CHEMISTRY LETTERS, pp. 847-850, 1986.

HETERO HEAD-TO-HEAD DIMER BY TOPOCHEMICAL PHOTOREACTION OF METHYL α-CYANO-4-[2-(2-PYRIDYL)ETHENYL]CINNAMATE

Satoshi KATO, Mitsunobu NAKATANI, Hatsuhiko HARASHINA,[††]
Kazuhiko SAIGO, Masaki HASEGAWA,* and Sadao SATO[†]
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
[†]Sankyo Co., Ltd., Analytical and Metabolite Research
Laboratories, 2-58, Hiromachi 1-chome, Shinagadwa-ku, Tokyo 140

Methyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate crytstal shows a high photoreactivity to form the dimer of single structure quantitatively. This result is a unique example in such point that the topochemical photoreaction of β-form diolefin crystals gives neither of the polymer nor the cyclic dimer, but the photostable diolefinic dimer.

Conjugated diolefin crystals arranged in α-type are known to give linear high polymers with 1,3-trans cyclobutanes in their main chains.1) In the topochemical photopolymerization of unsymmetrically substituted diolefinic compounds, the product is expected to be a highly stereospecific polymer having alternative substituents on cyclobutane rings,2) or having a chiral structure.3) Recently we found a number of unsymmetrically substituted photoreactive diolefinic crystals, exhibiting various photochemical behaviors to give such as homo- and hetero-adduct polymers or dimers.2,4) In the present paper, we report the photoreaction behavior of methyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate crystal. The structure of the photoproduct was investigated by spectroscopic and crystallographic analysis.

Methyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate (**1**) was prepared by successive condensation of terephthalaldehyde with 2-picoline and with methyl cyanoacetate (44% overall yield). Finely powdered crystals of **1**, recrystallized from methanol (mp 179-181 °C)5) were dispersed in 100 ml of water containing a small amount of surfactant (NIKKOL TL-10FF) and irradiated, with vigorous stirring, by a 500 W high pressure mercury lamp set outside of the flask through a Pyrex glass under nitrogen atmosphere at room temperature.

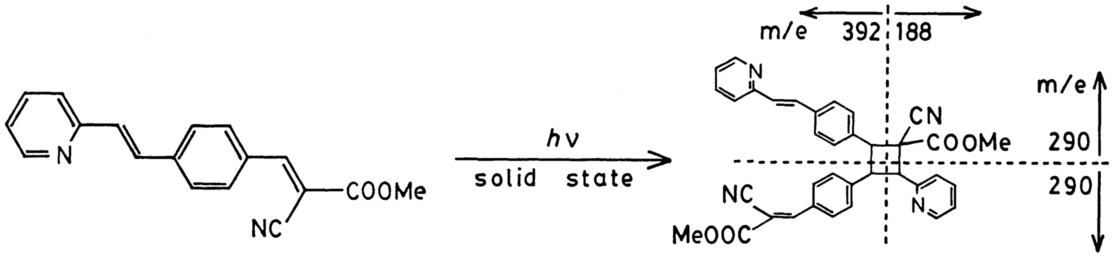
In the course of photoirradiation, a definite amount of the sample was withdrawn and analyzed by TLC and by ^1H NMR and UV spectra. In progress of the photoreaction, the ratio of olefinic proton signals decreased while new signals

---

[††] Present address: Polyplastics Co., Ltd., 973 Miyajima, Fuji-shi, Shizuoka 416.

corresponding to cyclobutane protons appeared and increased. The singlet of methyl protons of ester group at 3.94 ppm decreased, and two new singlet signals at 3.89 and 3.54 ppm appeared. The UV absorption band at 365 nm decreased and new absorption peak appeared at 313 nm. In addition, clear isosbestic points are seen in the spectra at 258 and 329 nm during the course of photoreaction. The photoreaction of the crystal of **1** is fast and the spectral change is leveled off within 2 h photoirradiation. Finally, TLC of photoproduct showed a single spot. These spectral data and TLC analysis indicate the progress of single reaction on photoirradiation of the crystal **1**.

