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Structural Effects on Photochemical Intermolecular Cycloaddition of Phenanthrenecarboxylic Lactones. Dual Collapse Processes of an Exciplex Leading to Cycloadducts

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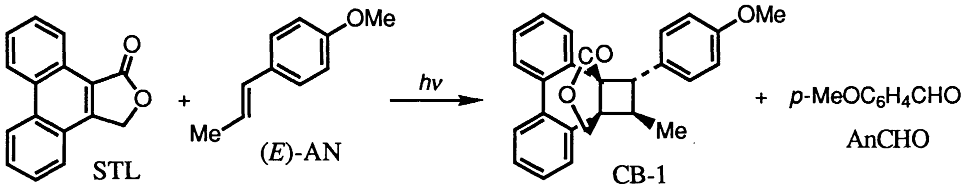
On irradiation with (*E*)-anethole in benzene 10-hydroxymethyl-9-phenanthrenecarboxylic lactone (STL) gave an intermolecular [2+2] cycloadduct, a cyclobutane derivative, while 8-hydroxymethyl-9-phenanthrenecarboxylic lactone (SCL) afforded both of a cyclobutane with the same conformation and an olefinic product derived from an oxetane precursor, the carbonyl adduct. The formation of cycloadducts of highly different structures in SCL was ascribed to competitive collapse of the involved exciplex to the products.

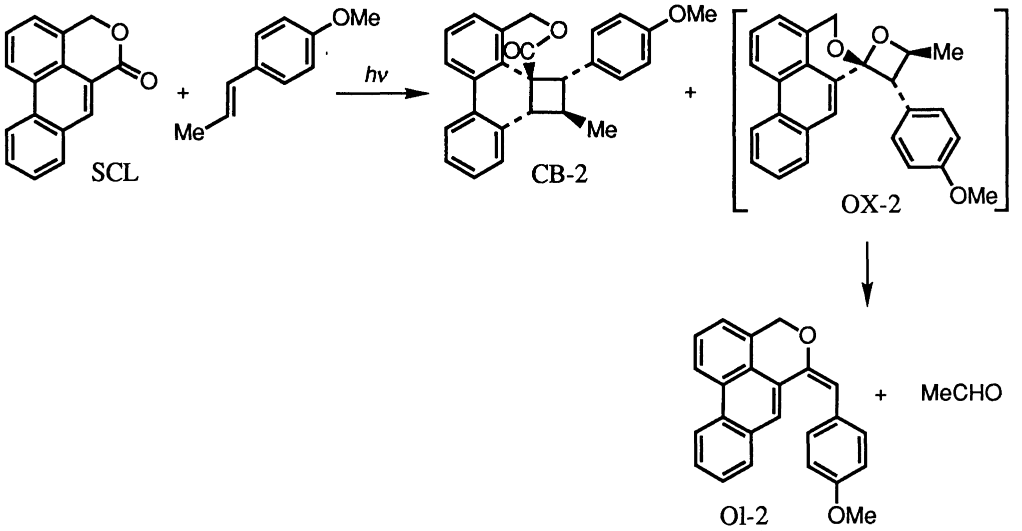
Photochemical [2+2] cycloaddition is one of the most important and well-studied reactions.[1–5] Exciplexes are intermediates in this cycloaddition, and the products formed are those of maximum overlap of the chromophores at the transition state for the reaction.[1–3] On excitation of methyl 9-phenanthrenecarboxylate (9-MCP) with (*E*)-anethole [(*E*)-1-(*p*-methoxyphenyl)propene, (*E*)-AN], only a cyclobutane derivative, the head-to-head cycloadduct, was obtained, but incorporation of the two chromophores in one molecule separated by a polymethylene chain brought about a new aspect of the competitive cycloaddition through intramolecular exciplexes involving carbonyl addition.[6] This can be ascribed to a change of the photochemical properties of the respective chromophores by imposing conformational constraints on intramolecular processes.

In order to get further insight into the structural factors controlling the carbonyl addition we undertook a study on behavior of *intermolecular* exciplexes arising from rigid planar phenanthrenecarboxylic lactones and (*E*)-AN. For 9-phenanthrenecarboxylates, a conformation in which the 9-10 bond of the phenanthrene ring and the carbonyl bond are s-trans is assumed to be preferable, and this is the case for 4-methoxyphenylalkenyl 9-phenanthrenecarboxylates which show the competitive intramolecular cycloadditions.[6,7] Esters in general strongly prefer a conformation for the C-O single bond in which the alkyl group and carbonyl group are s-cis, and the carbonyl and *O*-alkyl bonds are coplanar.

