Photoaddition Reactions of Pyromellitic Acid Tetramethylester to Olefins

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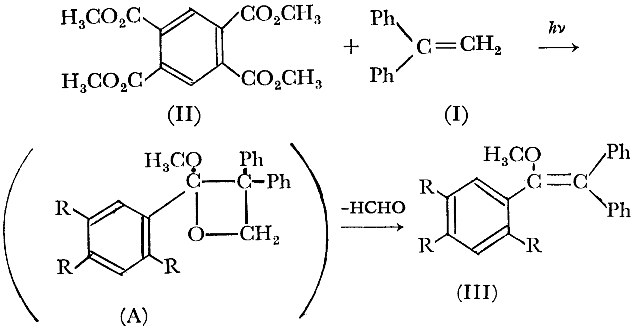
In our previous paper, we reported the photoadditions of some aromatic carboxylate esters with one or two electron-withdrawing groups to 1,1-diphenylethylene (I).[1] As part of our series of studies of the photochemistry of aromatic carboxylate esters, we will now report on the photoreactions of pyromellitic acid tetramethylester (II) with olefins.

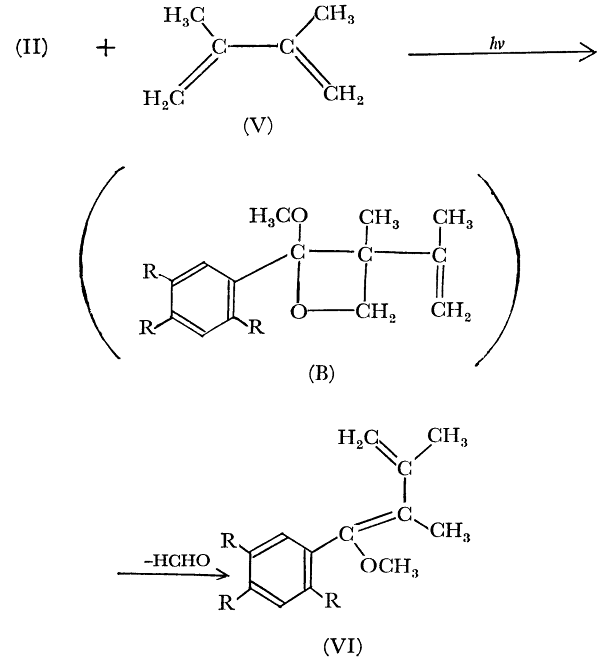
A mixture of 0.03 mol of II and 0.09 mol of I in acetonitrile was irradiated through a Pyrex filter with a 500-W high-pressure mercury lamp for 120 hr under a nitrogen atmosphere to give pale yellow needles (mp 108—109°C) in a 95% yield based on the reacted ester. This photoproduct was identified as the olefin (III) by a study of its IR, NMR, and mass spectra and by elemental analysis. Obviously, III would be derived from an intermediary oxetane (A) by deformylation due to the steric hindrance of the adjacent *o*-methoxycarbonyl group.



R=CO_2CH_3

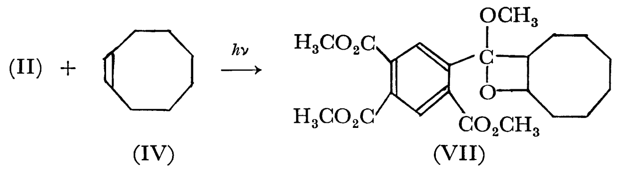
Recently Koltzenburg *et al.* reported that benzene reacted photochemically with butadienes at the 1,4-position of the aromatic ring to give cycloadducts.[2] On the other hand, we have observed a photocycloaddition of the aromatic ring of trimesic acid triesters to cyclooctene (IV).[3] In order to examine the possibility of photocycloaddition at the aromatic ring of II, the following photoreactions of II with some olefins were done.

First, a solution of 0.02 mol of II and 0.10 mol of 2,3-dimethylbutadiene (V) was irradiated for 20 hr under the conditions described above. The diene product (VI), consisting of S-*cis*- and S-*trans*-forms, was obtained in a 13% yield, together with large amounts of butadiene polymers, but no photocycloaddition reaction at the aromatic ring took place at all. It was also reasonable to consider that VI was formed *via* an unstable oxetane (B).



R=CO_2CH_3

Second, a solution of 0.03 mol of II and 0.09 mol of IV was irradiated in a similar manner, an unstable oxetane (VII) was thus obtained in a 16% yield as the sole detectable product.



From the facts that only one isomeric oxetane was formed in each photocycloaddition of II to olefins, and that acetone was produced by the photoreduction of II in 2-propanol, the reactive species of these reactions were assumed to be n-π^* in nature. Studies of the reactive species of polysubstituted aromatic carboxylate esters are currently in progress.

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[1] Y. Shigemitsu, H. Nakai, and Y. Odaira, *Tetrahedron*, **25**, 3039 (1969).

[2] K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, **1967**, 4357, 4723.

[3] Unpublished.