of about 1 nsec can be inferred[3] from O_2 quenching of the exciplex fluorescence.

Photoproduct formation is also attenuated by quenchers of the exciplex fluorescence. Stern–Volmer plots for the quenching of X (K) formation have the same slopes $(k_Q^R\tau_x)$ as those for exciplex fluorescence quenching $(k_Q^F\tau_x)$ for 2,3-dimethyl-but-2-ene, dihydropyran, and triethylamine as quenchers (Table I). The slopes for quenching of C and T formation deviate from linearity at high quencher concentrations (Figure 2). These observations can be quantitatively explained using the partial kinetic scheme[4]

$$P \xrightarrow{h\nu} P^1$$

$$P^1 \xrightarrow{k_{isc}} P^3$$

$$P^1 \xrightarrow{k_d + k_f} P + h\nu + heat$$

$$P^1 + F \xrightarrow{k_F} E^1$$

$$E^1 \longrightarrow P + F + h\nu \text{ or heat}$$

$$E^1 \longrightarrow C + T + X$$

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

$$P^3 + F \xrightarrow{\phi_{C+T}} C + T$$

in which no assumptions need be made as to the precise mechanism of formation of C, T, and X from the singlet exciplex (E^1).

In the absence of quenchers $\phi_{C+T} = 0.014$ at $0.1M$ F. From known[10] values of k_{isc}, k_d, k_f, k_F, and ϕ_{C+T} a residual quantum yield of C + T resulting from $p^1 \rightarrow p^3 \rightarrow C + T$ of 0.0019 can be calculated. Use of these parameters plus
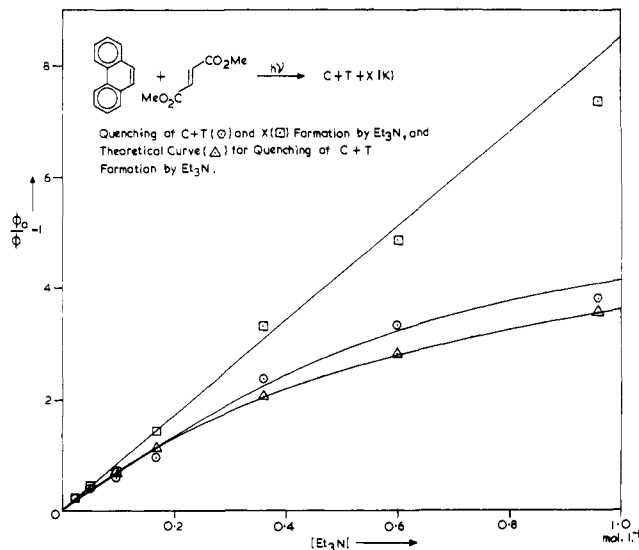
the Stern–Volmer slope for exciplex *fluorescence* quenching by triethylamine, allows calculation[11] of the dependence of ϕ_{C+T} on [Et_3N]. The fit between the calculated curve and the experimental points (Figure 2) offers strong support for the involvement of both the singlet exciplex and P^3 in the formation of C + T. Clearly the *exciplex is a viable precursor of all three products*. The singlet biradical suggested by Kaupp[7] does not readily explain the loss of stereochemical integrity, particularly when compared to other photochemically generated biradicals.[12] Since other P–olefin singlet exciplexes are known[3,6] to react stereospecifically, and the stereochemical consequences of the triplet sensitized reaction[4,5] of P and F are very similar to those of the direct[4] reaction, we believe that Farid's claim[4] of intersystem crossing in the P–F exciplex is correct.

Quenching of the exciplex is most probably a charge transfer phenomenon. In the exciplex $[P^{\delta+} \text{- -}{}^{\delta-}F]^*$, F is the donor and P the acceptor and the exciplex is quenched most effectively by another (ground state) donor. Electron acceptors such as dimethyl acetylenedicarboxylate ($k_Q\tau_x < 0.1$) and dimethyl fumarate itself ($k_Q\tau_x < 0.05$) are ineffective quenchers. These observations may imply a specific geometry for the *ter*molecular complex[13] (which we call an *exterplex*) most probably involved in the quenching. Other exciplexes show similar preference[14] for either electron donors or acceptors as efficient quenchers.

Further application of the method of exciplex quenching, both for emitting and nonemitting exciplexes, should lead to a better understanding of the role of exciplexes in photochemical reactions. We can now treat reactive exciplexes as distinct photoexcited entities. Electron and excitation transfer reactions of exciplexes, the perturbational effects of heavy atom and paramagnetic molecules on exciplexes, and other *termolecular* photochemical processes can now be explored.

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(11) This analysis leaves little room for enhanced intersystem crossing from an encounter complex preceding the exciplex. *cf.* (a) N. Orbach, R. Potashnik, and M. Ottolenghi, *J. Phys. Chem.*, **76**, 1133 (1972); (b) Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 591 (1972).

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Received July 26, 1974

The Cyclooctatetraene–Bicyclo[4.2.0]octatriene Equilibrium. A Striking Gradation in Secondary Deuterium Isotope Effects during Diels–Alder Reactions of Monosubstituted Derivatives

Sir:

The kinetically recognizable[1] disrotatory closure of cyclooctatetraene to *cis*-bicyclo[4.2.0]octatriene now serves as the basis for mechanistic discussion of its Diels–Alder reactivity. Empirical substituent effect data on this equilibrium are now appearing, chiefly as the result of investigations aimed primarily at unveiling positional specificity in such cycloadditions.[2] Supplementing these findings, we now report details of a secondary deuterium isotope effect study which reveals for the first time that fractionation factors associated with adduct formation are highly sensitive to the nature of the ring substituent and dienophile (DP).

