Registry No. 2, 83435-86-3; **3**, 83435-87-4; [Fe(TPP)]$_2$O, 12582-61-5; ferric perchlorate, 13537-24-1.

Supplementary Material Available: Listing of positional and thermal parameters (11 pages). Ordering information is given on any current masthead page.

Conformations and Competitive [2 + 2] Cycloadditions of Intramolecular Exciplexes of Some Anisylalkenyl 9-Phenanthrenecarboxylates

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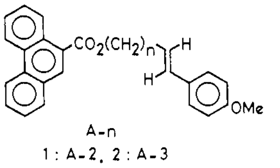
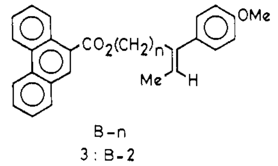
Exciplexes are intermediates in the [2 + 2] photocycloadditions of 9-cyanophenanthrenes with styrene derivatives, and the products formed are those of maximum "sandwich" overlap of the chromophores at the transition state for the reaction.[1] With 9-cyanophenanthrene and *trans*-anethole, only a "head-to-head" product was obtained, but substituents in some cases caused the formation of "head-to-tail" products.[2] Others[3] have amply demonstrated the value of interchromophoric links in studying geometric and conformational relationships between reacting chromophores. In the course of studying the effect of conformational constraints on the phenathrene–styrene reaction, we have found that interchromophoric links with an ester group bring about a novel aspect of the reaction, a competitive cycloaddition of intramolecular exciplexes involving carbonyl addition. We have prepared esters **1**–**3** from 9-phenanthrenecarbonyl chloride and the corresponding alcohols.[4] We have compared photochemical[5] and photophysical results for **1**–**3** with those for 9-(methoxycarbonyl)phenanthrene (**4**) and *trans*-anethole (**5**) as an unlinked model. In the B series, head-to-head cycloaddition can and does result, while in the A series cyclobutane photoproducts are not detected. The major photochemical process are in both series those of carbonyl addition.



A-n
1 : A-2, 2 : A-3



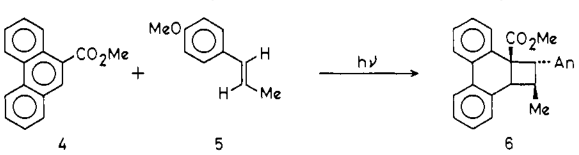
B-n
3 : B-2

Table I. Disappearance Quantum Yields and Photophysical Parameters for **1**–**4**

compd	ϕ(disapp)[a]	ϕ_f[b]	τ_f, ns[c]	λ_m(exciplex), nm[e]
1	0.36	0.07	3.9	NO[f]
2	0.61	0.04	3.2	450
3	0.70	0.06	5.2	450
4	0.11[d]	0.25	15.3	450

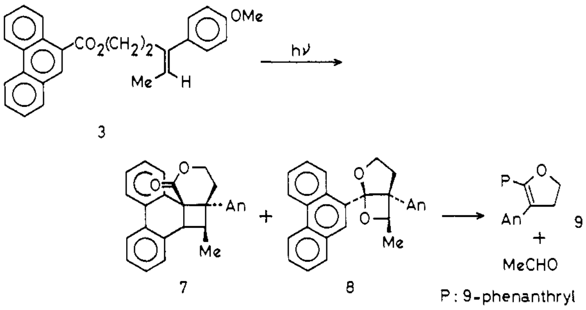
[a] In benzene at 366 nm vs. potassium ferrioxalate. Substrate concentration 5 × 10^{-4} M. [b] Recorded on a Hitachi MPF4 spectrofluorimeter and calculated relative to ϕ_f = 0.13 for phenanthrene; see: Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1971; p 376. [c] By single-photon counting with an Applied Photophysics SP-3X system. [d] Extrapolated to infinite anethole concentration. [e] Obtained by subtraction of the fluorescence spectrum of **4** after normalization. Results are identical for normalization at 367 (0, 0) or 383 nm (λ_{max}). [f] Not observed.

The photochemical cycloaddition of **5** to **4**[6] clearly affords a head-to-head adduct **6** of the expected[2] stereochemistry. The reaction is a singlet process. We observe $k_Q\tau$ = 46 M^{-1} for quenching of **4** fluorescence by **5**. Weak exciplex emission (λ_{max} 450 nm) was observed.



