

# Communications to the Editor

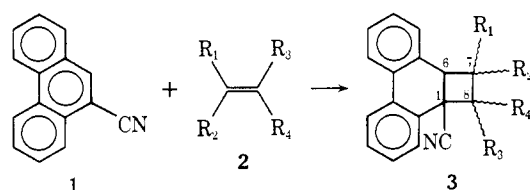
## Photocycloaddition of Olefins to 9-Cyanophenanthrene. Singlet Exciplex or Triplet Mechanism Depending on Olefins<sup>1</sup>

Sir:

Photocycloaddition to various aromatic nitriles, occurring across aromatic rings,<sup>2-5</sup> usually proceeds *via* excited singlet nitriles, and the mechanisms are discussed in relation with exciplexes.<sup>2,4</sup> However, it has been reported that benzonitrile undergoes photocycloaddition to tetrasubstituted, very electron-rich ethylenes at the nitrile function in an excited singlet state, whereas that occurs to less electron-rich olefins across the benzene ring from the  $\pi, \pi^*$ -triplet state.<sup>6</sup> This divergency in mechanisms depending on olefins is interesting, since exciplexes would appear to play important roles. In this paper, we wish to report the photoreactions of 9-cyanophenanthrene (**1**) with methyl vinyl ether (**2a**), ethyl vinyl ether (**2b**), 2-methyl-2-butene (**2c**), 2,3-dimethyl-2-butene (**2d**), and 2,5-dimethyl-2,4-hexadiene (**2e**) to yield common cyclobutane compounds **3a-e** in a stereoselective manner and show that the photoreactions with the former three olefins occur from triplet **1**, whereas in the latter two cases singlet exciplexes play important roles.

Irradiation of a benzene solution of **1** in the presence of **2a-e** gave a 1:1 adduct **3a-e** (Table I); in each case, only a single isomer was isolated.<sup>8</sup> Vpc and nmr analyses of photolysates or crude products showed that the other stereoisomer of **3a**, **3b**, **3c**, or **3e** could not be detected to any appreciable extent (<1-5%),<sup>9</sup> showing the stereoselective nature of the photocycloadditions.

The formation of compounds **3a**, **3b**, and **3c** was not only sensitized by Michler's ketone but also quenched



- 1  
 a,  $R_1 = R_2 = R_3 = H$ ;  $R_4 = OCH_3$   
 b,  $R_1 = R_2 = R_3 = H$ ;  $R_4 = OC_2H_5$   
 c,  $R_1 = H$ ;  $R_2 = R_3 = R_4 = CH_3$   
 d,  $R_1 = R_2 = R_3 = R_4 = CH_3$   
 e,  $R_1 = H$ ;  $R_2 = CH=C(CH_3)_2$ ;  $R_3 = R_4 = CH_3$

by isoprene,<sup>10</sup> apparently indicating the intermediacy of *triplet* **1**. In contrast, the photoreaction with **3d** could not be sensitized but was remarkably quenched by Michler's ketone. Moreover, quenching by isoprene was not so significant up to 1.0 M in the diene. Thus these results suggest a singlet mechanism. For the photocycloaddition of **2e** to **1**, a singlet mechanism was established by fluorescence quenching studies and quantum yield measurements,<sup>11</sup> which gave identical  $k_q\tau$  values, 162 and 168  $M^{-1}$ , respectively.

From a mechanistic point of view, it is noteworthy that the fluorescence quenching by **2e** was accompanied with enhancement of longer wavelength emission and appearance of an isoemissive point at 427 nm. Further increase in concentration of **2e** up to *ca.* 0.3 M resulted in appearance of a weak, broad emission at  $\lambda_{max}$  410-420 nm, demonstrating the formation of a *singlet exciplex*. This would therefore suggest that the photocycloaddition of **2e** to **1** proceeds *via* a *singlet exciplex*. This exciplex mechanism would be further supported by the observation that the photoreaction of **1** with **2e** in methanol gave 9,10-dihydro-9-cyanophenanthrene (**4**) and a solvent-incorporated product **5** in 90% yields which apparently arise from ion radicals.<sup>12</sup> It is well known that emissive singlet exciplexes possessing a charge transfer character dissociate into ion radicals in polar media.<sup>13,14</sup> This type of solvent effect could also be observed in the photoreaction with **2d**; irradiation of a methanolic solution of **1** in the presence of **2d** gave 50% of **4** and 20-30% of solvent-incorporated products **6** (cis and trans mixture) accompanied with *ca.* 10% of **3d**. Accordingly, a singlet exciplex mechanism would be favorable for the photoreaction with **2d**, though direct evidence is lacking. In contrast, any solvent-incorpo-

