A Novel Photochemical Reaction of 2-Alkoxynicotinates to **Cage-Type Photodimers**

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Irradiation of a benzene solution of 2-alkoxynicotinic acid alkyl esters gave cage-type photodimers in good yields, the structure of which was established by X-ray single-crystal analysis. The maximum quantum yield was 8.0×10^{-2} when a 5.0 M (almost neat) solution was used. Photolysis of phenyl 2-methoxynicotinate promoted photo-Fries rearrangement to give 1,3- and 1,5-rearranged products. Excimer emission of methyl 2-methoxynicotinate was observed at 77 K.

Introduction

The photochemical reaction of aromatic compounds has received much attention from both the mechanistic and synthetic perspectives,1-5 and the intra- and intermolecular photochemical addition reactions of carbon aromatics are well documented.⁶⁻¹¹ Photochemical addition of benzene derivatives with alkenes is a useful method for synthesizing natural products. Furthermore, $4\pi + 4\pi$ photodimerization of polycyclic aromatic systems, such as naphthalene and anthracene derivatives, are investigated not only for the fundamental photophysical and photochemical properties but also for a wide range of applications. However, in contrast, the dimerization of monocyclic aromatics, benzene and its derivatives, has not been successful in a photochemical reaction¹² because of the disadvantageously enormous loss of aromatic energy of two aromatic molecules. We are interested in new aspects of the photochemical cycloaddition of aromatic compounds and the application of the methodology to heteroaromatics and have reported a unique 2 + 2 photodimerization of 2-alkoxy-3-cyanopyridines.^{13,14} We have now found a new type of photodimerization of nicotinic acid esters leading to cage-type photodimers.

Results and Discussion

2-Alkoxynicotinates **1a**-**f** were conveniently prepared by alkoxylation and acid-catalyzed esterification from 2-chloronicotinic acid.^{15,16} Photochemical experiments were carried out by irradiation of an argon-degassed benzene solution at room temperature with a Pyrexfiltered light from 1000-W high-pressure mercury lamp. The consumption of the starting esters was checked by TLC; irradiation time depended on the concentration of the esters and needed 2-8 h. For example, when a benzene solution containing 100 mg of methyl 2-methoxyniconinate 1a (0.1 M) was irradiated for 2 h and the crude photolyzate was subjected to chromatography on silica gel, a dimer 2a, 5,11-dimethoxy-4,10-diazapentacyclo[6.4.0.0.^{2,7}0.^{3,12}0^{6,9}]dodeca-4,10-diene-6,12-dicarboxylic acid dimethyl ester, was isolated in 85% yield at 80% conversion yield as shown in Table 1, entry 1. Photolysis of other nicotinic acid esters 1b-d also gave the corresponding dimers **2b**-**d** in good yields (entries 2-4). The dimerization was influenced by the substituent on the 6-position of the pyridine ring. For the photolysis of 1e, the substitution of a methyl group at the 6-position resulted in low reactivity for the photoreaction, and the prolonged irradiation for 8 h gave an intractable mixture (Table 1, entry 5). The difference in reactivity might be attributed to the steric effect of the methyl group.

However, phenol ester 1f showed completely different photochemical behavior (Table 1, entry 6). When a 0.02 M benzene solution of 1f was irradiated, excitation of the molecule led to the reaction at the ester functionality instead of the pyridine ring, the photo-Fries rearrangement proceeded, and 1,3- and 1,5-rearranged products (3 and 3') were obtained in 47% and 29% yield, respectively, as the only isolable products.^{17,18}

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 Table 1. Photochemical Reaction of 2-Alkoxynicotinates

 1a-f in Benzene



entry	ester 1 ^a	\mathbb{R}^1	\mathbb{R}^2	\mathbb{R}^3	conv (%)	yields (%) ^b of 2 or (3 , 3 ') ^c
1	1a	Me	Me	Н	80	85
2	1b	Me	Et	Н	68	89
3	1c	Et	Me	Н	56	93
4	1d	Me	\mathbf{Pr}^{i}	Н	51	87
5	1e	Me	Me	Me	48	0^d
6	$1\mathbf{f}^{e}$	Me	Ph	Н	45	0 (47, 29) ^c

^{*a*} A benzene solution (0.1 M) was irradiated for 2 h. ^{*b*} The chemical yields were determined on the basis of consumed nicotinates 1. ^{*c*} Number in parentheses is the yield of photo-Fries rearrangement products 3 (1,3-rearrangement) and 3' (1,5-rearrangement). ^{*d*} Intractable mixture was formed after 8 h of irradiation. ^{*e*} Benzene solution (0.02 M) was irradiated for 0.5 h.

