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# PHOTOCLEAVAGE OF COUMARIN DIMERS

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trans-head-to-head Coumarin dimer cleaves into coumarin in chloroform by irradiation with the light of wavelength 277 nm in high yield. When a ring opened dimer, trans-3,cis-4-bis(2-hydroxyphenyl)-1,trans-2-cyclobutanedicarboxylic acid in aqueous solution is irradiated, a mixture of trans-2,2'-dihydroxystilbene and fumaric acid is obtained in high yield.

In the course of study on photocleavage of cyclobutane derivatives in this laboratory,[1,2] the photochemical behavior of coumarin dimers has been investigated. In the present work both "symmetric" and "unsymmetric" photocleavages of coumarin dimer derivatives were observed, in the first case to yield coumarin and in the second a stilbene derivative and fumaric acid.

trans-head-to-head coumarin dimer ( I ) was obtained from the irradiation of a benzene solution of coumarin with a small amount of benzophenone.[3] Krauch and his co-workers have reported nearly exclusive formation of the coumarin dimer ( I ) in chloroform by irradiation with the light of longer wavelength than 310 nm and the photocleavage of I to coumarin in dioxane by the light of shorter wavelength than 310 nm.[4] In "symmetric" photocleavage, irradiation of a chloroform solution of the coumarin dimer I with monochromatic light of 277 nm gave the original coumarin as a sole product in high yield. Fig.1 shows gradual change of the ultraviolet spectrum of a solution of the dimer I in chloroform ( $7.0 \times 10^{-5}$ mol·l$^{-1}$ ) during irradiation. The apparent reaction velocity of the dimer I decreased with the irradiation time because the absorption band of coumarin produced overlaps with that of the dimer. Thus, the yield of coumarin attains a maximum of only about 60 % under the present experimental conditions.

On the basis of this result, a photochemical reversible scheme was confirmed between coumarin and its dimer in chloroform. This reaction is similar to the reversibility between thymine and its dimer which depends on the wavelength of the light used.[5]

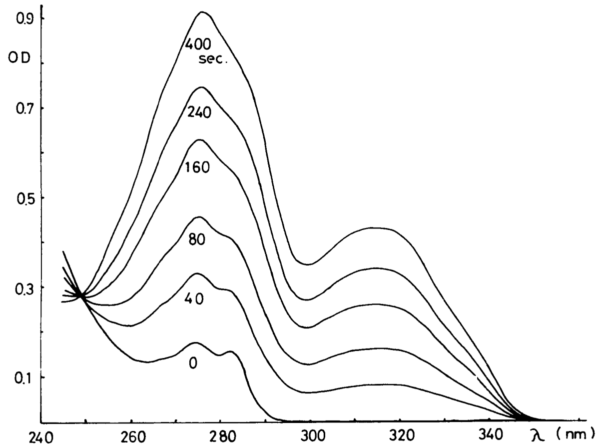


Fig. 1 UV absorption spectral change in photocleavage of the dimer I into coumarin by irradiation with light of 277 nm. Initial conc. of I : $7.0 \times 10^{-5}$ mol·l$^{-1}$ in chloroform.

Although the lactone ring of coumarin is opened only under rather drastic conditions, the ring in the coumarin dimer I is opened to give a ring opened dimer, trans-3,cis-4-bis(2-hydroxyphenyl)-1,trans-2-cyclobutanedicarboxylic acid ( II ) under mild conditions, e.g. in a dilute aqueous alkaline solution at room temperature.[3] In "unsymmetric" photocleavage, the ring opened dimer II, in either neutral or anionic form, was cleaved to give trans-2,2'-dihydroxystilbene ( III ) and fumaric acid ( IV ) in high yields by irradiation for several hours with the light of 277 nm. For example, a solution of 80 mg. of the ring opened dimer II in 50 ml of water on irradiation for twenty hours gave 35 mg. of III ( 68 % yield ) as white crystalline precipitate which was identified by melting point,[6] elementary analysis, and ir and nmr spectra. III, which is slightly soluble in water, was observed, in the present work, to be photoreactive in solution. No coumarin was detected in the residual solution by spectroscopic analysis.