(10) The photocycloaddition of benzene solutions 1.5-2.0 M in **2a-c** and 1.0 M in isoprene occurs at a rate only one-fourth that in the absence of added quencher. It was confirmed that isoprene was very inert to quenching of fluorescence of **1** ( $k_q\tau < 0.1 M^{-1}$ ) and photoreaction with **1**.

(11) Quantum yield for disappearance of **1** was determined for degassed cyclohexane solution containing various amounts of **2e** (1.0-0.0042 M) at 313 nm, using a potassium ferrioxalate actinometer. (12) Ionic nature for the formation of **4** was confirmed by irradiation of a methanol-*O-d* solution containing **1** and **2d** or **2e** which gave 4-9,10-*d\_2* in place of **4**.

(13) For review, see M. Ottolenghi, *Accounts Chem. Res.*, **6**, 153 (1973).

(14) The exciplex of **1** and **2e** can be considered to be a charge transfer complex in nature from the solvent dependent shift of the exciplex emission; solvents (dielectric constants,  $\lambda_{max} \pm 5$  nm) cyclohexane (2.023, 415), di-*n*-butyl ether (3.06, 425), diethyl ether (4.34, 435), and acetone (20.7, 483).

(1) Part XIX of Photochemical Reactions of Aromatic Compounds. Part XVIII: C. Pac, K. Mizuno, T. Tosa, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) (a) C. Pac, T. Sugioka, and H. Sakurai, *Chem. Lett.*, 39 (1972); (b) T. Sugioka, C. Pac, and H. Sakurai, *ibid.*, 667 (1972); (c) C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai, *ibid.*, 187 (1973); (d) K. Mizuno, C. Pac, and H. Sakurai, *ibid.*, 309 (1973); (e) C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai, *Bull. Chem. Soc. Jap.*, **46**, 238 (1973).

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(4) N. C. Yang, J. Libman, L. Barret, Jr., M. H. Hui, and R. L. Loesch, *J. Amer. Chem. Soc.*, **94**, 1406 (1972).

(5) J. G. Atkinson, D. E. Ayer, G. Buchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963).

(6) T. S. Cantrell, *J. Amer. Chem. Soc.*, **94**, 5929 (1972).

(7) A benzene solution (50 ml) containing 0.3 g of **1** and 5-10 ml of an olefin, placed in a test tube, was irradiated under nitrogen atmosphere at room temperature by a high-pressure mercury arc. In the case of **2e**, over irradiation led to accumulation of secondary products.

(8) For the products except **6**, sufficient analytical data were obtained. For all the products reported here, the spectral properties are in accord with the structures assigned, though endo or exo configuration of the C-substituents of **3c** and **3e** has not been determined yet. Endo location of the alkoxy group of **3a** and **3b** was tentatively assigned from comparison of nmr spectra with those of similar compounds; see ref 2d, 2e, and 20.

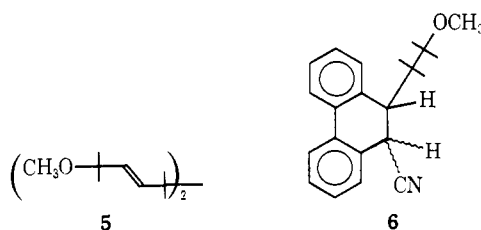
(9) In nmr analyses of reaction mixtures obtained by irradiation of **1** and **2b** or **2e**, difficulties were encountered, since some oligomeric and/or polymeric materials of the olefin were formed. However, there was observed no signal of epimers in nmr spectra of crude products, after such oligomeric materials had been removed by column chromatography on a short column of silica gel.