Table 2. Quantum Yields for Dimerization of 1a

solvent	concn (mol/L)	$\Phi_{ m dim.}$ ($ imes$ 10 ⁻³)
benzene	0.01	0.3
benzene	0.1	1.6
benzene	1.0	13
benzene	5.0	80
MeCN	0.1	1.8
$C_{6}H_{12}$	0.1	1.6
EtOH	0.1	2.2

The dimer structure 2a - d was determined on the basis of the spectral data. The structural analysis was exemplified by 2a; the HR-Mass (FAB) spectrum showed a molecular ion peak at 335.1211 (M + 1), which strongly suggested the dimeric structure. The ¹H NMR spectrum showed the methine protons at δ 2.89 (dt, J = 7.8 and 7.1 Hz, 2H, 2- and 8-H), 3.29 (t, J = 7.1 Hz, 2H, 1- and 7-H), and 5.23 (d, J = 7.8 Hz, 2H, 3- and 9-H) derived from cyclobutane substructure. The ¹³C NMR spectrum exhibited peaks at δ 27.1 (d, 2- and 8-C), 35.1 (d, 1- and 7-C), 55.6 (s, 6-, 12-C), and 57.7 (d, 3- and 9-C) derived from cyclobutane sp³ carbons, in addition to the sp² carbon peaks at 164.2 (s, C=N) and 172.3 (s, C=O). The assignment was made using the COSY sequence. These spectral data strongly supported the C-2 symmetrical structure of cage-type photodimer 2a.

Finally, the cage structure of **2a** was established by X-ray crystallographic analysis.¹⁹ The four-membered rings show a range of bond lengths from 1.522(3) to 1.592(3) Å and bond angles of 88.6–90.6°. Despite possessing three fused cyclobutane rings, the dimers were



Figure 1. (a) Fluorescence spectrum of **1a** at the concentration of 1.0×10^{-3} in EPA (ethanol/isopentane/ether 2:5:5) at room temperature, excitation at 290 nm, band-pass 3 nm. (b) Fluorescence spectrum of **1a** at the concentration of 1.0×10^{-3} in EPA at 77 K, excitation at 290 nm, band-pass 1.5 nm.

stable at room temperature for several weeks. However, when 2a was heated in refluxing toluene for 1 h or the acetonitrile solution was irradiated with short wavelength light (254 nm), the starting nicotinic acid ester 1a was obtained quantitatively.

The intermolecular photoreaction should be influenced by the concentration of the substrate. Table 2 shows the quantum efficiency for the formation of 2a under various concentrations. When a benzene solution of 2a at a concentration under 0.01 M was used, the cycloaddition was quite inefficient ($\Phi = 3 \times 10^{-3}$). The value increased according to the concentration linearly and was 1.6 imes 10^{-3} and 1.3×10^{-2} , at 0.1 and 1.0 M of concentration, respectively. The maximum quantum yield was 8.0 \times 10^{-2} when 5.0 M (almost neat) solution was used. Furthermore, it seems that a protic solvent is somewhat preferred for the dimerization; however, considerable differences have not been observed. In the case of 1f, irradiation of a higher concentrated benzene solution (0.5 M) did not give the corresponding dimers but also gave 1,3- and 1,5-rearrangement products, 3 and 3', in 48% and 39% yield, respectively, when the conversion yield reached at 23%.

