Diastereoselective Photocycloaddition using Memory Effect of Molecular Chirality Controlled by Crystallization

Masami Sakamoto,* Atsushi Unosawa, Shuichiro Kobaru, Yasuhiro Hasegawa, Takashi Mino, Yoshio Kasashima, and Tsutomu Fujita

Experimental

General. NMR spectra were recorded on CDCl$_3$ solutions on a BRUKER 300 operating 300 MHz, respectively, for $^1$H- and $^{13}$C-NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standards. IR spectra were recorded on a JASCO FT/IR-230 spectrometers as KBr disks.

General procedure for the preparation of naphthamides 1a and 1b. Both naphthamides 1a-1b were provided from the corresponding 2-alkoxynanthoic acids and proline methyl ester. A synthesis of 1a was exemplified as follows. To a THF solution containing 1.11 g (5.5 mmol) of naphthoic acid and triethylamine 0.67g (6.6 mmol) was added 0.79 g (6.6 mmol) of thionyl chloride at 0°C. The reaction mixture was stirred for 0.5 h, and then a THF solution containing 1.68 g of proline methyl ester (13.0 mmol) was added dropwise. After the reaction mixture was stirred for 2 h, water and ethyl acetate were added, and the organic layer was extracted in the usual manner. After the organic solvent was evaporated in vacuo, the residual mixture was subjected to chromatography on silica gel and the naphthamide 1a was separated. The structures of 1a and 1b were determined on the basis of spectral data, mass spectroscopy, and unequivocally X-ray single crystallographic analyses.

(S, aR) N-(2-Methoxy-1-naphthalencarbonyl)prolinecarboxilic acid methyl ester 1a
m.p. 109-112°C; IR (cm⁻¹, KBr) 1620, 1735; ¹H-NMR: (CDCl₃) δ 1.9-2.0 (m, 2H), 2.05-2.25 (m, 1H), 2.3-2.35 (m, 1H), 3.2-3.4 (m, 2H), 3.90 (s, 3H), 3.97 (s, 3H), 4.75-4.8 (m, 1H), 7.3-7.4 (m, 2H), 7.5-7.6 (m, 1H), 7.8 (d, J=8.2 Hz, 1H), 7.9-8.0 (m, 2H), ¹³C-NMR (CDCl₃) δ28.7, 33.9, 52.3, 56.3, 60.3, 62.9, 117.0, 123.6, 127.9, 128.5, 131.9, 132.2, 133.1, 135.0, 135.4, 156.9, 173.0, 177.1; EI-MS m/z (rel intensity): 313 (M⁺, 10); HRMS (FABMS) m/z calcd for C₁₈H₁₉N₀₄+H: 314.1392, found 314.1368.

(S, aR)-N-(2-Ethoxy-1-naphthalencarbonyl)prolinecarboxilic acid methyl ester 1b
m.p. 133-135°C; IR (cm⁻¹, KBr) 1053, 1248, 1446, 1628, 1749, 2871, 2971, 2973; ¹H-NMR: (CDCl₃) δ 1.4 (t, J=7.0 Hz, 3H), 1.85-2.0 (m, 2H), 2.05-2.2 (m, 1H), 2.35-2.5 (m, 1H), 3.15-3.25 (m, 1H), 3.3-3.4 (m, 1H), 3.89 (s, 3H), 4.2-4.3 (m, 2H), 4.75-4.8 (m, 1H), 7.3-7.45 (m, 2H), 7.5 (dt, J=1.1 and 7.6 Hz, 1H), 7.8 (d, J=8.2 Hz, 1H), 7.8-8.0 (m, 2H), ¹³C-NMR (CDCl₃) δ 19.0, 28.8, 34.0, 52.3, 56.4, 62.8, 69.1, 118.2, 124.1, 128.0, 128.5, 131.9, 132.2, 133.1, 135.1, 135.3, 156.1, 173.0, 177.2; EI-MS m/z (rel intensity): 327 (M⁺, 16); HRMS (FAB) m/z calcd for C₁₉H₂₁N₀₄ +H 328.1549, found 328.1535.

General procedure for the photochemical reaction of naphthamide 1a-b with 9-cyanoanthracene using the chiral crystal.
Crystals of 1 were added to a cooled THF solution of 9-cyanoanthracene (0.025 M), and the solution was irradiated with a 350-W ultra-high pressure mercury lamp under argon atmosphere for 30 min. After removing the solvent in vacuo, the crude photolysate was subjected to chromatography on silica gel. The 4+4 cycloadduct 2 was obtained in 100% chemical yield accompanied by a small amount of a dimmer of 9-cyanoanthracene. The chemical yield of 2 was determined on the basis of the consumed naphthamide 1.

