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PHOTOCHEMICAL REACTIONS OF AROMATIC ESTERS . V[1].
PHOTOCYCLOADDITIONS OF TRIMESIC ACID TRIESTERS TO CYCLOOCTENE

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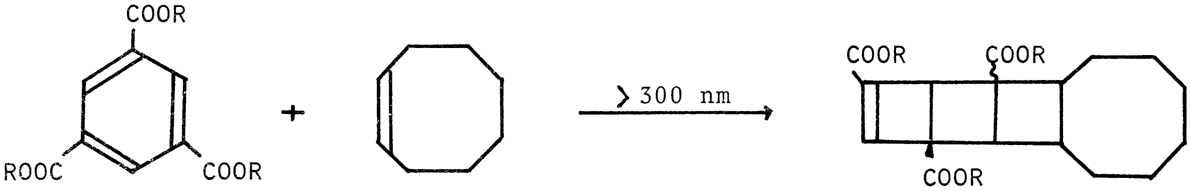
Irradiation of a benzene solution of trimesic acid triesters and cyclooctene yielded exclusively 1:1 cycloadducts without formation of oxetane derivatives. The photoadducts were shown to be tetracyclo[6.6.0.0.^{2,7}0^{3,6}]tetradec-4-ene derivatives. The reactive species of the present reaction was suggested to be an exciplex.

Although it has been reported with a great interest that photochemical condensation of aromatic compounds with olefins and acetylenes leads to formation of an additional ring,[2] in regard to the aromatic esters no successful examples are known at all. In a series of our studies on the photoreaction of aromatic esters with olefins, we previously reported that with some olefins, such as 1,1-diphenylethylene, the oxetane derivatives were given.[1,3] With cyclooctene, some aromatic esters undergo the photocycloaddition at aromatic ring. We wish to report here that the photoreaction of trimesic acid triesters (I) with cyclooctene (II) yielded a configurational mixture of tetracyclo[6.6.0.0.^{2,7}0^{3,6}]tetradec-4-ene derivatives (III).



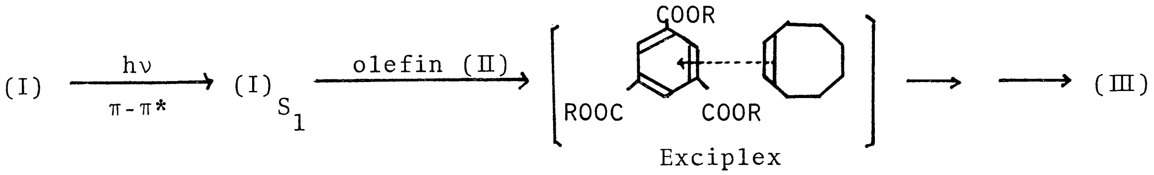
(I) (II) (III)

a) R=Et, b) R=Me a) R=Et, R=Me

A mixture of 0.025 mole of trimesic acid triethylester (Ia) and 0.10 mole of (II) in benzene (200 ml) was irradiated with a 500 W high pressure mercury lamp through a Pyrex filter for 70 hr under a nitrogen atmosphere to give a mixture of adducts (IIIa) (a colorless oil) in a 93 % yield based on the reacted ester.[4] The mass spectrometry and elemental analysis of (IIIa) were in agreement with formula $C_{23}H_{32}O_6$ (MW 404), corresponding to a 1:1 adduct. Peroxy-acid titration indicated the presence of one double bond. The ir spectrum of (IIIa) showed absorption bands at 1625 cm^{-1} (C=C), 1145 and 1060 cm^{-1} (ring skeletal vibration), and no bands attributed to the aromatic ring. The nmr spectrum of (IIIa) in CCl_4 showed three singlets in olefinic region at τ 3.40, 3.50 and 3.53 (3:1:1; one proton). Examination of the nmr spectrum indicated that (IIIa) was composed of three isomers, but they were not completely separable by column chromatograghic and g.l.c. technique. In the catalytic hydrogenation of (IIIa) under the various conditions, only 1 mole eq. of hydrogen[5] was always taken up by all components of (IIIa) to yield a mixture of the corresponding saturated compounds, and the above fact was proved by examination of ir, nmr and mass spectra of hydrogenated product and by its elemental analysis. Spectral evidence outlined above and the results of the catalytic hydrogenation indicate that (IIIa) consists of three stereo-isomers having the tetracyclo[6.6.0.0^{2,7}0^{3,6}]tetradec-4-ene structure.[6]