The photochemical cycloadditions of many aromatic compounds proceed via a singlet excimer or exciplex. In the fluorescence spectra of **1a** at room temperature (Figure 1(a)), only strong emission derived from an excited monomer was observed at 326 nm without any new emissions. On the other hand, when the fluorescence was measured at 77 K, a new emission assignable to that from the excimer was observed at 430 nm accompanied with fluorescence from the monomer (Figure 1(b)). It seems that dimerization could be faster than emission from the excimer at room temperature. Quenching of the dimerization by 0.02 M of 2,5-dimethylhexa-2,4-diene ($E_{\rm T}$ 58.7 kcal mol⁻¹) was quite inefficient, whereas pyridine has triplet energy at 84.7 kcal mol^{-1.20} This fact also indicated that the dimerization proceeds via the singlet excited state by direct irradiation.

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Figure 2. (a) Fluorescence spectrum of **1f** at the concentration of 1.0×10^{-3} in EPA at room temperature, excitation at 290 nm, band-pass 3 nm. (b) Fluorescence spectrum of **1f** at the concentration of 1.0×10^{-3} in EPA at 77nK, excitation at 290 nm, band-pass 1.5 nm.

Contrary to the above, phenyl ester **1f** did not exhibit any emission at room temperature (Figure 2(a)); however, emissive excimer was observed at 77 K (Figure 2(b)). Photo-Fries rearrangement of **1f** proceeded from its singlet excited state, which was also determined by sensitization and quenching experiments. These results indicate that photo-Fries rearrangement initiated by homolytic cleavage of the bond between carbonyl and oxygen from the singlet excited state could be faster than dimerization or fluorescence emission at room temperature. The difference in the reaction course was clearly due to the stability of the radical pair intermediate making the C(=O)-O bond cleavage process a more facile process.

The regioselectivity and stereoselectivity in many singlet photoadditions can be explained by orbital interactions.^{25,26} Frontier-MO calculations by the PM3 method help to explain the photocycloaddition.²⁷ The orbital surfaces of the HOMO and LUMO of **1a** were obtained from the PM3 Hamiltonian contained within MacSpartan as shown in Figure 3. The orbital interaction between each LUMO supports the photocycloaddition leading to isolable dimer **2a**. The coefficient values of C3 and C6 positions of LUMO are bigger than the other positions, and the interaction of these positions are suggested; however, both the $4\pi + 4\pi$ addition between C3–C6' and the C6–C3' (path A mechanism) and $2\pi + 2\pi$ cyclo-addition between C3–C4 and C6'-C5' (path B mechanism) are supported as shown in Scheme 1.

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Figure 3. Orbital surface diagram of methyl 2-methoxynicotinate **1a** obtained from the PM3 Hamiltonian contained within MacSpartan.

Scheme 1



Pac et al. and Noh et al. individually investigated the cycloaddition of 1-cyanonaphthalene to furan and detected two diastereomeric $4\pi + 4\pi$ adducts by NMR spectroscopy.^{21–23} Furthermore, recently we reported the photochemical addition of cyanopyridine with furan,²⁴ where the $4\pi + 4\pi$ photocycloadducts are also directly detected by NMR spectra. A deuterated benzene solution of 1a was irradiated with and without 2,5-dimethylhexa-2,4-diene as a triplet quencher, because in the case of the cyanopyridine-furan system, a $4\pi + 4\pi$ photocycloadduct was detected only in the presence of a triplet quencher.²⁴ Actually, irrespective of the presence of a triplet quencher, only the peaks derived from the dimer 2a were observed even if the reaction was checked in an early step of the reaction. Under these conditions, it seems that the absorbance of nonconjugated intermediate 4 is small and most of the light is absorbed by the starting nicotinate 1; these facts indicate that an effective cyclization to dimer **2** involves two consecutive $2\pi + 2\pi$ photocycloadditions via path B mechanism. In this case, conjugated ester function and the diene chromophore of intermediated **5** can react subsequent $2\pi + 2\pi$ photocycloaddition effectively.