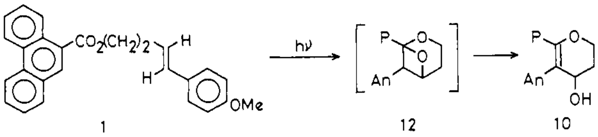
An : p-anisyl

Irradiation of **3** in benzene[5] afforded a cyclobutane (**7**, 15% yield) and a bicyclic acetal (**8**, 65%). The structure of **7** is analogous to **6** as demonstrated by comparison of their NMR spectra. Compound **8** is a [2 + 2] cycloadduct between the ester carbonyl group and the olefinic double bond.[7] During the measurement of an NMR spectrum in CDCl$_3$, **8** slowly decomposed to give a dihydrofuran **9** (loss of acetaldehyde). Repeated chromatography of **8** on silica gel with CHCl$_3$ gave **9** (51% yield based on **3** consumed).[8]



P : 9-phenanthryl

Irradiation of esters **1** and **2** in benzene gave a dihydropyranol (**10**, 54%) and a dihydrooxepine (**11**, 57%) respectively.[5] There



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[1] Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45.

[2] Caldwell, R. A.; Ghali, N. I.; Chien, C.-K.; DeMarco, D.; Smith, L. *J. Am. Chem. Soc.* **1978**, *100*, 2857.

[3] Van den Auweraer, M.; Gilbert, A.; DeSchryver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4007. McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1980**, *102*, 7780 and references cited therein.

[4] Synthetic procedures will be reported elsewhere. Spectral data and elemental analyses were satisfactory.

[5] Preparative irradiations were carried out at 5 × 10^{-4} M with a high-pressure mercury lamp. Product structures were assigned from spectral data and are consistent with elemental analyses.

[6] At 0.02 M **4** and 0.03 M **5** in 9:1 benzene–isoprene with a low-pressure mercury lamp. Analysis was satisfactory and the NMR spectrum was nearly identical (except for the ester methyl) with that for the 9-cyanophenanthrene–**5** photoadduct.[2]

[7] Shigemitsu, Y.; Katsuhara, Y.; Odaira, Y. *Tetrahedron Lett.* **1971**, 2887. Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. Lewis, F. D.; Johnson, D. E. *Ibid.* **1978**, *100*, 983. Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. L. R. *Ibid.* **1975**, *97*, 3697.

[8] Bichan, D.; Winnik, M. *Tetrahedron Lett.* **1974**, 3857.

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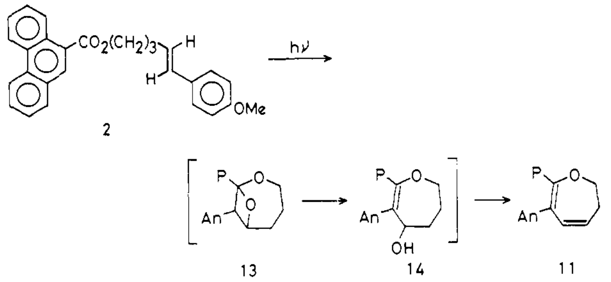

was no spot in the TLC of either reaction mixture that could be ascribed to a cyclobutane adduct. The only unidentified spots showed $R_f \sim 0$ and corresponded to small amounts of material. The products **10** and **11** can be rationalized by the initial formation of **12** and **13**, respectively, analogous to the **3** → **8** reaction, followed by obvious polar rearrangements and (for **11**) dehydration. That **10** and **11** are not primary photoproducts is shown by their absence in TLC of reaction mixtures.

Disappearance quantum yields and photophysical parameters for **1–4** are given in Table I.[9] The lower ϕ_f and shorter τ_f for **1–3** compared to **4** clearly demonstrate dominant intramolecular singlet interaction between the chromophores, and the high ϕ(disapp) values confirm its ultimate chemical nature. That exciplexes are indeed intermediates in at least the formation of the oxetanes from **1** and **2** is strongly suggested by a 10–20% greater quenching of product formation than of the phenanthroate fluorescence by molecular oxygen.[10]

Formation of cycloadducts is very efficient from the exciplexes. The lifetimes in the table and the reasonable assumption of a structure-independent fluorescence rate constant for the phenanthroate chromophore afford intramolecular quenching probabilities for **1**, **2**, and **3** of 0.74, 0.80, and 0.69. The corresponding exciplex → product probabilities are 0.49, 0.76, and 1.0, respectively.

That structures so different as cyclobutanes **6** and **7** and oxetanes **8** and **13** arise from exciplexes with identical fluorescence maxima suggests that the energies of these exciplexes are rather insensitive to their geometries. The intramolecular cycloadditions of McCullogh behave analogously.[3] Various photophysical measurements for intramolecular exciplexes[11] afford the same conclusion.