After irradiation for 2 h, the product (**2**) was isolated and purified by column chromatogrophy on aluminium oxide, followed by recrystallization from benzene/hexane (yield: 90%). The IR spectrum of the photoproduct showed the decrease of carbon-carbon double bond (1600 and 980 cm^{-1}) and the shift of carbonyl and cyano groups to higher wave number (from 1720 to 1740 and from 2210 to 2220 cm^{-1}, respectively), indicating the formation of a saturated ester. These spectral results coinside with the exclusive progression of [2+2] cycloaddition between a pair of double bonds. The mass spectrum shows peaks at *m*/*e* 188 and 392 due to asymmetric cleavage of the cyclobutane ring in addition to the peaks originated in symmetric cleavage at *m*/*e* 290 ($M^+/2$) and 580 (M^+). The mass spectral result of **2**[6] corresponds to the structure of hetero head-to-head dimer, namely, methyl 1-cyano-3-[4-(2-cyano-2-methoxycarbonylethenyl)phenyl]-2-(2-pyridyl)-4-[4-[2-(2-pyridyl)ethenyl]phenyl]cyclobutanecarboxylate.



1 **2**

To ascertain the structure of **2**, the X-ray crystallographic analysis of **1** was carried out.[7] The crystal structure viewed along the c axis is shown in Fig. 1. The reactive double bonds, separated by 3.886(7) Å for C(7)···C(15') and 3.807(7) Å for C(8)···C(16'), are non-parallel while these distances are within those of normal reactive bonds. Other distances of intermolecular olefin double bonds are 4.926(7) Å for C(8)···C(16"), 4.906(7) Å for C(7)···C(15") and 4.719(6) Å for C(7)···C(8"). These distances is so long for the limit of photoreactive double bonds accepted at present.[8] And other short distances between carbon atoms, which are 4.141(6) Å for C(7)···C(7") and 4.281(6) Å for C(8)···C(15"), are out of the question because these carbon atoms do not lie in the disposition of reactive olefinic double bonds on neiboring molecules. Every pair of two reactive molecules is arranged in β-type packing and the other neighboring molecule is too far to react as illustrated in Fig. 2. The nonparallel arrangement of reactive double bonds is deviated from generally accepted principle for topochemical [2+2] reaction[8] and has been reported only in a few articles for the last few years.[9] Moreover, only a few examples are

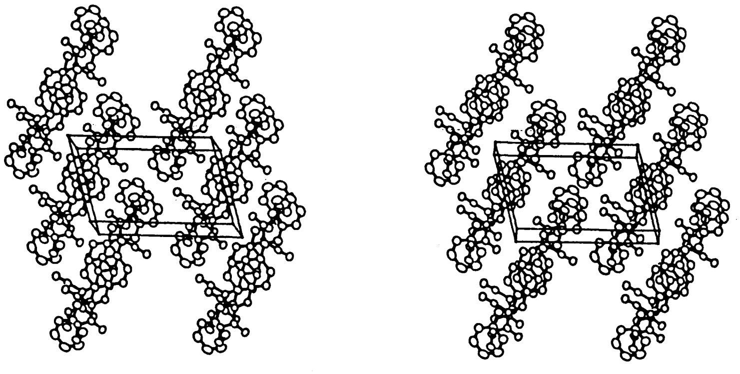


Fig. 1. The crystal structure viewed along the **c** axis. The origin is at upper left (back-ground), with **a** horizontal and **b** vertical.

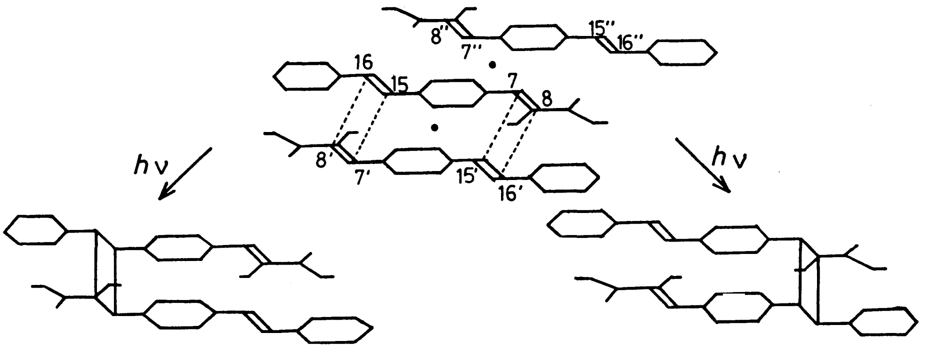


Fig. 2. Schematic illustration of the formation of racemic dimer (2) from **1**.