Table I

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

<sup>a</sup> Quenching of **1** fluorescence by olefins; aerated cyclohexane solution; **1** concentration,  $5 \times 10^{-5}$  M; excitation at 310 nm. <sup>b</sup> Yields are based on unrecovered **1** and estimated by vpc. Numerals in parentheses are isolated yields. <sup>c</sup> K. Watanabe, T. Nakayama, and J. R. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962). <sup>d</sup> J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **81**, 2064 (1959). <sup>e</sup> 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;<sup>15</sup> 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<sup>16–19</sup> which occurs from triplet phenanthrene<sup>18</sup> or triplet exciplexes<sup>19</sup> 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;<sup>20</sup> 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.

(16) D. Bryce-Smith and B. Vickery, *Chem. Ind. (London)*, 429 (1961).

(17) T. Miyamoto, T. Mori, and Y. Odaira, *J. Chem. Soc., Chem. Commun.*, 1598 (1972).

(18) S. Farid, J. C. Doty, and J. L. R. Williams, *J. Chem. Soc., Chem. Commun.*, 711 (1972).

(19) R. A. Caldwell, *J. Amer. Chem. Soc.*, **95**, 1690 (1973).

(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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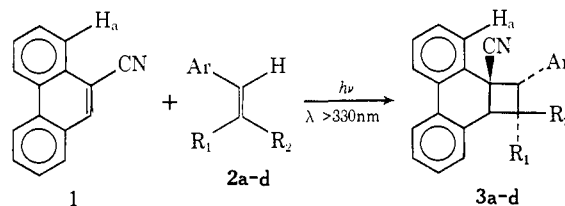
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### Photocycloaddition of 9-Cyanophenanthrene to Substituted $\beta$ -Methylstyrenes. An Obligatory Exciplex Intermediate

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 excimers<sup>1</sup> and exciplexes,<sup>2,3</sup> but evidence has largely been indirect.<sup>4</sup> One observation<sup>5a</sup> of exciplex emission in a [2 + 2] photocycloaddition system has recently been questioned;<sup>5b</sup> another report<sup>6</sup> indicated no products. We now report the reactions<sup>7</sup> **1** + **2a–d**  $\rightarrow$  **3a–d**, in which exciplex emission



**2a**, Ar = C<sub>6</sub>H<sub>5</sub>; R<sub>1</sub> = H; R<sub>2</sub> = CH<sub>3</sub>

**b**, Ar = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; R<sub>1</sub> = H; R<sub>2</sub> = CH<sub>3</sub>

**c**, Ar = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; R<sub>1</sub> = CH<sub>3</sub>; R<sub>2</sub> = H

**d**, Ar = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>

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 regioselectivity<sup>8</sup> and stereoselectivity occur (>98% with **2a** and **2b**, >95% with **2c**). Structure proofs follow from nmr

(1) Th. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969), and references therein.

(2) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

(3) M. Ottolenghi, *Accounts Chem. Res.*, **6**, 153 (1973), and references therein.

(4) See, for example, (a) P. DeMayo, *Accounts Chem. Res.*, **4**, 41 (1971), and references therein; (b) O. L. Chapman and R. D. Lura, *J. Amer. Chem. Soc.*, **92**, 6352 (1970); (c) D. O. Cowan and R. L. E. Drisko, *ibid.*, **92**, 6281, 6286 (1970); (d) C. D. DeBoer, *ibid.*, **91**, 1855 (1969); (e) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *ibid.*, **92**, 4106 (1970); (f) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971); (g) W. Ferree, Jr., J. R. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971); (h) R. A. Caldwell, *ibid.*, **95**, 1690 (1973); (i) T. Sugioka, C. Pac, and H. Sakurai, *Chem. Lett.*, 667 (1972); (j) K. Mizuno, C. Pac, and H. Sakurai, *ibid.*, 309 (1973). For evidence in [4 + 4] systems, see (k) N. C. Yang, J. Libman, and M. F. Savitzky, *J. Amer. Chem. Soc.*, **94**, 9226 (1972); (l) J. Saltiel and D. E. Townsend, *ibid.*, **95**, 6140 (1973).

(5) (a) S. Farid, J. C. Doty, and J. L. R. Williams, *J. Chem. Soc., Chem. Commun.*, 711 (1972); (b) G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **12**, 765 (1973).

(6) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

(7) All new compounds gave satisfactory analyses.

(8) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 5624 (1973).