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Formation of a Tricyclic [2.2]Paracyclophane Derivative in the Low-Temperature Photoreaction of an Unsymmetric Diolefin Crystal

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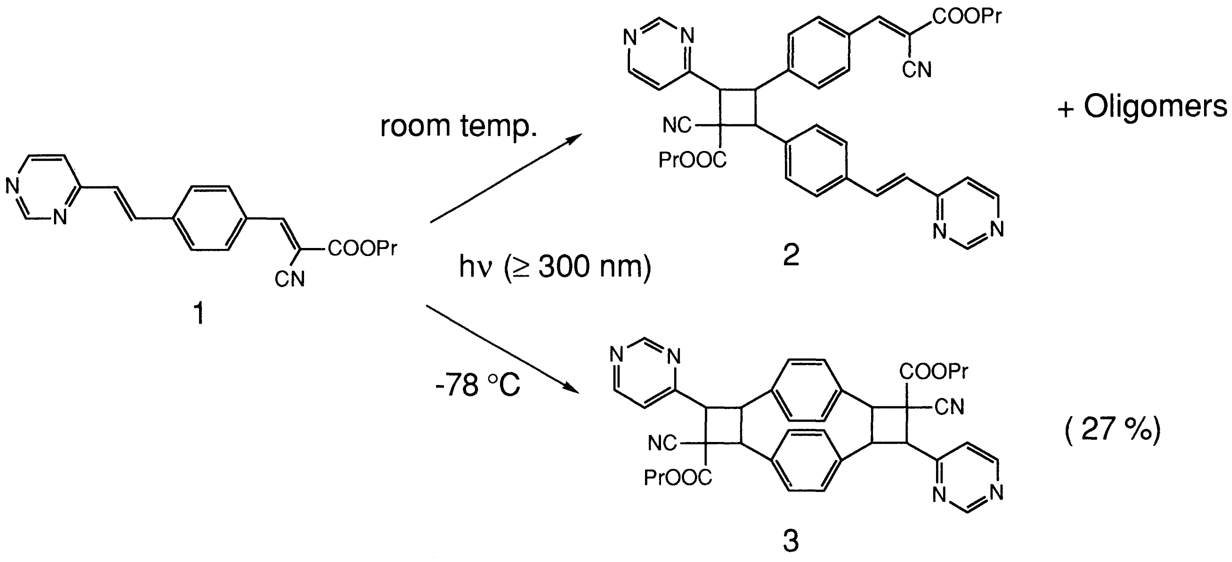
Propyl α-cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamate crystal afforded a tricyclic [2.2]paracyclophane derivative upon photoirradiation at low temperatures even though it gave a monocyclic dimer and oligomers at room temperature. This result is very significant in understanding of photochemical behavior of organic crystals at low temperature and in development of a new synthetic route of highly strained [2.2]paracyclophane derivative.

Topochemical photoreaction in organic crystals has become of interest in recent years as one mean of organic synthesis because the reaction proceeds regio- or stereo-selectively under the control of the crystal lattice. We recently found a number of unsymmetrically substituted 1,4-divinylarene crystals affording such products as polymers, racemic or optically active dimers, or cyclophanes through [2+2] cycloaddition.1)

Amorphous oligomers have been generally obtained from β-type packing crystals2) of 1,4-divinylarene derivatives when the wavelength of irradiating light was controlled so that dimeric (or oligomeric) molecules might be excited. This result can be explained by the following reason; cyclodimerization of diolefin molecules in the β-packing crystals results in large displacement of two chains having a residual double bond from each other because of the strained bond angle of cyclobutane skeleton.3) Such a large molecular motion disrupts regular molecular arrangement. The subsequent reactions between the dimer and its neighboring molecules occur at random in the disordered solid state, leading to the formation of indefinable oligomers.

On the other hand, the thermal motion of reacting molecules must be taken into account when the photochemical reaction of organic crystals is dealt with, because the reaction is deeply related to molecular dynamics during the reaction process. That is to say, such a molecular motion accompanying dimerization is considered to be restricted to some extent at low temperatures. Study of temperature effect on topochemical reaction4) must be an useful tool in understanding molecular dynamics in the course of photoreaction of organic crystals as well as in visualizing a possibility of formation of well defined products. In this connection, the temperature dependence of photoreaction was investigated on propyl α-cyano-4-[2-(4-pyrimidyl)ethenyl] cinnamate (**1**) crystal. Although the X-ray crystal structure analysis of starting **1** has not been successful, the structure of resulting dimer **2** suggests that the crystal of **1** consists of β-type packing monomers.5)

Crystal **1** was highly photoreactive and afforded dimer **2** in quantitative yield on photoirradiation for 2.5 h with a cut-off filter (≥ 410 nm) at room temperature (Scheme 1 , Table 1). It was confirmed that all the reactions of **1** carried out in the previous and the present studies gave only one type of dimer **2**, suggesting that the crystal lattice control worked throughout the dimerization reaction,[5)] although the starting crystals were gradually transformed into an amorphous product with the proceeding of reaction. Upon photoreaction with $\lambda \geq 300$ nm at room temperature, indefinable oligomers were formed. At -78 °C, however, a [2.2]paracyclophane **3** was found to be formed (27% yield) on irradiation for 12 h.[6)] **3** was obtained in 6% yield at -40 °C, indicating that the yield of **3** increases with decreasing the photoirradiation temperature.



Scheme 1.

Table 1. Photoirradiation Conditions and Products in the Reaction of Crystal **1**

Photoirradiation[a)]			Products
Wavelength /nm	Time/h	Temp/°C	(Yield/%)
≥410	1	r.t.	**2**(≈100)[b)]
≥300	8	r.t.	oligomers[c)]
≥300	1	-40	**3**(6), **2**, oligomers[d)]
≥300	12	-78	**3**(27), oligomers[d)]

a) A 500 W super-high-pressure mercury lamp set outside of the flask was used. b) Upon photoirradiation with $\lambda \geq$ 410 nm, the monomer molecules are exclusively excited. Prolonged irradiation did not afford **3**. c) At the initial stage of the reaction (≈ 2 h), **2** could be isolated from the photoproduct. d) The amount of **3** in the product decreased gradually upon prolonged photoirradiation.

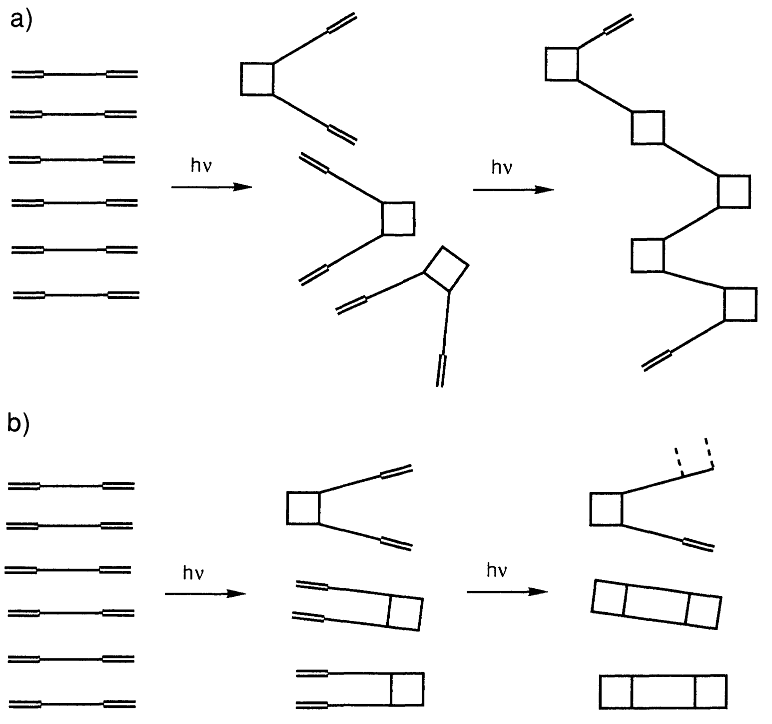


Fig. 1. Schematic illustration of the photoreaction of crystal **1** upon photoirradiation a) at room temperature and b) at -78 °C.

The elution time of **3** in GPC measurement coincided with that of **2**, implying that **3** corresponds to dimeric compound. The IR absorption spectra showed no peak corresponding to the olefinic double bond. In the ^{1}H NMR spectrum of **3**, no signal of olefinic double bond exists and the range of signals of the benzene and cyclobutane rings over 7.25-6.76 ppm and 5.52-4.57 ppm, respectively, are almost identical to those of a tricyclic [2.2]paracyclophane derivative, which is derived from a mixed crystal of ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates.[7,8] From these results, **3** was concluded to be a highly strained [2.2]paracyclophane derivative.

