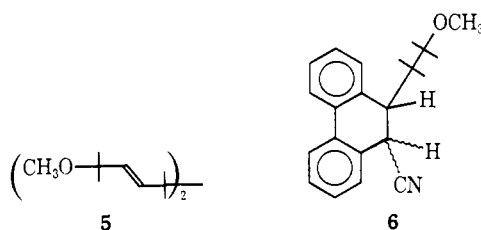


Table I

Olefin	IP, eV	$K_{q\tau}$, ^a M^{-1}	Adducts	Yield, ^b %	Mp, °C
2a	8.93 ^c		3a	80 (60)	141
2b		0.1	3b	80 (60)	117–118
2c	8.89 ^d	0.16	3c	–100 (>90)	212–213
2d	8.53 ^d	0.42	3d	–100 (>90)	186–188
2e	7.84 ^e	96.5	3e	–100 (65)	97.5–98.5

^a Quenching of **1** fluorescence by olefins; aerated cyclohexane solution; **1** concentration, 5×10^{-5} M; excitation at 310 nm. ^b Yields are based on unrecovered **1** and estimated by vpc. Numerals in parentheses are isolated yields. ^c K. Watanabe, T. Nakayama, and J. R. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962). ^d J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **81**, 2064 (1959). ^e D. A. Labianca, G. N. Taylor, and G. S. Hammond, *ibid.*, **94**, 3679 (1972).

rated product was not formed by irradiation of a methanolic solution of **1** in the presence of **2a**, **2b**, or **2c**, suggesting again a different mechanism from that of the photoreactions with **2d** and **2e**.



Thus the mechanism of these photocycloadditions depends on electron densities of olefins, *i.e.*, ionization potentials. This divergency in mechanism would be interpreted in terms of competition between the exciplex formation and intersystem crossing as well as efficiencies to final products from exciplexes;¹⁵ the higher the ionization potential of olefin, the slower the exciplex formation and the lower the efficiency will become. In line with this, **2b** and **2c**, possessing higher ionization potential, are very poor quenchers for fluorescence of **1**. Finally it should be noted that the photocycloaddition of **2a**, **2b**, and **2c** to **1** is commonly stereoselective, in sharp contrast to that of electron deficient olefins to phenanthrene^{16–19} which occurs from triplet phenanthrene¹⁸ or triplet exciplexes¹⁹ to yield mixtures of cyclobutane compounds. Although reasonable discussion of this stereoselectivity requires concrete determination of structures of the cycloadducts, a triplet exciplex mechanism would render an attractive speculation;²⁰ for example, triplet exciplexes of **1** and **2a–c** might be expected to be more strongly bonded than those of phenanthrene and electron deficient olefins.

(15) The exciplex to cycloadduct probabilities are very low for reactions of phenanthrene singlet with electron-poor olefins: R. A. Caldwell, private communication.

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(20) Alternatively, this stereoselectivity could be simply interpreted by steric factors. However, the exclusive formation of the sterically unfavorable endo adducts **3a** and **3b** cannot be reasonably interpreted. In this regard, it is noteworthy that photocycloaddition of **1** to trimethylsilyl vinyl ether, containing more bulky group than **2a** and **2b**, gave both endo and exo cycloadducts in a ratio of 3:2

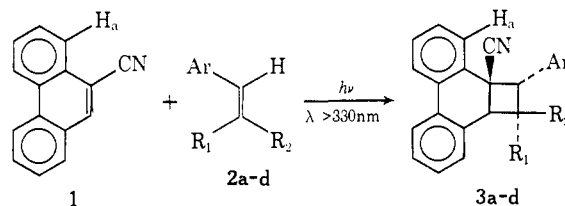
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Photocycloaddition of 9-Cyanophenanthrene to Substituted β -Methylstyrenes. An Obligatory Exciplex Intermediate

Sir:

The [2 + 2] photocycloaddition has often been interpreted as involving prior formation of a complex. The electronically excited nature of such a complex has been implied by analogy to know excimers¹ and exciplexes,^{2,3} but evidence has largely been indirect.⁴ One observation^{5a} of exciplex emission in a [2 + 2] photocycloaddition system has recently been questioned;^{5b} another report⁶ indicated no products. We now report the reactions⁷ **1** + **2a–d** \rightarrow **3a–d**, in which exciplex emission



- 2a**, Ar = C₆H₅; R₁ = H; R₂ = CH₃
b, Ar = *p*-CH₃OC₆H₄; R₁ = H; R₂ = CH₃
c, Ar = *p*-CH₃OC₆H₄; R₁ = CH₃; R₂ = H
d, Ar = *p*-CH₃OC₆H₄; R₁ = R₂ = CH₃

and photocycloaddition occur simultaneously, together with kinetic evidence that the exciplex is an obligatory intermediate in photocycloaddition.

