(m, 1 H, H on dihydrofuran β-C), 4.80 (dd, 1 H, H on dihydrofuran α-C, J = 7, 15 Hz), 7.41–7.62 (m, 5 H, aromatic H), 4.98–8.07 (m, 1 H, aromatic H), 8.49–8.67 (m, 2 H, aromatic H); mass spectrum, m/e (relative intensity) 302 (P, base), 260 (15), 141 (80).

Anal. Calcd for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 87.54; H, 7.28.

C. Thermolysis of 2g. The mixture of **2g** (0.20 mmol, 60.4 mg) and TMEDA (23 mg) was heated at 230–245 °C for 5 min. After separation of tar by column chromatography on silica gel with dichloromethane, GLC and NMR analysis indicated the presence of **1g** (19%) and **15g** (58%).[3]

D. Thermolysis of 2i. The mixture of **2i** (0.20 mmol, 70 mg) and TMEDA (23 mg) was heated at 270–280 °C for 5 min. After separation of tar by column chromatography on silica gel with dichloromethane, NMR analysis indicated the presence of **15i**: 51% yield; colorless cubes; mp 84–85 °C (hexane); IR (CCl₄) 1630, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 1.88 (d, 1 H, bridge CH₂, J = 10 Hz), 2.07 (d, 1 H, bridge CH₂, J = 10 Hz), 3.73 (s, 1 H, bridgehead CH), 3.79 (s, 1 H, bridgehead CH), 3.94 (d, 1 H, H on dihydrofuran β-C, J = 8 Hz), 5.17 (d, 1 H, H on dihydrofuran α-C, J = 8 Hz), 7.08–8.15 (m, 10 H, aromatic H), 8.54–8.65 (m, 2 H, aromatic H); mass spectrum, m/e (relative intensity) 334 (P, 25), 209 (50), 117 (100).

Anal. Calcd for $C_{25}H_{18}O$: C, 89.79; H, 5.43. Found: C, 90.03; H, 5.64.

E. Thermolysis of 21. The mixture of **21** (0.40 mmol, 127 7g) and TMEDA (46 mg) was heated at 220–230 °C for 5 min. After separation of tar by column chromatography on silica gel with dichloromethane, GLC analysis indicated the presence of **11** (49%).

Photochemistry of Stable Pyridinyl Radicals. