NOTES *Bull. Chem. Soc. Jpn.*, **58**, *3399—3400 (1985)*

Convenient Synthesis of β-Truxinic Acid *via* Photodimerization of *p*-Nitrophenyl Cinnamate in the Crystalline State

Tadatomi NISHIKUBO,* Eiji TAKAHASHI, Takatoshi MIYAJI, and Takashi IIZAWA
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221

(Received June 13, 1985)

Synopsis. β-Truxinic acid was synthesized in extremely high yield *via* a topochemical photodimerization of *p*-nitrophenyl cinnamate crystals, followed by the hydrolysis of the obtained dimer.

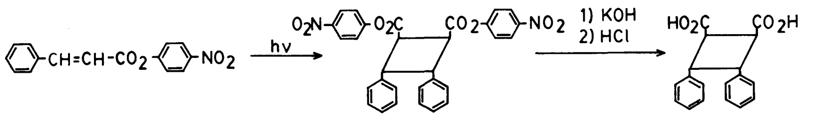
Since topochemical photodimerizations of cinnamic acid derivatives have been investigated extensively by Schmidt and his co-workers,[1] the photodimerizations of cinnamic acids and other olefinic compounds in the crystalline state, which is very interesting as crystal engineering, have been reported. The stable α-form of (E)-cinnamic acid gives α-truxillic acid selectively whereas the metastable β-form of (E)-cinnamic acid yields pure β-truxinic acid at low temperature. However, the metastable form of (E)-cinnamic acid is transformed to the stable form at temperatures higher than 50 °C in the crystalline state. Recently, although many substituted α-truxillic acids or β-truxinic acids were prepared[2–5] by the topochemical photodimerizations of the corresponding forms of substituted (E)-cinnamic acids, the unsubstituted β-truxinic acid has not been obtaind by topochemical photodimerization on a preparative scale so far due to the above transformation.

This article reports on the successful photodimerization of *p*-nitrophenyl cinnamate (NPC) in a crystalline state at various temperatures to give β-truxinic acid in high yield per reaction. As shown in Fig. 1, the rate of photochemical reaction of NPC embeded in KBr pellet was much faster than those of cinnamic acid (CA) and phenyl cinnamate (PC). This means that NPC has a high photochemical reactivity in the crystalline state.

Therefore, the photochemical reaction of NPC has been carried out under various conditions. The results are summarized in Table 1. The yield of bis(*p*-nitrophenyl) β-truxinate (BNPT) was not affected by the reaction temperature, the solvent and air. However, the yield was dependent on the irradiation time. The yield of BNPT was also affected by the amounts of NPC suspended in hexane, because a small amount of the suspended NPC was soluble in hexane. (E)–NPC in a hexane solution changed to the (Z)-isomer (confirmed by HPLC) upon irradiation by UV light.

According to the intensity of the X-ray diffraction patterns, the crystallinity of NPC decreased extremely along with the progress of the reaction. Then, new weak peaks, which seem to be peaks of the dimer crystal, appeared. However, the diffraction pattern of as-prepared BNPT was quite different from that of the recrystallized BNPT. This is good evidence that the reaction of NPC proceeded topochemically.

Recently, we have found[6] that the pendant 4-nitrophenoxide moiety acts as an excellent photosensitizer for a pendant cinnamic ester in a polymer film and a diluted solution of the polymer. From these results, it seems that 4-nitrophenoxide on NPC



(NPC) (BNPT)

TABLE 1. PHOTOCHEMICAL REACTION OF NPC IN THE CRYSTALLINE STATE

Run No.	Cinnamic ester/g/l	Dispersant	Irradiation conditions Temp/°C	Time/h	Yield %
1	NPC (4.0)	Hexane	30	3	67.3
2	NPC (12.0)	Hexane	30	3	80.2
3	NPC (20.0)	Hexane	30	3	88.9
4	NPC (40.0)	Hexane	30	3	84.4
5	NPC (40.0)	Hexane	30	3	85.2[a]
6	NPC (40.0)	Hexane	−10	3	89.9
7	NPC (40.0)	Hexane	50	3	90.7
8	NPC (40.0)	Hexane	30	6	99.2
9	NPC (80.0)	Hexane	30	10	91.1
10	NPC (40.0)	Water	10	3	89.4

a) The reaction was carried out in N_2.

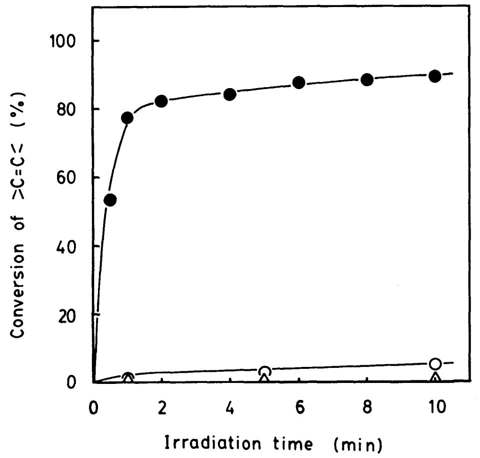


Fig. 1. The rates of disappearance of C=C group in cinnamic acid and its esters.
(△): CA, (○): PC, (●): NPC.

also acted as a photosensitizer in the crystalline state.

The BNPT obtained by a photodimerization reaction in a crystalline state was successfully hydrolyzed in high yield to give *β*-truxinic acid using excess potassium hydroxide in methanol.

From these results, we reveal here that NPC is an excellent starting compound for obtaining an unsubstituted *β*-truxinic acid by crystal engineering.

Experimental

NPC (mp 144—145 °C)[7] was prepared through a reaction of cinnamoyl chloride with 4-nitrophenol. Then it was recrystallized twice from methanol.

Measurement of the Rate of Photochemical Reaction of NPC in KBr Pellet. NPC (10^{-6} mol) with KBr (0.089 g) was ground and molded into pellet form. The pellet fastened to a plate was irradiated using 250-W high-pressure mercury lamp (Ushio Electric Co., USH-250D) at a distance of 30 cm. The rate of the disappearance of the absorption peak due to a C=C group at 1640 cm^{-1} was measured by IR spectrometry (JASCO model A-202).

Synthesis of BNPT by Photodimerization of NPC in the Crystalline State. NPC crystals (1.6—80 g) were dispersed in hexane (400 ml) in a Pyrex flask. The flask was then irradiated with a 100-W high-pressure mercury lamp (Ushio Electric Co., UM-102) at various temperatures. Then the progress of the reaction was monitored by measuring the decrease of NPC and the increase of BNPT by HPLC [JASCO model; Twincl, detecter; uvidec-100-III, column (4.6 mm×250 mm) packed with a silicagel-ODS-10, elutant; water-acetonitrile (ratio; 4/6)] and/or from UV spectrum of NPC (absroption maximum; 271 nm in THF) by the spectrometry (Shimazu model; UV-240). The final product was filtered off, washed with hot methanol, and recrystallized twice from 2-butanone. Mp 192—193 °C. IR (KBr) 1750 (C=O), 1520 and 1350 ($-NO_2$), 1150 cm^{-1} (C-O-C). NMR ($CDCl_3$) δ=4.6 (s, 2H, C-CH-C), and 7.1—8.5 (m, 9H, aromatic protons). Found: C, 66.51; H, 4.10; N, 5.10%. Calcd for $C_{30}H_{22}N_2O_8$: C, 66.91; H, 4.12; N, 5.20%.

Synthesis of β-truxinic acid by Hydrolysis of BNPT. BNPT (53.8 g; 0.1 mol) and potassium hydroxide (28.1 g; 0.5 mol) were dissolved in methanol (250 ml). Then, the solution was refluxed for 5 h. The reaction mixture was poured into water (750 ml) the PH of the solution was adjusted to 3 with concd HCl solution. The precipitated *β*-truxinic acid was filtered off, washed with water, and dried. Yield: 28.6 g (96.7%). The crude *β*-truxinic acid was recrystallized twice from acetic acid. Mp 209—210 °C (Lit,[8] 209—210 °C).

The authors thank professor M. Hasegawa of the University of Tokyo for his helpful advice.

References

1) a) G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971); b) G. M. J. Schmidt *et al.* "Solid State Photochemistry," Verlag Chemie, New York (1976).

2) M. D. Cohen, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, **1964**, 2000.

3) a) F. Nakanishi, H. Nakanishi, M. Tsuchiya, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **49**, 3096 (1976); b) F. Nakanishi, M. Ishii, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **57**, 3335 (1984).

4) J. P. Glusker D. E. Zacharias, and H. L. Carrell, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 68.

5) a) J. A. R. P. Sarma and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, **1984**, 145; b) G. R. Desiraju, R. Kamala, B. H. Kumari, and J. A. R. P. Sarma, *J. Chem. Soc. Perkin Trans. 2*, **1984**, 181.

6) T. Iizawa, T. Nishikubo, E. Takahashi, and M. Hasegawa, *Makromol. Chem.*, **184**, 2297 (1983).

7) M. L. Bender, G. R. Schonbaum, and B. Zerner, *J. Am. Chem. Soc.*, **84**, 2540 (1962).

8) H. Stobbe, *Ber.*, **55**, 2225 (1922).