Photocycloaddition is a singlet reaction with **2b** and **2c**; isoprene is not a quencher, but Michler's ketone is. Similar experiments revealed both singlet and triplet components with **2a**. In all cases, high regioselectivity⁸ and stereoselectivity occur (>98% with **2a** and **2b**, >95% with **2c**). Structure proofs follow from nmr

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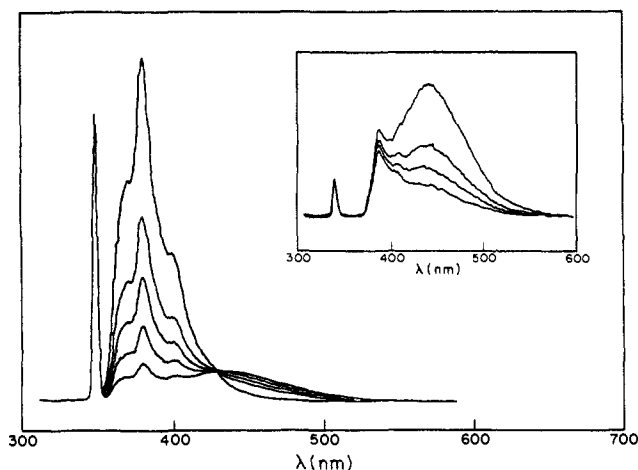


Figure 1. Attenuation of 9-cyanophenanthrene fluorescence by anethole and the concomitant exciplex emission. Insert: quenching of the exciplex emission by dimethyl acetylenedicarboxylate.

spectra, especially from the marked upfield shifts in **3** for H_a (δ 6.35–6.6) and R₁ methyls (δ 0.7) resulting from the various aromatic ring currents.

Table I summarizes the results of fluorescence quench-

Table I. Quenching of 9-Cyanophenanthrene Fluorescence by Styrene Derivatives

Quencher	$k_{QT},^a$ M^{-1}	Exciplex λ_{max}, nm	IP, ^c eV
2a	2.3		8.23
2b	90	435 ^b	7.62
2c	20	420 (est)	7.94
2d	67	448	

^a In air-saturated benzene. ^b Isooctane, 418 nm; neat anethole, 456 nm; acetone, 468 nm (weak). ^c Adiabatic values, measured on a Perkin-Elmer PS-18 photoelectron spectrometer. We thank Dr. J. N. A. Ridyard of P.-E. Ltd. for his kind cooperation. The IP of **1** was determined to be 8.44 eV.

ing experiments. On the addition of **2b**, **2c**, or **2d** to a solution of **1**, the fluorescence of **1** is quenched and a new long-wavelength emission appears. Isoemissive points indicate a stoichiometric relationship between **1** fluorescence and each new emission. This emission is absent in the fluorescence spectra of **2a–c**. The new emissions (cf. Figure 1) thus arise from 1:1 exciplexes. Solvent effects on **1:2b** exciplex fluorescence clearly demonstrate charge-transfer binding (Table I).⁹ Quenching of **1** fluorescence by **2a** was dramatically less efficient and afforded no new emission.

Exciplex formation and cycloaddition could be parallel and unrelated paths for quenching of singlet **1** by **2b**. Alternatively, the emitting exciplex could be a precursor of cycloadduct; this latter case in fact obtains. The exciplex emission is sharply attenuated by dimethyl acetylenedicarboxylate (**6**) ($k_{QT} = 64 \pm 5 M^{-1}$ in air-saturated benzene; cf. Figure 1). Since k_{QT} for quenching of singlet **1** by **6** is only $2.2 M^{-1}$, the quenching must be due to an interaction of **6** with the exciplex. An identical ($62 \pm 5 M^{-1}$) Stern–Volmer slope was obtained

(9) The effect of additional substituents in **1** is fully consistent with the solvent effect: R. A. Caldwell and N. I. Ghali, unpublished results.

