ENHANCEMENT OF REACTIVITY OF THE ESTER CARBONYL GROUP BY INTERCHROMOPHORIC LINKS IN PHOTOCHEMICAL CYCLOADDITIONS. INTERMEDIACY AND ROLES OF PLURAL INTRAMOLECULAR EXCIPLEXES

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Abstract—9-Phenanthrenecarboxylic esters as well as naphthalenecarboxylic esters linked with p-methoxystyrene derivatives exert an intramolecular competitive or exclusive oxetane formation through carbonyl addition, although the carbonyl addition is not observed in the corresponding intermolecular systems. The reaction proceeds from the excited singlet state involving plural intramolecular exciplexes. The new aspect of carbonyl addition, i.e., the enhancement of reactivity of the ester carbonyl group by interchromophoric links, is discussed on the basis of photochemical and photophysical observations as well as MO calculations.

1. INTRODUCTION

Exciplexes are intermediates in [2+2] photocycloadditions, and the products are formed from those of maximum "sandwich" overlap of the chromophores at the transition state for the reaction [1-4]. Incorporation of two chromophores in one molecule separated by a certain number of atoms changes photochemical properties of the respective chromophores by imposing new restrictions on intramolecular processes [5-7]. Some series of arencarboxylic esters linked with styrene derivatives exert a competitive or exclusive oxetane formation, though the carbonyl addition is not observed in the corresponding intermolecular systems [8-12]. This phenomenon is understood in terms of enhancement of reactivity of the ester carbonyl group by interchromophoric link; the link causes some restrictions to the formation of exciplexes with the same conformations as those achieved in the intermolecular systems and therefore, the exciplexes preferable for carbonyl addition take an important role in the reaction course.
In this paper we describe features of the intramolecular carbonyl addition in arenecarboxylic esters linked with styrene derivatives and discuss the role of exciplex intermediates in the cycloaddition.

2. INTRAMOLECULAR CYCLOADDITIONS OF BICHROMOPHORIC PHENANTHRENE- AND NAPHTHALENE-CARBOXYLATES

Competitive Cycloadditions Forming a Cyclobutane and an Oxetane

The photochemical cycloaddition of methyl 9-phenanthrenecarboxylate (9MCP) to (E)-anethole ((E)-AN) affords a head-to-head adduct (9PCB0) of the expected stereochemistry in good yield in 9:1 benzene-isoprene (Scheme 1, X = H) [8]. The reaction is a singlet process; 9MCP behaves similarly to 9-cyanophenanthrene [13] with (E)-AN. The photochemistry of methyl 6-cyano-9-phenanthrenecarboxylate (CN9MCP) is quite similar to that of 9MCP (Scheme 1, X = CN) [12].

The competitive cycloadditions take place on irradiation of (E)-3-(p-methoxyphenyl)-3-pentenyl 9-phenanthrenecarboxylate (9PC2αA) at 366 nm in 9:1 benzene-isoprene to afford a cyclobutane (9PCB2, 15% yield) and a bicyclic acetal (9POX2α, 65%) (Scheme 2, X = H) [8]. The structure of 9PCB2 is analogous to that of 9PCB0 obtained from 9MCP and (E)-AN. Acetal 9POX2α is a [2+2] cycloadduct between the carbonyl group and the olefinic double bond, and is slowly decomposed in chloroform to a dihydrofuran (9PDHF) and acetaldehyde.

(E)-3-(p-Methoxyphenyl)-3-pentenyl 6-cyano-9-phenanthrenecarboxylate (CN9PC2αA) gives also a cyclobutane (CN9PCB2, 39%) and a bicyclic acetal (CN9POX2α, 35%) on irradiation of the phenanthrene moiety at 366 nm (Scheme 2, X = CN) [12]. The product ratio (CN9PCB2/CN9POX2α) at ambient temperature is ≈1.1 in contrast with 9PCB2/9POX2α ≈ 0.23.

The competitive cycloadditions are also observed on irradiation of (E)-4-(p-methoxyphenyl)-4-hexenyl 9-phenanthrenecarboxylate (9PC3αA) and (E)-5-(p-methoxyphenyl)-5-heptenyl 9-phenanthrenecarboxylate (9PC4αA) in 9:1