Fig.2 shows change in the spectrum of an aqueous potassium hydroxide solution of the ring opened dimer II ( anionic form ) during the "unsymmetric" photocleavage. After acidification the resultant absorption curve was identical with that of III in the range of 220 — 380 nm, indicating almost quantitative conversion of the dimer II into the "unsymmetric" photocleavage products.

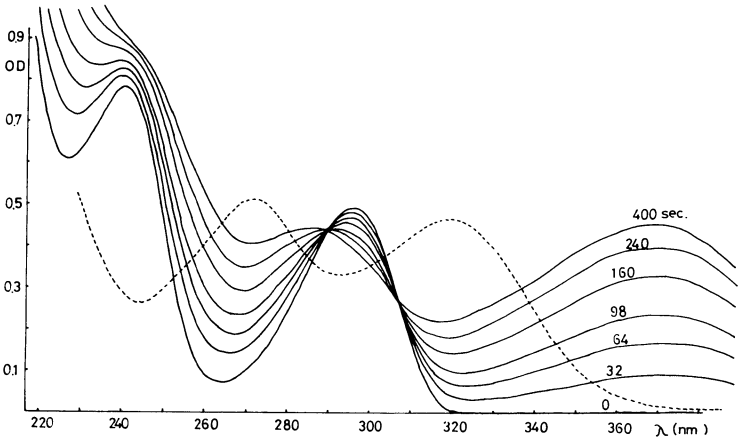
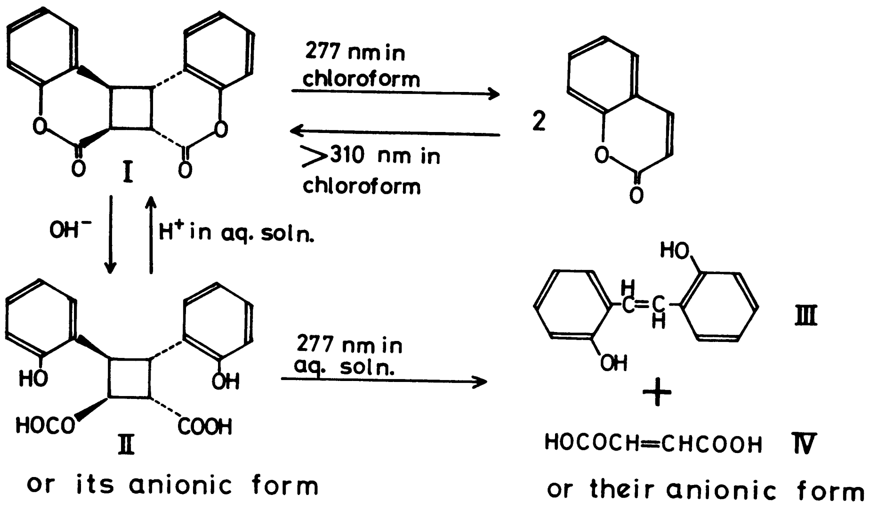


Fig. 2 UV absorption spectral change in photocleavage of the ring opened dimer II into III and IV by irradiation with light of 277 nm. Initial conc. of II : $5.0 \times 10^{-5}$ mol·l$^{-1}$ in 1 % aq. KOH solution. Dotted line : acidified after 400 sec. irradiation.

The results are summarized in the following scheme :



It is noteworthy that such structural difference between I and II determines the mode of photocleavage of the cyclobutane ring system. Solvents other than those described here affected both the mode and the quantum yield of the photocleavage reaction to a certain extent. Similar results have been obtained with cis-head-to-head coumarin dimer and other ring opened dimer ( II ) derivatives such as the corresponding ester and amide.

Further work is in progress and the results will be published in the near future.

## References

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