As rigid planar substrates, 10-hydroxymethyl-9-phenanthrenecarboxylic lactone (STL) and 8-hydroxymethyl-9-phenanthrenecarboxylic lactone (SCL) were prepared; STL and SCL have conformations where the 9-10 and carbonyl bonds are s-trans and s-cis, respectively, and the *O*-alkyl moiety and carbonyl group are fixed to be s-trans (Schemes 1 and 2). On irradiation with (*E*)-AN, STL afforded only a [2+2] cyclobutane adduct, whereas the exciplex of SCL collapsed competitively to a cyclobutane and an oxetane.



Scheme 1.



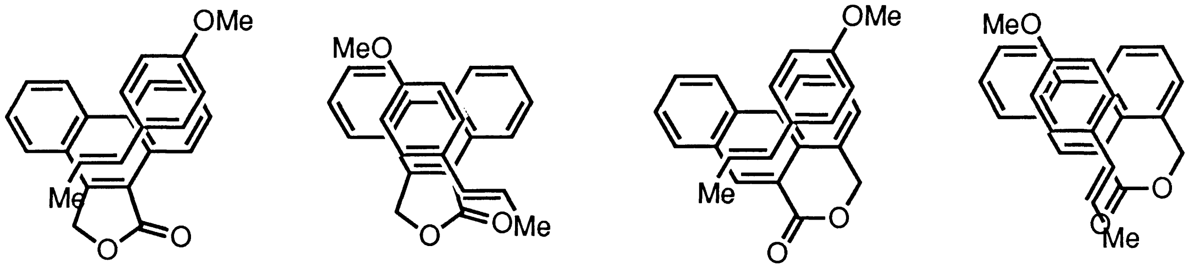
Scheme 2.

On irradiation of STL (4×10^{-3} mol dm^{-3}) in benzene in the presence of (*E*)-AN (5×10^{-3} mol dm^{-3}) under nitrogen with 366-nm light from a 450-W high-pressure mercury lamp through a uranium glass wall, a cyclobutane[8] (CB-1) was produced in 15% yield together with *p*-methoxybenzaldehyde[9] (AnCHO, 10% yield) (Scheme 1). CB-1 has the same conformation as the head-to-head cycloadduct from 9-MCP with (*E*)-AN.[6] Similar irradiation of SCL (3×10^{-3} mol dm^{-3}) with (*E*)-AN (3×10^{-3} mol dm^{-3}) in benzene, however, gave both of a cyclobutane[10] (CB-2, 19%) and an olefin[11] (Ol-2, 23%) (Scheme 2). The products were isolated by preparative HPLC [SiO_2, hexane-ethyl acetate (5:1)] and identified on the basis of the various spectral data. CB-1 and CB-2 are [2+2] head-to-head cycloadducts at the 9-10 bond of the lactones, and Ol-2 is a secondary product which might be derived from the carbonyl adduct OX-2 through elimination of acetaldehyde during the separation. Similar cleavage was observed for an oxetane, the intramolecular carbonyl adduct of (*E*)-3-(*p*-methoxyphenyl)-3-pentenyl 9-phenanthrenecarboxylate.[6a,12]

The efficiencies of reaction were very low for STL (limiting quantum yield for disappearance at [(*E*)-AN]$\rightarrow\infty$, $\phi^r \le 10^{-3}$), but much higher for SCL ($\phi^r = 0.13$). The latter value is comparable to that for the photocycloaddition of 9-MCP to (*E*)-AN. Similarity of STL in reaction mode to 9-MCP could be ascribed to their analogous conformations in which the 9-10 and carbonyl bonds are s-trans.

The cycloadditions proceed through exciplexes formed from the lactone singlets. The lactones, STL and SCL, exhibited their fluorescence spectra in benzene in the wavelength region similar to that of 9-MCP; that of STL appears in slightly shorter wavelengths. The fluorescence lifetime (τ_f) and quantum yield (ϕ_f) were also similar in the two lactones; τ_f=22.0 ns and ϕ_f=0.26 for STL and τ_f=15.5 ns and ϕ_f=0.20 for SCL. The fluorescence spectra of STL and SCL were efficiently quenched by (*E*)-AN in benzene ($k_q = 7.1\times10^9$ and 6.1×10^9 M^{-1} s^{-1}, respectively) with an isoemissive point (455 and 470 nm, respectively) and weak exciplex emissions were observed in the longer wavelength region (430-480 and 450-500, respectively). There are no large differences in physical properties of the excited singlet state of STL, SCL, and 9-MCP, and all the three compounds afford the head-to-head cycloadducts. Nevertheless, only SCL gives the oxetane in addition to the cyclobutane.