In the previous case, a [2.2]paracyclophane derivative crystal was formed quantitatively even at room temperature, by virtue of a lattice-controlled steric compression of neighboring molecules.[7] However, the molecular packing in the mixed crystal is a very unusual β-type; the β-packing crystals generally afford amorphous oligomers as mentioned above.[9] The most plausible explanation for the present cyclophane formation is as follows. If a sufficient thermal energy is supplied, the first cycloaddition of one pair of reactive double bonds makes large the distance between two residual double bonds in order to release the strained bond angles around cyclobutane ring, leading to further reaction with neighboring molecules (Fig. 1 a). At low temperatures, however, the thermal motion of dimer is restricted; the motion of two chains having a residual double bond is "frozen" to some extent, and restricted owing to "steric compression" of neighboring molecules, keeping the favorable distance between olefinic bonds for intramolecular reaction (Fig. 1 b). This result concerning the temperature-dependent formation of cyclophane is of significant interest and important, in connection with not only further understanding the photochemical behavior of organic crystals but also demonstration of a new synthetic route of highly strained [2.2]paracyclophane derivatives.

Further investigation of the temperature dependence of photoreaction is currently under way on the other unsymmetric diolefin crystals in order to establish this new method of cyclophane synthesis at low temperature.

References

1) M. Hasegawa, *Pure Appl. Chem.*, **58**, 1179 (1986); M. Hasegawa, "Photopolymerization and Photoimaging Science and Technology," ed by N. S. Allen, Elsevier Applied Science, London and New York (1989), p.187; M. Hasegawa, C.-M. Chung, N. Muro, and Y. Maekawa, *J. Am. Chem. Soc.*, **112**, 5676 (1990).
2) The crystal in which molecules are superimposed without displacement in the direction of long molecular axis is termed β-type packing crystal.
3) Intramolecular cycloaddition between two residual olefins does not occur because of the large distance between them. Such a large distance could be demonstrated by the X-ray crystal structure analysis of several dimers of the same type diolefinic molecules. Distance between double bonds of reacting molecules must be within ca. 4.2 Å for cycloaddition to occur in the solid state (For a review on this empirical principle of organic photochemistry in the solid state, see; G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 2014).
4) A model for topochemical reaction probability was proposed, which is explained in terms of temperature factor; M. Hasegawa and S. Shiba, *J. Phys. Chem.*, **86**, 1490 (1982).
5) The characterization for **1** and its dimer as well as the photoreaction of **1** were reported in the previous paper; M. Hasegawa, Y. Endo, M. Aoyama, and K. Saigo, *Bull. Chem. Soc. Jpn.*, **62**, 1556 (1989).
6) [2.2]Paracyclophane **3**: IR (KBr) 2240, 1735, 1580, 1390, 1240 cm^{-1}; ^1H NMR (CF_3COOD) δ 9.68 (s, 2H, pyrimidyl), 9.23 (d, 2H, J = 6.4 Hz, pyrimidyl), 8.21 (d, 2H, J = 6.4 Hz, pyrimidyl), 7.25 (d, 2H, J = 8.7 Hz, phenylene), 7.16 (d, 2H, J = 8.3 Hz, phenylene), 7.04 (d, 2H, J = 7.8 Hz, phenylene), 6.76 (d, 2H, J = 8.2 Hz, phenylene), 5.52 (d, 2H, J = 10.5 Hz, cyclobutane), 5.35 (dd, 2H, $J_1 = J_2$ = 10.1 Hz, cyclobutane), 4.57 (d, 2H, J = 9.2 Hz, cyclobutane), 4.46-4.32 (m, 4H, methylene), 1.87 (m, 4H, methylene), 1.12 (t, 6H, J = 7.3 Hz, methyl).
7) Both the molecular packing in the mixed crystal and the structure of the reference cyclophane were confirmed by X-ray crystal structure analysis; M. Hasegawa, Y. Maekawa, S. Kato, and K. Saigo, *Chem. Lett.*, **1987**, 907; Y. Maekawa and M. Hasegawa, 59th National Meeting of the Chemical Society of Japan, Yokohama, April 1990, Abstr., No. 2F229; Y. Maekawa, S. Kato, and M. Hasegawa, *J. Am. Chem. Soc.*, in press.
8) The shift of the chemical shifts of benzene rings to lower values (≈6.76 ppm) is typical in the ^1H NMR spectrum of cyclophane derived from this type of diolefins. The proton signals of benzene rings appears beyond 7.00 ppm even in the case of polymer derived from crystals of the same type of diolefin compound.
9) By the systematic studies of the correlation between crystal structure and photoproduct, it was found that oligomers was obtained from β-type packing crystals in which molecules are superimposed to make plane-to-plane stack as shown in Fig. 1. In the structure of the mixed crystal, however, two molecules make a molecular pair, which is related to the neighboring pairs by glide plane. This type of molecular packing is very unusual in β-packing crystal.

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