related to the photoreactions of unsymmetrically substituted diolefins arranged in β-form.3e,10)

The crystal structure of **1** sufficiently supports the structure of the photodimer (**2**) expected from the spectral studies if the topochemical process is assumed in the photoreaction. Highly photostable behavior of **2** is quite reasonable because, after one pair of double bond reacted, then the residual pair will be rearranged far outside of the photoreactive arrangement in the crystal. Quantitative formation of the dimer (**2**) of single structure indicates that the photoreaction of **1** is strictly controlled by the crystal lattice although the final photoproduct is amorphous.

Although the dimer (2) has asymmetric carbon atoms, the photoproduct from large single crystal of **1** did not show detectable values of optical rotation and circular dichroism. As the center of symmetry exists between two molecules arranged in β-form, and as two pairs of double bonds are equivalent in reactivity, both enantiomers should be equivalently formed from **1** if none of chiral induction exists in this system (Fig. 2).

References

1) M. Hasegawa, Chem. Rev., **83**, 507 (1983); W. L. Dilling, Chem. Rev., **83**, 1 (1983).

2) M. Hasegawa, S. Kato, N. Yonezawa, and K. Saigo, J. Polym. Sci., Polym. Lett. Ed., in press.

3) a) L. Addadi and M. Lahav, J. Am. Chem. Soc., **100**, 2838 (1978); b) L. Addadi and M. Lahav, ibid., **101**, 2152 (1979); c) J. van Mil, L. Addadi, M. Lahav, and L. Leiserowitz, J. Chem. Soc., Chem. Commun., **1982**, 584; d) L. Addadi, J. van Mil, and M. Lahav, J. Am. Chem. Soc., **104**, 3422 (1982); e) J. van Mil, L. Addadi, E. Gati, and M. Lahav, ibid., **104**, 3422 (1982).

4) M. Hasegawa, H. Harashina, S. Kato, and K. Saigo, Macromolecules, accepted for publication.

5) ^{1}H NMR ($CDCl_3$) δ 3.92 (3H, s), 7.05-8.10 (9H, m), 8.18 (1H, s), 8.52-8.79 (1H, m) ppm.

6) Dimer (**2**): mp 186-189 °C; ^{1}H NMR ($CDCl_3$) δ 3.54 (3H, s), 3.88 (3H, s), 4.76 (1H, d), 4.98 (1H, d), 5.23 (1H, t), 7.02-7.84 (16H, m), 8.12 (1H, s), 8.58 (1H, d), 8.64 (1H, d) ppm; MS *m/e* 580 (M^+), 392 (asymmetric cleavage of the cyclobutane ring), 290 ($M^+/2$ symmetric cleavage), 188 (asymmetric cleavage).

7) Crystal data of **1**: $C_{18}H_{14}N_2O_2$ = 290.3, $P\bar{1}$, triclinic, $a = 12.269(2)$, $b = 7.489(1)$, $c = 8.486(2)$ Å, $\alpha = 97.74(1)$, $\beta = 92.42(1)$, $\gamma = 74.41(1)°$, $U = 743.8$ Å^3, $Z = 2$, $D_x = 1.30$ g.cm^{-3}, $R = 0.080$, μ (Cu Kα) = 0.7 mm^{-1}.

8) M. D. Cohen and G. M. J. Schmidt, J. Chem. Soc., **1964**, 1996; G. M. J. Schmidt, Pure Appl. Chem., **27**, 647 (1971).

9) For example: N. Ramasubbu, T. N. G. Row, K. Venkatesan, V. Ramamurthy, C. N. R. Rao, J. Chem. Soc., Chem. Commun., **1982**, 178; M. Hasegawa, K. Saigo, T. Mori, H. Uno, M. Nohara, and H. Nakanishi, J. Am. Chem. Soc., **106**, 2788 (1985).

10) M. D. Cohen, A. Elgavi, B. S. Green, Z. Ludmer, and G. M. J. Schemidt, J. Am. Chem. Soc., **94**, 6776 (1972); F. Nakanishi, T. Tanaka, F. Miyagawa, and H. Nakanishi, Nippon Kagaku Kaishi, **1981**, 412.

(Received February 15, 1986)