The difference in photochemical behavior might arise from the structure of exciplexes involved and their collapse processes. In intermolecular cycloadditions the precursor exciplexes can generally take a conformation of maximum overlap of the chromophores at the transition state for the reaction.[1-3] For STL and 9-MCP the cyclobutane derivatives are produced, though the efficiencies are very much different, through an exciplex with the most stable conformation, but the formation of oxetanes might require another exciplex with a less stable conformation. Thus, the latter process could not compete with the former. The higher stability of the former conformation for cyclobutane is confirmed by application of perturbation theory,[13,14] which estimates overlap interactions of molecular orbitals involved in bond formation in the conformations with an appropriate distance between the chromophores.[15,16] Dreiding models show that interconversion between the two conformations favorable for cyclobutane and oxetane formation needs a rotation of 180° about the long molecular axis and a rotation of 60° about the axis perpendicular to the molecular plane of one of the partner molecules (Fig. 1a). Accordingly, only the exciplex leading to cyclobutane is essentially formed. For SCL, the conformations of maximum overlap resulting in cycloadducts (Fig. 1b) are in a similar situation to the case of STL; however, these two conformations can be easily converted to each other by a 60° rotation of either component molecule about the axis perpendicular to the molecular plane with keeping the parallel relation. Furthermore, the interorbital interaction integral between carbon and oxygen atoms, γ_{CO}, is much lower at a long distance like 350 pm than that between carbon atoms, γ_{CC}; however, at a very close distance like 150 pm, γ_{CO} exceeds γ_{CC}.[19,20] This might affect the transition state of carbonyl addition.



a) STL b) SCL

Fig. 1. Conformations of intermediates favorable for formation of the cycloadducts in STL and SCL.

In the intramolecular cases, the exciplex affording a cyclobutane and that giving an oxetane are similar in energy due to the conformational constraints, and each product might arise from a particular exciplex; *the formation of exciplexes might be competitive.* In the present intermolecular case, however, we believe that a sole exciplex contributes to the formation of both cycloadducts by *competitive exciplex→product collapse.*

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7) This is supported by comparison of NMR data for these compounds together with methyl 8-methyl-9-phenanthrenecarboxylate and methyl 10-methyl-9-phenanthrenecarboxylate.

8) CB-1: ^{1}H-NMR ($CDCl_3$) δ 1.33 (d, 3H, CH_3), 3.23 (m, 1H, Me-CH), 3.68 (s, 3H, OCH_3), 3.72–3.83 (m, 3H, CH_2 and An-CH), 6.85 (m, 4H, Phenyl H), 7.19-8.20 (m, 8H, Phenanthryl H); IR ($CHCl_3$) 1780 cm^{-1} ($\nu_{C=O}$); Mass, *m/z* 382 (M^+).

9) The aldehyde is an oxygenation product from (*E*)-AN. The mechanism for aldehyde formation will be reported elsewhere.

10) CB-2: ^{1}H-NMR ($CDCl_3$) δ 1.23 (d, 3H, CH_3), 2.45 (m, 1H, Me-CH), 3.67 (s, 3H, OCH_3), 3.67-4.10 (m, 2H, 10-H and An-CH), 4.52 (br. s, 2H, CH_2), 6.60 (m, 4H, Phenyl H), 7.10-8.03 (m, 7H, Phenanthryl H); IR ($CHCl_3$) 1730 cm^{-1} ($\nu_{C=O}$); Mass, *m/z* 382 (M^+).

11) Ol-2: ^{1}H-NMR ($CDCl_3$) δ 3.78 (s, 3H, OCH_3), 5.30 (s, 2H, CH_2), 6.62 (s, 1H, C=CH), 6.87–8.53 (m, 13H, Aryl H); Mass, *m/z* 338 (M^+).

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15) The overlap interactions between the lowest L_b singlets of phenanthrene derivatives[17,18] and ground-state (*E*)-AN were estimated at a distance of 350 pm by using the interorbital interaction integrals[19,20] and the atomic orbital coefficients obtained from MNDO calculations for planar molecular geometries.[19] Under the above conditions, irradiation leads to the lowest singlet states of lactones.

16) The difference in reactivity between STL and SCL cannot be predicted only by this estimation; however, a shallower energy minimum on the reaction coordinate is predicted for SCL than for STL when the phase matching in LUMO-LUMO interactions of the cycloaddends is taken into account.

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