Furthermore, to look into the formation of a diastereomeric dimer, low-temperature photolysis was tried. When a deuterated toluene solution of **1a** was irradiated in the NMR tube at -60 °C, the dimerization proceeded quite slowly and formed only **2a**, and no other products such as a diastereomer could be detected. In this photodimerization, the dipole–dipole interaction, the steric repulsion between two ester groups and the secondary photochemi-

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cal reaction may be important factors responsible for the diastereoselective formation of $\mathbf{2}$.²⁸

In conclusion, we have provided the first example of the photochemical dimerization of 2-alkoxynicotinates leading to *C*2-symmetrical cage-type photodimers. The substituents on the pyridine ring exert considerable influence on the photodimerization, and an additional methyl group at the 6-position or an exchange to a phenyl ester prevents the dimerization. Furthermore, we also examined the photochemical reaction of 2-methoxy-4pyridinecarboxylic acid methyl ester, methyl nicotinate, 2-methoxynicotinic acid; however, they are inert toward photolysis under the same conditions.^{29,30} We were now continuing investigations to explore this unique photodimerization.

Experimental Section

Melting points are uncorrected. FT-IR spectra are reported in cm⁻¹. ¹H and ¹³C NMR spectra were obtained in CDCl₃ solutions at 300 MHz. Chemical shifts are reported in δ units, parts per million (ppm) relative to the TMS as internal standard. An Eikohsya 500-W, 1000-W high-pressure and a 100-W low-pressure mercury lamps were used as irradiation source.

Preparation of 2-Alkoxy Nicotinic Acid Esters 1a–f. Nicotinates **1a–f** were obtained by substitution of 2-chloronicotinic acid with sodium alkoxide, followed by esterification with sulfuric acid in the corresponding alcohol. Nicotinates **1a–c** were identified by the accordance of its spectral data.^{15,16}

Isopropyl 2-Methoxynicotinate 1d. HRMS (FAB) calcd for C₉H₁₂NO₃ (MH⁺) 182.0817, found 182.0811. (Colorless oil) bp 40–45 °C/4 mmHg. IR (CHCl₃): 1583, 1729. ¹H NMR (CDCl₃): 1.36 (d, J = 6.2 Hz, 6H, CH(*CH*₃)₂), 4.04 (s, 3H, OMe), 5.25 (sep, J = 6.2 Hz, 1H, *CH*(CH₃)₂), 6.94 (dd, J = 4.9 and 7.5 Hz, 1H, 5-H), 8.12 (dd, J = 2.0 and 7.5 Hz, 1H, 4-H), 8.29 (dd, J = 2.0 and 4.9 Hz, 1H, 6-H). ¹³C NMR: 22.3, 54.4, 69.0, 115.1, 116.6, 141.2, 150.8 162.9, 164.8.

Methyl 2-Methoxy-6-methylnicotinate 1e. MS (FAB) calcd for $C_{10}H_{14}NO_3$ (MH⁺) 196, found 196. (Colorless oil) bp 35–40 °C/6 mmHg. IR (CHCl₃): 1594, 1733. ¹H NMR: 2.48 (s, 3H, 6-Me), 3.88 (s, 3H, COOMe), 4.03 (2-OMe), 6.78 (d, J= 7.7 Hz, 1H, 5-H), 8.08 (d, J= 7.7 Hz, 1H, 4-H). ¹³C NMR: 24.8, 52.4, 54.3, 110.8, 115.9, 141.9, 161.6, 162.3, 166.0.

Phenyl 2-Methoxynicotinate 1f. HRMS (FAB) calcd for $C_{13}H_{12}NO_3$ (MH⁺) 230.0817, found 230.0813. Mp 120–125 °C. IR (CHCl₃): 1583, 1739. ¹H NMR: 4.08 (s, 3H, OMe), 7.00–7.03 (m, 1H), 7.20–7.27 (m, 3H), 7.40–7.43 (m, 2H), 8.36–8.40 (m, 2H). ¹³C NMR: 54.6, 116.8, 122.1, 126.3, 129.8, 142.1, 151.2, 151.9, 163.3, 163.7, 182.8.

General Procedure for the Photochemical Reaction of 2-Alkoxynicotinates 1a–f. A benzene solution containing 2-alkoxynicotinate 1 was deaerated by bubbling argon for 15 min and was irradiated by Pyrex filtered light with a 1000-W high-pressure mercury lamp at 15–20 °C. After irradiation, the solvent was removed in vacuo, and the residual mixture was subjected to chromatography on silica gel (eluant, *n*hexane/ethyl acetate). The crystalline photoproducts were recrystallized from a mixture of chloroform and hexane. The structure of photoproducts was determined on the basis of the spectral data. Furthermore, the structure of 2a was established by X-ray crystallographic analysis.