We believe that the strong preference for oxetane rather than cyclobutane formation from **1–3** arises from the conformational constraints of the aroyl ester group.[12-16] Esters in general strongly prefer a conformation for the C–O single bond in which the alkyl group and carbonyl oxygen are cis and the carbonyl and *O*-alkyl bonds are coplanar.[12-16] In all such conformations, the formation of cyclobutane is precluded as can readily be seen from Dreiding models. That **7** forms at all is evidence that this conformation is not absolutely enforced. It is also possible that restricted rotation around the phenanthrene–carbonyl bond[17] contributes to the disfavoring of cyclobutane formation, since models show that such rotation is probably necessary for close approach of the C=C double bonds. Finally, the models show that access of the carbonyl oxygen to the β position of the *p*-methoxystyryl moiety, which leads to all the oxetanes, can be accomplished in the favored conformation of the ester C–O single bond without serious difficulty.

Acknowledgment. We thank Dr. Takashi Tamaki, Research Institute for Polymers and Textiles, for valuable assistance with the fluorescence studies. R.A.C. acknowledges helpful conversations with Professor M. A. Winnik. Work at The University of Tsukuba was financially supported in part by a Grant-in-aid from the Ministry of Education, Science, and Culture of Japan. Work at the University of Texas at Dallas was partially supported by The Robert A. Welch Foundation (Grant AT-532).

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(9) Fluorescence lifetimes and quantum yields of esters A-1, A-4, B-1, B-3, and B-4 were also measured. Intramolecular fluorescence quenching was ineffective for all compounds except for B-3. Ester B-3 was similar to B-2 in photochemical and photophysical behavior according to preliminary results. Ester A-4 showed weak exciplex emission, but preparative irradiation[5] afforded almost quantitative recovery of starting material even on prolonged irradiation.

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(14) Riveros, J. M.; Wilson, E. B., Jr. *J. Chem. Phys.* **1967**, *46*, 4605.

(15) Curl, R. F., Jr. *J. Chem. Phys.* **1959**, *30*, 1529.

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(17) Although apparently undocumented for esters, the analogous restriction for benzaldehydes and acetophenones is well-known,[13,14] as is its relevance to aryl ketone photochemistry.[18]

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Evidence for Oxide Transfer from Coordinated CO_2 to Coordinated CO in an Anionic CO_2 Complex

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We recently reported that CO_2 could be reduced to coordinated CO by reaction with transition-metal carbonylate dianions and suggested that the reactions might involve formation of intermediate carbon dioxide complexes such as $[W(CO)_5CO_2]^{2-}$ ($\mathbf{1}^{2-}$, eq 1).[1] We now report experiments that support the intermediacy

$$\underset{\mathbf{2}^{2-}}{[W(CO)_5]^{2-}} \xrightarrow{CO_2} \underset{\mathbf{1}^{2-}}{[W(CO)_5CO_2]^{2-}} \xrightarrow{CO_2} \underset{\mathbf{3}}{[W(CO)_6]} + CO_3^{2-} \qquad (1)$$

of a species with a composition corresponding to that of $\mathbf{1}^{2-}$ in the reaction of $Li_2[W(CO)_5]$ ($Li_2\mathbf{2}$) with CO_2, spectral studies consistent with its formulation as an η^1-CO_2 complex, and labeling studies that suggest that transfer of oxide from coordinated CO_2 to coordinated CO is facile in this anionic complex.

The infrared spectrum shown in Figure 1 is obtained when 1 equiv of CO_2 is added slowly (30 min) to a 0.05 M solution of $Li_2[W(CO)_5]$[2] in tetrahydrofuran (THF) at −78 °C and the mixture allowed to warm to room temperature. The spectra of such solutions have been observed to remain unchanged after storage for 40 h at 0 °C, and since the characteristic absorptions of $Li_2\mathbf{2}$ are not observed[4] and only small quantities of $[W(CO)_6]$ have been formed, this suggests the formation of a relatively thermally stable complex whose composition is that of the simple CO_2 adduct $Li_2[W(CO)_5CO_2]$ ($Li_2\mathbf{1}$).

The spectrum in Figure 1 is consistent with formulation of $\mathbf{1}^{2-}$ as a species with C_{4v} symmetry.[5,6] The absorptions at 1899 (vs) cm^{-1} and 1865 (s) cm^{-1} can be assigned to the IR-active E symmetry stretch of the equatorial carbonyls and the A_1 symmetry stretch of the axial carbonyl, respectively, in agreement with the relative intensities of the bands, while the weak band at 2043 cm^{-1} can be assigned to the A_1 stretching mode of the equatorial

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† Fellow of the Alfred P. Sloan Foundation, 1982–1984.

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(2) Typically prepared on a 1-mmol scale by lithium napthalide reduction of $[W(CO)_5NMe_3]$.[3]

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(6) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: New York, 1975; Chapter 7 and references therein.