Polyolefins **1b–d** were prepared in a high state of isotopic

a, R = CH$_3$; **b**, R= C$_6$H$_5$; **c**, R = COOCH$_3$; **d**, R = CN
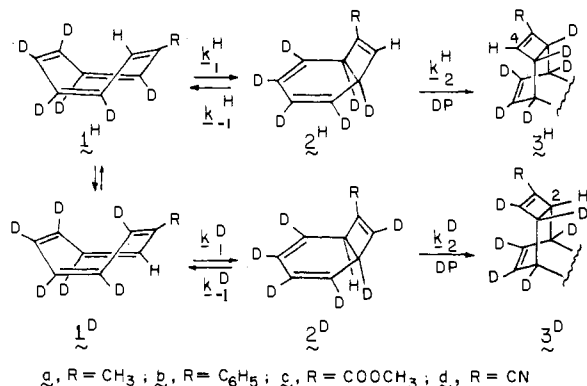
purity by suitable irradiation of the substituted acetylene in benzene-d_6[3] while methyl derivative **1a** was obtained by

further transformation of the ester. The direct involvement of **2** requires that production of adducts **3** be controlled by the kinetic expression

$$\frac{\mathrm{d}3^H/\mathrm{d}t}{\mathrm{d}3^D/\mathrm{d}t} = \frac{[1^H]}{[1^D]}\frac{k_1^H k_2^H (k_{-1}^D + k_2^D[\mathrm{DP}])}{k_1^D k_2^D (k_{-1}^H + k_2^H[\mathrm{DP}])} \tag{1}$$

which complicated function, herein referred to as case II behavior, has two limiting extremes. If the valence tautomerism occurs rapidly so that the cycloaddition is rate determining ($k_{-1} \gg k_2[\mathrm{DP}]$, case I), the rate equation simplifies to

$$\frac{\mathrm{d}3^H/\mathrm{d}t}{\mathrm{d}3^D/\mathrm{d}t} = \frac{[1^H]}{[1^D]}\frac{k_1^H k_2^H k_{-1}^D}{k_1^D k_2^D k_{-1}^H} \tag{2}$$

Conversely, when the cycloaddition rate is very fast ($k_2[\mathrm{DP}] \gg k_{-1}$, case III), closure to bicyclic form **2** becomes the rate-determining step

$$\frac{\mathrm{d}3^H/\mathrm{d}t}{\mathrm{d}3^D/\mathrm{d}t} = \frac{[1^H]}{[1^D]}\frac{k_1^H}{k_1^D} \tag{3}$$

The dienophiles employed were maleic anhydride (MA), tetracyanoethylene (TCNE), and dicyanomaleimide (DCMI). This trio represents a sliding scale of dienophilic capability ranging from the rather unreactive MA through the moderately reactive TCNE to DCMI which sometimes, but not always (*vide infra*), attains limiting case III behavior.[4] Of importance herein, all three undergo cycloaddition to **1** with exclusive capture of the 7-substituted bicyclo[4.2.0]octatrienes (**2**).[5]

Table I summarizes the available data. The cycloadditions were performed using 5–12-fold excess of the dienophile and the products were isolated by a combination of column chromatography and recrystallization. That variations in the amount of DP in this range do not measurably affect the ratios is seen for example in the **1c**-MA reaction where combination at equimolar levels afforded a fractionation factor of 1.50. Temperature and solvent effects are also of little consequence since this same cycloaddition in ethyl acetate at 131°, benzene at 131°, and chlorobenzene at 161° gave results of 1.49 ± 0.08, 1.51 ± 0.06, and 1.54 ± 0.07, respectively, nor are the spectral determinations biased in a direction which gives excess weighting to the H$_4$ signal because of some special magnetic factor (*e.g.*, altered transition probability).[6] Finally, a significant departure of the $1^H \rightleftarrows 1^D$ equilibrium from unity does not contribute to the partitioning of protium in the adducts. When **1c** was examined by pmr techniques at −41° (in CDCl$_3$),[7] the two signals due to 1^H (δ 7.14) and 1^D (6.07) were equally intense (K = 1.0 ± 0.01).

In the case of the **1b**-DMCI reaction, the limiting case III profile is reached.[1] On this basis, the isotope effect is exclusively k_1 dependent (eq 3) and its magnitude (1.08) ac-

Table I. Deuterium Isotope Effect Data ($3^H/3^D$)^a

| Compd | Dienophile^b | | |
	MA^c	TCNE^d	DCMI^e
1a	1.26 ± 0.05	1.08 ± 0.05	1.08 ± 0.04
1b	1.30 ± 0.04	1.11 ± 0.02	1.09 ± 0.03
1c	1.55 ± 0.05	1.39 ± 0.08	1.20 ± 0.03
1d	1.55 ± 0.06	1.41 ± 0.06	1.23 ± 0.08

^{a} Values relate to the intensity ratios of the H$_4$ and H$_2$ singlet absorptions (H$_4$/H$_2$) as determined by repeated integration of expanded scale 100-MHz pmr spectra. ^{b} All unlabeled counterparts of the 12 adducts have been prepared and fully characterized; mass spectra of the d_6 adducts show no loss of deuterium content. ^{c} Chlorobenzene solvent at reflux (132°). ^{d} Ethyl acetate solvent at reflux (77°). ^{e} Benzene solvent at reflux (80°).