© *1988 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 61, 1005—1007 (1988)*

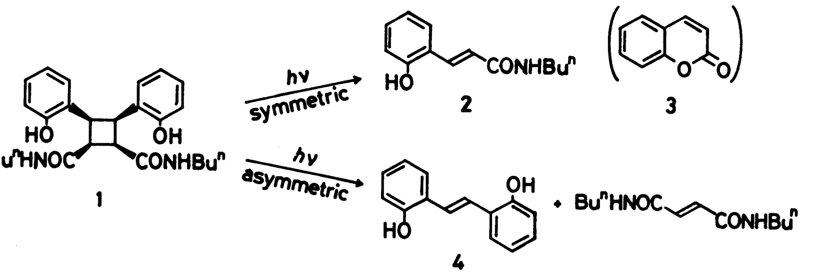
Solvent- and Wavelength-Dependence of the Photocleavage of the Cyclobutane Ring in *N,N'*-Dibutyl-*c*-3,*c*-4-bis-(2-hydroxyphenyl)-*r*-1,*c*-2-cyclobutanedicarboxamide

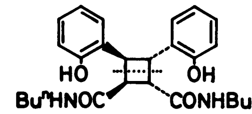
Noriyuki Yonezawa,† Masataka Kubo,†† Kazuhiko Saigo, and Masaki Hasegawa*
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

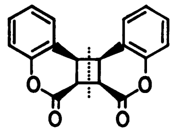
(Received March 31, 1987)

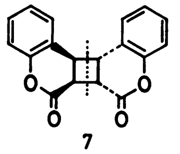
Synopsis. The ratio between two photocleavage directions of the cyclobutane ring in the title compound varies with the solvent polarity and the irradiation wavelength, and the effect of the solvent polarity appears much larger in protic solvents than aprotic ones.

Head-to-head type cyclobutane compounds have two possible cleavage modes, namely, symmetric and asymmetric cleavages.[1)] Most of the lactone-opened derivatives of head-to-head coumarin dimers have only one photocleavage direction, but the derivatives, of which all the substituents are situated in the cis positions to each other on the cyclobutane ring such as *N,N'*-dibutyl-*c*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*c*-2-cyclobutanedicarboxamide (**1**), were confirmed to undergo symmetric and asymmetric photocleavages competitively.[2–4)] To clarify the factors which govern the photocleavage mode of these compounds, the photoscission reaction of **1** was investigated under various conditions by comparing with those of *N,N'*-dibutyl-*t*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*t*-2-cyclobutanedicarboxamide (**5**) and syn and anti head-to-head coumarin dimers **6** and **7**.




5


6


7

Results and Discussion

Irradiation of **1** was carried out in alcohols (protic) and MeCN (ε 37.5)/dioxane (ε 2.2) mixed solvents (aprotic). The products of photolysis were confirmed by comparing their retention times of HPLC analysis with those of the authentic samples. The conversions and the ratios between photocleavage modes were estimated by the area of elution bands and the molar absorptivities of the starting material, the products, and the standard sample as shown in the Eqs. 1 and 2, respectively:

conversion

$$= [S_h/\varepsilon_h + (S_c/\varepsilon_c + S_{cis}/\varepsilon_{cis} + S_{trans}/\varepsilon_{trans})/2]/(aS_s/\varepsilon_s) \quad (1)$$

symmetric fission/asymmetric fission

$$= (S_c/\varepsilon_c + S_{cis}/\varepsilon_{cis} + S_{trans}/\varepsilon_{trans})/(2S_h/\varepsilon_h) \quad (2)$$

where S is the area of the elution band recorded by the UV detector at 320 nm and ε is the molar absorptivity at 320 nm; h, c, cis, trans, s, and a denote **4**, **3**, *cis-N*-butylcoumaramide, **2**, standard meterial, and the ratio of the starting material to the standard material, respectively.

The molar absorptivity of *cis-N*-butylcoumaramide was determined by HPLC analysis of the solution of **2** after irradiation using Eq. 1. The isolation of *cis-N*-butylcoumaramide was unsuccessful because of its spontaneous relactonization to coumarin at room temperature, and the isomerization of **4** was not observed in our experiments.

The ratio between the two photocleavage modes of **1** varied with the solvent polarity and the wavelength of light as shown in Fig. 1. Though the symmetric cleavage mode was predominant in every case, asymmetric one gradually increased with shortening the wavelength, and protic solvents were favorable for asymmetric cleavage as compared to aprotic solvents.

---

† Present address: Nippon Kokan K. K., Kawasaki-ku, Kawasaki 210.

†† Present address: Mie University, Tsu, Mie 514.