Photoadduct of 1a with 9-cyanoanthracene 2a
Decomp. 103-105°C; IR (cm⁻¹, KBr) 1655, 1737; ¹H-NMR: (CDCl₃) δ 1.5-1.9 (m, 3H), 2.1-2.25 (m, 1H), 2.6-2.7 (m, 1H), 2.85-2.95 (m, 1H), 2.95 (s, 3H), 3.88 (s, 3H), 4.36 (d, J=7.6 Hz, 1H), 4.65-4.75 (m, 2H), 5.91 (s, 1H), 6.8-7.0 (m, 6H), 7.2-7.3 (m, 4H), 7.35-7.4 (m, 1H), 7.6-7.65 (m, 1H), ¹³C-NMR (CDCl₃) δ 25.8, 29.2, 48.2, 52.7, 54.2, 54.5, 55.7, 56.0, 60.6, 64.7, 98.4, 122.0,
125.0, 125.3, 126.3, 126.9, 127.2, 127.3, 127.4, 128.7, 129.3, 139.3, 140.2, 140.6, 140.9, 142.0, 143.2, 164.3, 168.5, 173.7; FAB-MS \( m/z \) (rel intensity) 517 (\( M^+ + 1 \), 11); HRMS (FAB-MS) \( m/z \) calcd for C\(_{33}\)H\(_{28}\)N\(_2\)O\(_4\) + H 517.2127, found 517.2007.

**Photoadduct of 1b with 9-cyanoanthracene 2b**

Decomp. 126-130°C; IR (cm\(^{-1}\), KBr) 1174, 1413, 1635, 1747, 2237, 2979; \(^1\)H-NMR: (CDCl\(_3\)) \( \delta \) 1.0 (8, \( J=7.0 \) Hz, 3H), 1.45-1.6 (m, 1H), 1.45-1.85 (m, 2H), 2.1-2.3 (m, 1H), 2.55-2.7 (m, 2H), 2.9-3.0 (m, 1H), 3.2-3.35 (m, 1H), 3.87 (s, 3H), 4.33 (d, \( J=7.6 \) Hz, 1H), 4.55-4.7 (m, 2H), 5.89 (s, 1H), 6.75-7.0 (m, 6H), 7.15-7.3 (m, 4H), 7.35-7.4 (m, 1H), 7.55-7.6 (m, 1H), \(^{13}\)C=NMR (CDCl\(_3\)) \( \delta \) 14.7, 25.9, 29.3, 48.2, 52.7, 54.3, 54.5, 55.7, 60.7, 64.4, 64.7, 98.3, 122.1, 124.9, 125.2, 126.3, 126.9, 127.0, 127.1, 127.2, 127.3, 127.4, 128.8, 129.4, 139.4, 140.2, 140.6, 140.9, 142.0, 143.3, 163.6, 168.5, 173.8; FAB-MS \( m/z \) (rel intensiy) 532 (\( M^+ + 1 \), 27); HRMS (FAB-MS) \( m/z \) calcd for C\(_{34}\)H\(_{30}\)N\(_2\)O\(_4\) + H 531.2284, found 531.2261.
Figure S1. $^1$H NMR spectrum of 1a before crystallization
Figure S2. $^1$H NMR spectrum of 1a immediately after dissolving crystals in CDCl$_3$
Figure S3. $^1$H NMR spectrum of 1b before crystallization
Figure S4. $^1$H NMR spectrum of 1b immediately after dissolving crystals in CDCl$_3$
Figure S5. $^1$H NMR spectrum of 2a
Figure S6. $^{13}$C NMR spectrum of 2a
Figure S7. $^1$H NMR spectrum of 2b
Figure S8. $^{13}$C NMR spectrum of 2b
Crystal data for 1a (recrystallized from a mixture of CHCl₃ and hexane); C₁₈H₁₉NO₄, Mr = 313.34, monoclinic, space group P2₁, a = 11.0267(17) Å, b = 6.9804(11) Å, c = 11.2114(17) Å, β = 116.392(2)°, V = 773.0(2) Å³, Z = 2, ρ = 1.346 Mgm⁻³; in the final least-square refinement cycles on F², the model converged an R₁ = 0.0352, wR₂ = 0.0884 for 4315 reflections.

Figure S9. View of 1a showing the atoms and thermal ellipsoids at 40% probability.
Crystal data for 1b (recrystallized from a mixture of CHCl₃ and hexane); C₁₉H₂₁NO₄, Mr = 327.37, Monoclinic, space group P2₁, a = 7.6617(7) Å, b = 12.7932(12) Å, c = 9.0838(8) Å, β = 99.4840(10)°, V = 878.20(14) Å³, Z = 2, ρ = 1.238 Mgm⁻³; in the final least-square refinement cycles on F2, the model converged an R₁ = 0.0462, wR₂ = 0.0834 for 3567 reflections.

Figure S10. View of 1b showing the atoms and thermal ellipsoids at 40% probability.
Crystal data for 2b (recrystallized from a mixture of CHCl₃ and hexane); C₃₄H₃₀N₂O₄, $Mr = 530.60$, Orthorhombic, space group $P2_12_12_1$, $a = 10.1985(5)$ Å, $b = 12.5024(6)$ Å, $c = 21.8216(10)$ Å, $V = 2782.4(2)$ Å³, $Z = 4$, $\rho = 1.267$ Mgm⁻³; in the final least-square refinement cycles on F2, the model converged an $R_1 = 0.0443$, $wR_2 = 0.1204$ for 6395 reflections.

Figure S11. View of 2b showing the atoms and thermal ellipsoids at 40% probability.