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PHOTOCHEMICAL REACTIONS OF AROMATIC ESTERS. IV[1]
THE OXETANE FORMATION INVOLVING AN EXCIPLEX

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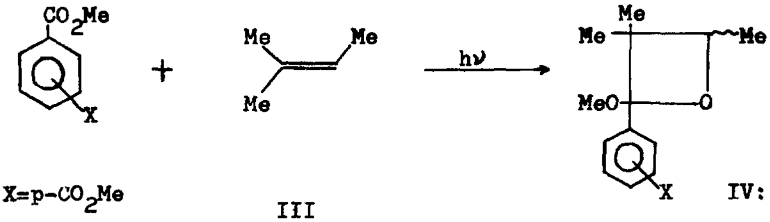
The photocycloaddition of ketones to olefins yielding oxetanes has been studied extensively in the recent years[2]. Ketone triplets are generally thought to be reactive species in these reactions, except for a few cases of nucleophilic attacks of $n-\pi^*$ singlet states of alkyl ketones[3]. In our previous studies on the photochemistry of carboxylate esters, we found that both ethyl cyanoformate[4] and diethyl oxalate[5] as well as ketones also underwent the Paterno-Büchi reaction with several olefins. Furthermore, we have recently reported that aromatic carboxylate esters, having more than one electron-withdrawing substituent such as a cyano or an alkoxycarbonyl group, photochemically added to 1,1-diphenylethylene to give new oxetanes and that $n-\pi^*$ excited states of the aromatic carboxylate esters were presumed to be reactive species in these reactions[6]. In the present work, our attention has been paid to the nature of the reactive species of the above interesting Paterno-Büchi reaction of the aromatic carboxylate esters. For this purpose, we have studied photocycloadditions of dimethyl terephthalate (I) and dimethyl isophthalate (II) with 2-methyl-2-butene (III).

Irradiation of an acetonitrile solution of I (0.03 mole) and III (0.1 mole) with a 500-W high pressure mercury arc through a Pyrex filter led to the formation of a mixture of two isomeric oxetanes (IV) in 45 % yield based on the unrecovered ester (isomer ratio, 1:1.2). Similar photocycloaddition of II (0.05 mole) with III (0.2 mole) gave a mixture of two isomeric oxetanes (V) in 70 % yield (isomer ratio, 1:1). All of the oxetanes obtained were characterized by



I: X=p-CO_2Me
II: X=m-CO_2Me
III
IV: X=p-CO_2Me
V: X=m-CO_2Me

elemental analysis, i.r., n.m.r., and mass spectra.

Phosphorescence spectra of I and II were observed at 77°K in methanol-ethanol glass (1:4) (0–0 band at 73.1, 77.0 Kcal mole^{-1}, respectively). The long radiative lifetime (1–2 sec) and the vibrational spacing verify that the lowest lying triplet states of I and II are π-π^* in nature. The failure of the triplet sensitization with xanthone (E_T=74.2 Kcal mole^{-1}) for the formation of IV would exclude the lowest triplet state of I as one of the reactive states. Consequently, an excited singlet state or a higher triplet one must be considered as the candidate for the reactive species of this oxetane formation.

Broad fluorescence emission spectra of I and II having maximum at around 380 mµ were also measured at room temperature in several solvents. For the fluorescence emission of II, a small bathochromic shift was observed on changing the solvent from ether to acetonitrile, whereas no solvent effect on that of I was detected. These facts are indicative that the lowest excited singlet states of I and II are also π-π^* in nature. These fluorescence emissions in acetonitrile solution were quenched by the olefin III. The Stern-Volmer plots of F_0/F against the concentration of III were linear, and hence the following equation is valid for the present systems.

$$F_0/F = 1 + k_q\tau[\mathrm{III}] \qquad (1)$$

where F_0 and F are the fluorescence intensities in the absence and presence of III, k_q is the bimolecular quenching rate constant, and τ is the singlet lifetime in the absence of III. The slopes, corresponding to $k_q\tau$ in eq. (1), were 55 M^{-1} for I and 2 M^{-1} for II. From the following facts, to account for this quenching we would like to propose an exciplex or an excited charge-transfer complex formation between the electron-deficient aromatic ring of the π-π^* excited singlet state of I or II and the olefin III. First, an exothermic singlet-singlet energy transfer from I or II to III is energetically unfavorable. Second, there is no evidence for a charge-transfer complex formation between the ground state aromatic ester and the olefin III from uv spectra measurements. Furthermore, quenching of the fluorescence of aromatic compounds by dienes[7] and amines[8] is generally ascribed to such excited charge-transfer complex formation. Therefore, it seems reasonable to conclude that the excited charge-transfer complex formation may also occur in our system. This is probably the first case of the Paterno-Büchi reaction which may proceed via an interaction of a π-π^* lowest excited singlet state of a carbonyl component with an olefin. There has been current interest in the photochemical reactions involving an excited charge-transfer interaction of an excited aromatic compound with a π-electron donor. For example, Wagner has suggested that α-trifluoroacetophenone has been photoreduced by alkylbenzenes through a charge-transfer interaction of the triplet state of the former with the benzene ring of the latter[9].

$$\begin{tikzcd}
\text{Ester} \arrow[r, "h\nu", "\pi-\pi^*"'] & \left[\text{Ester}\right]_{S_1} \arrow[r, "\text{Olefin}"] & \left[\text{Complex}\right] \arrow[dl, "\text{Path B}"'] \arrow[d, "\text{Path A}"] & \text{VI} \\
& \text{Oxetane} & \left[E_{T_2}(n-\pi^*)\cdot \text{Ol}\right] \arrow[l] &
\end{tikzcd}$$

Although the inclusion of the complex VI in the initial step of the present oxetane formation has become apparent, two possible paths of the collapse of VI to the oxetanes may be suggested at the present time. Path A involves an n-π^* higher triplet state of the aromatic ester which may be produced by the intersystem crossing from the complex VI. The other possible Path B involves the direct collapse of the complex VI to the oxetanes. The only present evidence is not sufficient to decide which path will be more favorable. Further work on the mechanism of this interesting Paterno-Büchi reaction involving an excited charge-transfer interaction is in progress and will be reported shortly.

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