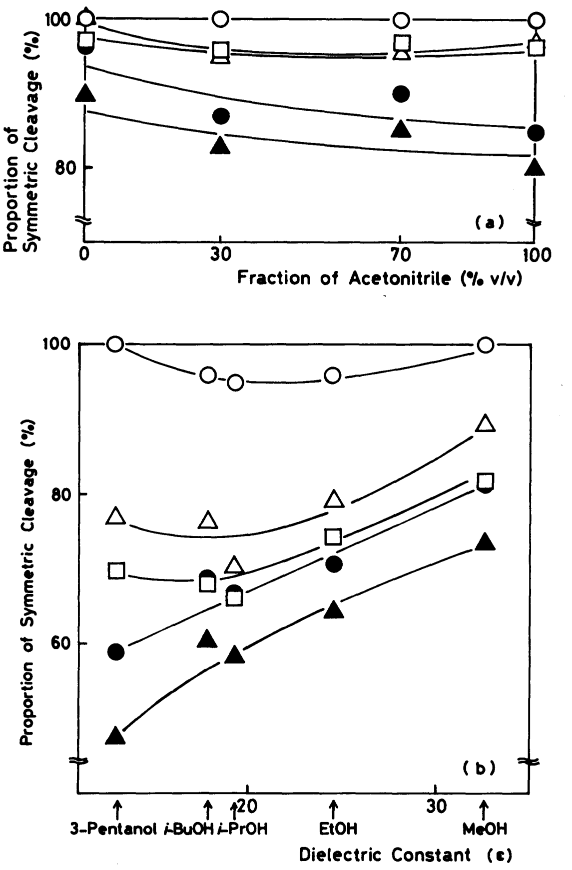


Fig. 1. The ratio between symmetric and asymmetric modes of the cyclocleavage reaction of **1** in (a) MeCN–dioxane and (b) alcohols (○: 330 nm, △: 304 nm, □: 277 nm, ●: 251 nm, and ▲: 224 nm).

The effects of solvent polarity appeared more remarkably at the range of shorter wavelength in both protic and aprotic solvents.

In protic solvents symmetric cleavage became more advantageous as the polarity of the solvent increased. In addition, the quantum yields for the formation of olefins in MeOH, calculated on the basis of Eq. 1, had also distinct dependence on the irradiation wavelength, i.e., $\phi_{224}=0.27$, $\phi_{251}=0.06$, $\phi_{277}=0.33$, and $\phi_{304}=0.05$. These results indicate that there exist at least two routes for this cyclocleavage reaction. On the other hand, the proportion of asymmetric photocleavage was almost constant in aprotic solvents.

In contrast, the exclusively asymmetric cleavage of the cyclobutane ring in **5** did not change by the wavelength nor by the solvent (dioxane, MeCN, or MeOH). And the irradiation of **6** or **7** in MeCN or dioxane solution always gave coumarin (**3**) as a sole product of the exclusively symmetric cleavage.

When the irradiation was carried out with the light of 251±10 nm wavelength using benzene as a sensitizer, the photocleavage reaction of **5**—**7** was accelerated by 3.2—3.5 times. But, the photocleavage reaction of **1** was sensitized by only 1.4 times. From the phosphorescence spectra of **1** and **5**, the triplet excited energies in MeOH were estimated to be 70 and 66 kcal mol^{-1}, respectively. Furthermore, the photocleavage reaction of **1** was not quenched by biacetyl and hardly sensitized by acetone or acetophenone. These results suggest that the cyclocleavage reaction of **1** proceeds predominantly via singlet excited state although the sensitization of the reaction with benzene indicates the existence of the reaction route via triplet excited state.

The dependence of the quantum yields on the irradiation wavelength and the different wavelength dependence between aprotic and protic solvents are considered to be attributed to the abilities of the solvents to stabilize **1** in both ground state and/or excitation process and the intermediates in the cyclocleavage reaction, presumably through hydrogen bonding interaction. In the ground state and the early stage of excitation, 2-hydroxyphenyl chromophore should interact with butylcarbamoyl group in several manners causing at least two excitation states in the ratio determined in accordance with the property of the medium. Moreover, one possible intermediate in the photocleavage reaction of **1** is an intramolecular excimer as observed in the cycloaddition of coumarin in ethanol to yield **6**.[5] But the evidence for the formation of the intramolecular excimer could not be obtained by the emission spectra. These phenomena show that in both protic and aprotic solvents at least two intermediates should exist and indicates that particularly in protic solvents the minor reaction routes was probably accelerated. The competitive photocleavage of **1** is distinctly different from exclusively one-directioned photocleavages of other lactone-opened derivatives of **6** and **7**.[2,4] This characteristic photochemical behavior of **1** was clearly brought in by the largely hindered cis-syn-cis configuration on the cyclobutane ring of **1**, which might make **1** to have peculiar conformations enabling the formation of intramolecular excimer and highly reactive intermediate by interaction of 2-hydroxyphenyl and carbamoyl groups, reflecting the hydrogen bonding and electrostatic effects of solvents.

