Synthesis of Macrocyclic Rings by Internal Photocycloaddition of α,ω-Dicinnamates

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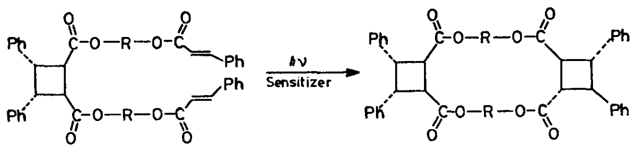
Summary α,ω-Dicinnamates in which the chromophoric groups are separated by 21, 27, 31, and 35 bonds have been cyclized by photosensitized intramolecular addition.

Many recent publications[1,2] have dealt with the study of intramolecular photochemical interaction between chromophores separated by many bonds. Until recently, instances in which such interaction led to chemical reaction (*e.g.* addition) had been limited to a separation of 14 bonds. We have shown elsewhere[3] that an α,ω-dicinnamate in which the double bonds are separated by 17 bonds can be successfully cyclized to an 18-membered ring by photosensitization. In this communication, we report that such an approach can be extended to synthesize rings with as many as 36 atoms.



(1) (2)

a; R = $[CH_2]_{10}$, **c**; R = $[CH_2CH_2OCH_2CH_2]$
b; R = $[CH_2]_{12}$, **d**; R = $[CH_2(CH_2OCH_2)_2CH_2]$

SCHEME

The photocyclization reaction can, in general, be written as shown in the Scheme. The α,ω-dicinnamates (**1a**—**d**) were prepared from β-truxinic acid by esterifying first with an excess of the dihydric alcohol in the presence of toluene-*p*-sulphonic acid followed by cinnamoylation of the dihydric diester alcohol with cinnamoyl chloride. Photocyclization was carried out at 350 nm with benzophenone as the sensitizer. The solvents used were chloroform, acetone or ether, the preferred one being $CDCl_3$ since it allowed the reaction to be followed by n.m.r. spectroscopy. Concentrations were 10^{-1}—10^{-2}M. Chemical yields of the macrocyclic tetraester ranged from 40 to 50% at this concentration. The effect of dilution was not investigated.

One point of interest in these syntheses is the stereochemistry at the point of closure. The earlier observation[4] that closure in solution phase led predominantly to δ-addition in the 10-membered ring was extended by us to the 18-membered ring.[3] In (**2a**—**c**) a consideration of the cyclobutane proton in the ^{1}H n.m.r. spectrum ($CDCl_3$) clearly pointed to δ-addition† in these 32-, 36- and 24-membered products. The stereochemistry in (**2d**) could not be elucidated from the cyclobutane protons since these were obscured by other mid-field protons, but the distribution of the aromatic protons suggested that the closure may be δ in nature in this instance as well. A second point of interest is the trend in the quantum yields with increasing separation between the chromophores. In confirmation of similar results in systems studied in other laboratories,[1] the quantum yield decreased by <50% with increasing chain length.

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† In δ-truxinic acid and its esters, two-proton absorptions fall farther upfield than in β-truxinic or α-truxillic acid or their esters. The splitting pattern in the δ-acid is also unique.

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[4] M. Freedman, Y. Mohadger, J. Rennert, S. Soloway, and I. Waltcher, *Org. Prep. and Proc.*, 1969, **1**, 267.