5,11-Dimethoxy-4,10-diazapentacyclo[6.4.0.0^{2,7}.0^{3,12}.0^{6,9}]dodeca-4,10-diene-6,12-dicarboxylic Acid Dimethyl Ester **2a.** HRMS (FAB) calcd for $C_{16}H_{19}N_2O_6$ (MH⁺) 335.1243, found 335.1211. Mp 156–157 °C. IR (CHCl₃): 1652, 1743, 2956, 2996. ¹H NMR: 2.89 (dt, J = 7.8 and 7.1 Hz, 2H, 2- and 8-H), 3.29 (t, J = 7.1 Hz, 2H, 1- and 7-H), 3.68 (s, 6H, C(=N)OMe), 3.80 (s, 6H, COOMe) and 5.23 (d, J = 7.8 Hz, 2H, 3- and 9-H). ¹³C NMR: 27.1, 35.1, 52.7, 53.3, 55.6, 57.7, 164.2, 172.3.

5,11-Dimethoxy-4,10-diazapentacyclo[**6.4.0.0**^{2,7}**.0**^{3,12}**.0**^{6,9}]**dodeca-4,10-diene-6,12-dicarboxylic Acid Diethyl Ester 2b.** HRMS (FAB) calcd for C₁₈H₂₃N₂O₆ 363.1556 (MH⁺), found 363.1550. Mp 113–115 °C. IR (CHCl₃): 1657, 1736, 2943, 2989. ¹H NMR: 1.28 (t, J = 7.1 Hz, 6H, CH₂*CH*₃), 2.89 (dt, J = 7.8and 7.0 Hz, 2H, 2- and 8-H), 3.27 (t, J = 7.0 Hz, 2H, 1- and 7-H), 3.68 (s, 6H, C(=N)O*Me*), 4.24 (m, 4H, *CH*₂CH₃) and 5.24 (d, J = 7.8 Hz, 2H, 3- and 9-H); ¹³C NMR: 12.9, 26.0, 34.0, 52.0, 54.5, 56.3, 60.4, 163.2, 170.7.

5,11-Diethoxy-4,10-diazapentacyclo[6.4.0.0^{2,7}.0^{3,12}.0^{6,9}]**dodeca-4,10-diene-6,12-dicarboxylic Acid Dimethyl Ester 2c.** HRMS (FAB) calcd for C₁₈H₂₃N₂O₆ (MH⁺) 363.1556, found 363.1565. Mp 113–115 °C. IR (CHCl₃): 1651, 1739, 2978. ¹H NMR: 1.21 (t, J = 7.1 Hz, 6H, CH₂*CH*₃), 2.87 (dt, J = 7.8 and 7.0 Hz, 2H, 2- and 8-H), 3.28 (t, J = 7.0 Hz, 2H, 1- and 7-H), 3.78 (s, 6H, O*Me*), 4.11 (m, 4H) and 5.21 (d, J = 7.8 Hz, 2H, 3and 9-H). ¹³C NMR: 14.0, 27.1, 35.1, 52.6, 55.7, 57.6, 61.5, 163.6, 172.5.

5,11-Dimethoxy-4,10-diazapentacyclo[**6.4**.0.**0**^{2,7}**.0**^{3,12}**.0**^{6,9}]**dodeca-4,10-diene-6,12-dicarboxylic** Acid Diisopropyl Ester 2d. HRMS (FAB) calcd for C₂₀H₂₇N₂O₆ (MH⁺) 391.1869, found 391.1856. Mp 114–115 °C. IR (CHCl₃): 1660, 1734, 2987. ¹H NMR: 1.24 (d, J = 6.3 Hz, 6H, CH(*CH*₃)₂), 1.25 (d, J = 6.3 Hz, 6H, CH(*CH*₃)₂), 2.90 (dt, J = 8.0 and 7.1 Hz, 2H, 2and 8-H), 3.23 (t, J = 7.1 Hz, 2H, 1- and 7-H), 3.67 (s, 6H, O*Me*), 5.13 (sep, J = 6.3 Hz, 2H, C*H*(CH₃)₂), 5.23 (d, J = 8.0Hz, 2H, 3- and 9-H). ¹³C NMR: 21.7, 22.0, 27.5, 35.5, 53.3, 56.0, 57.7, 69.3, 164.8, 171.7.