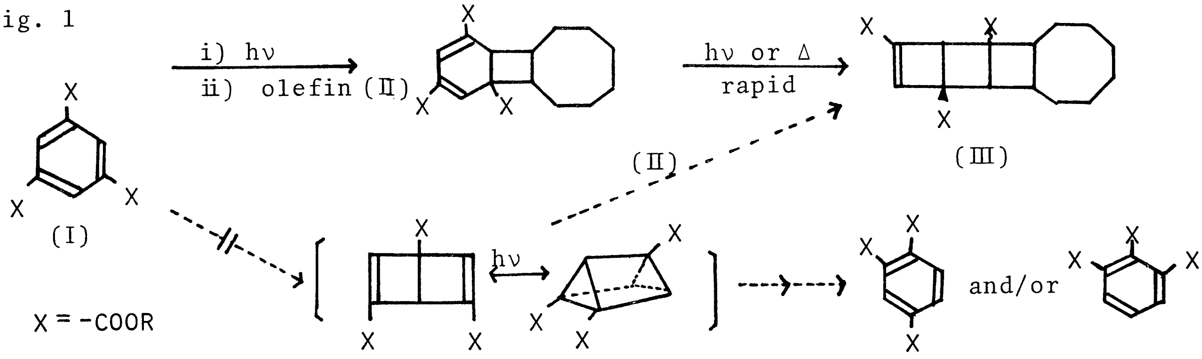
In addition, the photocycloaddition of trimesic acid trimethylester (Ib) with (II) gave (IIIb) in an 83 % yield.[7]

In order to obtain some informations about a reactive species of the present reaction, the quenching of the fluorescence of (Ib)[8] by (II) was performed. The Stern-Volmer plots of Fo/F against the concentration of (II) were linear (slope 25.7 mol^{-1}), where F and Fo were the fluorescence intensities at 358 nm (emission maximum) in the presence and absence of (II), respectively. An exothermic singlet-singlet energy transfer from (I) to (II) is energetically unfavorable. Furthermore, no new absorption bands attributable to the charge-transfer complex of (I) and (II) in the electronic ground states were detected. The above results indicate that (I) in the lowest excited singlet state interacts with (II) in the ground state. In the charge-transfer complex formation, molecules in the electronic excited states will generally be better donors and acceptors than in their electronic ground states.[2c] As a conclusion, we would like to propose that charge-transfer follows the excitation of (I) to form an exciplex, which is the reactive species of the present reaction, as shown in the following scheme.



It is not yet clear whether (III) is primary product or not, but (III) may arise presumably via a rapid further cyclization of the primary 1,2-cycloadduct,[9] because no isomeric aromatic esters were detected (Fig. 1). The more detailed investigations are now in progress and will be reported shortly.

Fig. 1



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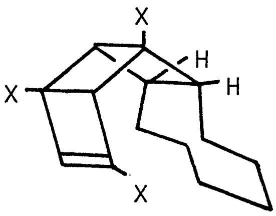
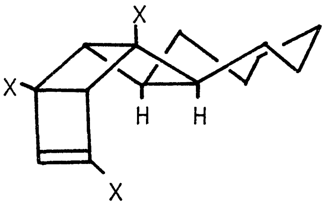
3) (a) Y.Shigemitsu, H.Nakai, and Y.Odaira, *Tetrahedron*, 25, 3039 (1969).
   (b) Y.Katsuhara, Y.Shigemitsu, and Y.Odaira, *Bull. Chem. Soc. Japan*, 44, 1169 (1971).

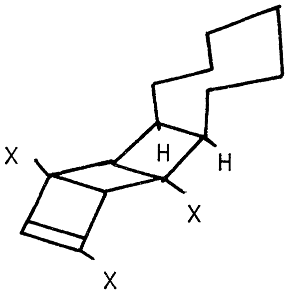
4) No oxetane derivatives were obtained at all.

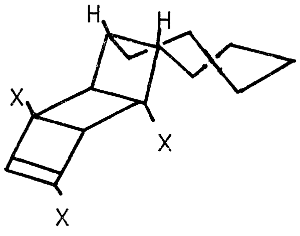
5) If the photoadducts had the other structure (that is, the structure of 1,2-, 1,3- and 1,4-cycloadduct), it should take up easily 2 mole eq. of hydrogen.[2]

6) Though an individual structural assignment is not yet done, a detailed analysis of nmr spectrum and a consideration of models for the possible isomers lead us to favor structure i)-iv) as the probable components of the mixture.









X = -COOR

i) syn, syn, *cis*- ii) syn, anti, *cis*- iii) anti, syn, *cis*- iv) anti, anti, *cis*-

7) Irradiation of a benzene solution of dimethyl isophthalate and cyclooctene also has caused a similar cycloaddition reaction.

8) The lowest excited singlet state of (I) was concluded to be π-π^* in nature from the study on the solvent effect of the fluorescence.

9) It has been pointed out that 1,2-photoaddition of ethylenes to benzenes has only been observed in systems where either the ethylene or the aromatic component has marked acceptor properties,[2c] and that the intervention of an exciplex would cause relaxation of orbital-symmetry restrictions.[2d] Our present results may not be contradictory to these conceptions.

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