Experimental

Irradiation was carried out with a JASCO CRM-FA spectroirradiator at room temperature. UV spectra were recorded on a Hitachi Model 100-60 spectrophotometer. Emission and phosphorescence spectra were recorded on a Hitachi MPF-4 fluorescence spectrophotometer. HPLC analysis was performed on a steel column (4 mm×250 mm) packed with LiChrosorb SI60 (5 μm, Merck and Co.) and the absorbance at 320 nm was monitored on a TOYO SODA UV8 Model II spectrophotometer at a flow rate of 0.4 ml min^{-1} using benzene–ethyl acetate (70:30 v/v) as an eluent.

Spectrograde solvents were used for reaction and UV measurement without further purification. **1** and **5**—**7** were prepared according to the literatures.[6,7] Standard and authentic samples for HPLC analysis, 4-ethoxycarbonyl-, and 4-phenoxycarbonylchalcones,[8] *trans*-*N*-butylcoumaramide (**2**),[9,10] and 2,2′-dihydroxystilbene (**4**),[2] were prepared according to the methods in the literatures. Other reagents were purified by the ordinary methods.[11]

Photolysis of 1 and 5—7. Through a solution of **1**, **5**—**7** (ca. 5×10^{-5} mol dm^{-3}) in a quartz cell, anhydrous nitrogen was bubbled for ca. 1 min. The photocleavage reaction was monitored by the UV spectrophotometer during the irradiation. Before the new absorption reached a maximum, the irradiation was stopped, and the solution was concentrated under reduced pressure. Then the residue was dissolved in benzene–ethyl acetate (70:30 v/v) containing a constant amount of a standard material (4-ethoxycarbonylchalcone, or 4-phenoxycarbonylchalcone) and analyzed by HPLC.

Quantum Yield. The quantity of the light absorbed was measured by the chemical actinometry.⑫ The quantum yields for the formation of olefins in the photocleavage of MeOH solution **1** was determined as follows: Two quartz cells were set in series along the line of the irradiation light, where the former cell was for the photoreaction or blank, and the second for chemical actinometry. The photoirradiation of MeOH solution of **1** and MeOH alone performed under exactly same conditions. The quantum of the light absorbed by **1** was calculated on the basis of the difference of the quantities of the light absorbed by the solution in the second cell. The amount of total olefins calculated by Eq. 1 and the quantity of light absorbed by **1** afforded the quantum yield.

The relative rates of the photocleavage were determined as follows: Two quartz cells were set in the same manner as the quantum yield measurement described above. First, only the solvent was placed in the former cell and the solution of the cyclobutane compounds containing sensitizer or quencher in the second cell, then the photoirradiation was undertaken. Then, solvent containing same amount of sensitizer or quencher was placed in the former cell and the solution of substrate in the second cell, and photoirradiation was undertaken under the exactly same conditions. Relative rate was calculated by the ratio of conversion between above two photoirradiation.

References

1) E. Schaumann and R. Ketcham, *Angew. Chem., Int. Ed. Engl.*, **21**, 225 (1982).

2) N. Yonezawa, T. Yoshida, and M. Hasegawa, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1083.

3) M. Hasegawa, K. Saigo, H. Katsuki, N. Yonezawa, and T. Kanoe, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2345 (1983).

4) N. Yonezawa, T. Yamashita, T. Kanoe, K. Saigo, and M. Hasegawa, *Ind. Eng. Chem., Prod. Res. Dev.*, **24**, 593 (1985).

5) G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Am. Chem. Soc.*, **86**, 3103 (1964).

6) C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, **99**, 625 (1966).

7) N. Yonezawa and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **56**, 367 (1983).

8) M. Hasegawa, H. Arioka, H. Harashina, M. Nohara, M. Kubo, and T. Nishikubo, *Isr. J. Chem.*, **25**, 302 (1985).

9) W. Schultz, *J. Pharm. Sci.*, **52**, 503 (1963).

10) V. A. Zagorevskii and V. L. Sarel'ev, *J. Gen. Chem. USSR (Engl. Transl.)*, **34**, 2302 (1964).

11) D. D. Perrin, W. L. F. Armarego, D. R. Perrin, "Purification of Laboratory Chemicals," 2nd ed, Pergamon Press, Oxford (1980).

12) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).