3-(2-Hydroxybenzoyl)-2-methoxypyridine 3f. HRMS (FAB) calcd for $C_{13}H_{12}NO_3$ (MH⁺) 230.0817, found 230.0822. Mp 103–105 °C. IR (CHCl₃): 1581, 1625, 3100 (br). ¹H NMR: 3.93 (s, 3H, O*Me*), 6.8–6.85 (m, 1H), 7.01–7.07 (m, 2H), 7.45–7.50 (m, 1H), 7.63–7.66 (m, 1H), 8.33–8.35 (m, 1H), 12.01 (s, 1H, OH). ¹³C NMR: 54.2, 116.8, 118.7, 119.3, 120.1, 122.1, 133.7, 137.3, 138.5, 149.7, 160.8, 163.4, 200.5.

3-(4-Hydroxybenzoyl)-2-methoxypyridine 3'f. HRMS (FAB) calcd for $C_{13}H_{12}NO_3$ (MH⁺) 230.0817, found 230.0812. Mp 164–165 °C. IR (CHCl₃): 1576, 1643, 3363. ¹H NMR: 3.90 (s, 3H, O*Me*), 6.76 (brs, 1H, O*H*), 6.87 (d, J = 10.8 Hz, 2H, Ph), 7.00 (dd, J = 5.1 and 7.2 Hz, 1H, 5-H), 7.68 (dd, J = 1.9 and 7.2 Hz, 1H, 4-H), 7.76 (d, J = 10.8 Hz, 2H, Ph), 8.31 (dd, J = 1.9 and 5.1 Hz, 1H, 6-H). ¹³C NMR: 53.7, 115.4, 116.5, 123.0, 129.9, 132.7, 138.6, 148.8, 160.9, 161.0, 193.6.

X-ray Crystallographic Analysis of 2a. The dimer **2a** gave prismatic crystals of monoclinic space group $P2_1/c$ (No. 14), a = 12.661(4) Å, b = 7.399(1) Å, c = 16.810(10) Å, $\beta = 92.08(3)^{\circ}$, V = 1573(1) Å³, Z = 4, $\rho = 1.411$ gcm⁻³, μ (Cu K α) = 1.09 cm⁻¹, F(000) = 704.00. The structure was solved by direct methods and expanded by full-matrix least-squares, where the final *R* and *Rw* values were 0.057 and 0.069, respectively, for 2499 reflections.

Quantum Yield Measurement of 1a. All quantum yields were determined at <20% conversion of the nicotinate using light filtered through a K_2CrO_4/Na_2CO_3 solution with a 500-W high-pressure mercury lamp. The light flux was calibrated using a valerophenone actinometer. The amount of products formed in each irradiation was determined by NMR spectroscopy.

Sensitization Experiments of Nicotinates 1f. Sensitization was carried out by irradiating a benzene solution of nicotinates with light at 313 nm using a K_2CrO_4/Na_2CO_3 solution filter. A benzene solution of 1f (0.02 M) and triplet sensitizers (3-methoxyacetophenone) was irradiated under conditions where the sensitizers should absorb >95% of the incident light. After the solvent was removed in vacuo, the crude reaction mixture was analyzed by ¹H NMR spectroscopy, with response for product distribution.

Quenching Experiments of Nicotinates 1a and 1f. The irradiation was performed at 313 nm using a K₂CrO₄/Na₂CO₃

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solution filter. A benzene solution of **1a** (0.05 M) or **1f** (0.02 M) containing triplet quenchers (0.02 M) was irradiated. The quenchers do not absorb light in the excitation region of nicotinates. The reactions were monitored by ¹H NMR spectroscopy.

Supporting Information Available: Crystal structure data for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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