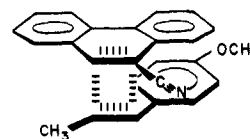


Figure 2.

for the attenuation of **3b** formation, demonstrating conclusively that the exciplex precedes cycloaddition. Further, oxygen quenching of the two processes is substantially the same; a ratio of N₂ to air-saturated exciplex emission intensity of 1.42 compares well with 1.54 for the cycloadduct formation rate ratio. Appropriate controls established that CT complexes involving **6** are not relevant. The inefficient quenching by **6** of the 380-nm emission (residual **1** monomer fluorescence), interestingly, demonstrates that exciplex formation here is largely or entirely irreversible.

The structures of **3a–d** may thus be understood on the basis of the "sandwich" exciplex (Figure 2). A similar geometry has been assigned to arene excimers^{1,10} and to the anthracene–naphthalene exciplex.¹¹ Significantly, an excellent match occurs in both phases and amplitudes for the highest bonding MO and lowest antibonding MO of the phenanthrene chromophore respectively with the corresponding MO's of the styrene chromophore.

Quantum yield studies afford estimates of exciplex → cycloadduct probabilities: **1:2b** → **3b**, 0.41; **1:2c** → **3c**, 0.3–0.4; **1:2d** → **3d**, 0.04–0.07. Clearly any comprehensive theory of reactivity in photocycloaddition must consider both factors which influence the rate of exciplex formation and factors which influence the rates of reactions of exciplexes: emission, collapse to cycloadducts, and collapse to the component cycloaddends. The result with **2b** suggests that collapse to cycloadduct can indeed be efficient when the exciplex binding is relatively strong, steric hindrance is absent, and the exciplex geometry is favorable. The aryl group may be very useful in helping the proper orientation of the two reacting bonds to be attained. We note that singlet exciplexes of phenanthrene with electron-poor alkenes containing no arene moieties give extremely low probabilities of cyclobutane formation.^{5a,12}

Exciplex lifetimes would be of great interest but have not yet been measured. Assuming diffusion-controlled oxygen quenching, the effect of air saturation on fluorescence intensity affords an estimate of 11 nsec for the **1:2b** exciplex and 36 nsec for **1:2d**. The quenching of **1:2b** by **6** then is estimated to have a rate constant of $ca. 8 \times 10^9 M^{-1} sec^{-1}$, i.e., also diffusion controlled. The longer lifetimes for **1:2d** requires that the low quantum yield for **3d** be due to slower collapse of **1:2d** to **3d** and not to rapid competing collapse to cycloaddends. A rationale based on steric hindrance to collapse seems attractive.

Observation of the same product structure for both the singlet and the triplet component of the reaction of **1** with **2a** might conceivably mean that a triplet exciplex, subject to the same geometric constraints as the singlet

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exciplex, is involved. If so, the apparent difference between the present result and other triplet arene [2 + 2] photocycloadditions for which exciplexes have been postulated, e.g., indene dimerization,^{4d} in which exo orientation of the aryl moieties occurs,¹³ remains obscure and merits close scrutiny.

Finally, both our observation of quenching of exciplexes by solute molecules and that of others⁴¹ offer good prospects for the detection of nonemitting exciplexes (by the demonstration of quenching by a molecule which does not quench the initially excited chromophore) plus an obvious *caueat* regarding the incautious interpretation of quenching experiments where long-lived exciplexes may be involved.

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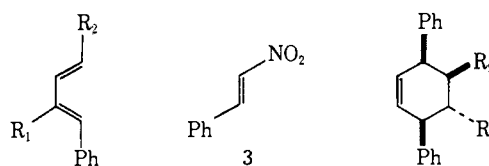
Some Novel Aspects of the Diels–Alder Reaction with 1,4- and 1,2-Diphenylbutadienes under Thermal and Lewis Acid Catalyzed Conditions¹

Sir:

A great deal of attention has been paid by theoretical chemists to explain the experimental facts of regio- and stereoselectivity of the Diels–Alder reaction ever since the propounding of the empirical rules by Alder and Stein,² and two of the recent and more successful such treatments are those of Herndon³ and Houk.⁴ It was reported earlier by us⁵ that in the addition of β -nitrostyrenes to 1,4-diphenylbutadiene electron withdrawing substituents in the 4'-position of the dienophile introduce striking stereoselectivity and lead to the formation of only the phenyl endo adducts (4). The work presented now shows some novel aspects of the stereoselectivity introduced by the Lewis acids and the steric control exerted by the 2-phenyl moiety in the addition of 1,2-diphenylbutadiene to β -nitrostyrene and cinnamic acid. These effects have been explained on the basis of the preferred geometry of the transition state. Any unified theoretical treatment will have to encompass these facts.

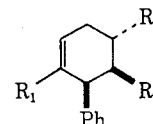
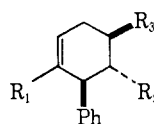
The addition reaction of 1 and 3 in benzene at 0° in presence of 1 molar equiv of SnCl₄ or AlCl₃ gave exclusively the nitro endo adduct 5, in contrast to the formation of equal proportions of both the phenyl endo

(4) and nitro endo (5) adducts under thermal conditions.^{5a} Treatment of the adducts formed under thermal conditions with Lewis acids did not change their stereochemistry.



- 1, R₁ = H; R₂ = Ph
2, R₁ = Ph; R₂ = H
10, R₁ = CH₃; R₂ = H

- 4, R₁ = NO₂; R₂ = Ph
5, R₁ = Ph; R₂ = NO₂
15, R₁ = CO₂H; R₂ = Ph



- 6, R₁ = Ph; R₂ = Ph; R₃ = NO₂
7, R₁ = R₂ = Ph; R₃ = NO₂
11, R₁ = CH₃; R₂ = Ph; R₃ = NO₂
14, R₁ = Ph; R₂ = Ph; R₃ = CO₂H
8, R₁ = R₂ = Ph; R₃ = NO₂
9, R₁ = R₂ = Ph; R₃ = NO₂
12, R₁ = CH₃; R₂ = Ph; R₃ = NO₂
13, R₁ = CH₃; R₂ = NO₂; R₃ = Ph

Reaction of 2 and 3 by heating in *o*-dichlorobenzene gave, of the four possible adducts 6–9, only 6 and 7, in a ratio of 72:25. 6 mp 159–160°; nmr (CCl₄)⁶ 4.78 (m, 5-H), 5.45 (dd, 4-H), 5.8 (d, 3-H); $J_{6e,5} = 6$, $J_{6a,5} = 10.5$, $J_{4,5} = 12$, $J_{3,4} = 10.5$ Hz. 7 mp 162–163°; nmr (CCl₄) 5.0 (dd, 4-H), 5.37 (d, 3-H), 6.38 (m, 5-H); $J_{3,4} = 10.5$, $J_{4,5} = 12.5$, $J_{5,6a} = 10.5$, $J_{5,6e} = 5$ Hz. These assignments were confirmed by introducing deuterium at 4 and 5 positions of the adducts by using α - and β -deuterio- β -nitrostyrenes as dienophiles in this condensation. The formation of 6 and 7 having 3,4 trans geometry is unusual; according to the usually accepted mode of Diels–Alder reaction, an ortho-cis product should be formed.⁷ When the addition of 2 to 3 was carried out in the presence of 1 molar equiv of SnCl₄ or AlCl₃, isomer 8 was the exclusive adduct: mp 162–163°; nmr (CCl₄) 4.55 (q, 4-H), 5.3 (d, 3-H), 6.5 (m, 5-H); $J_{3,4} = 5.5$, $J_{4,5} = 12$, $J_{5,6a} = 11$, $J_{5,6e} = 5$ Hz.

Lewis acids are known to cause rate acceleration⁸ of Diels–Alder reactions and markedly alter the isomer ratio,⁹ forming in some cases a larger ratio of the isomer not expected on steric considerations.¹⁰ A striking reversal of usual orientation in Diels–Alder reaction by Lewis acids has recently been reported by Dickinson, *et al.*¹¹ The formation of 8 under Lewis acid catalysis, having stereochemistry different from that of either of the adducts formed under thermal conditions, is thus novel and noteworthy.

(6) Nmr spectra were recorded at 60 and 220 MHz using Me₄Si as standard. Chemical shift is expressed in τ and J in Hz. Only relevant signals have been given.

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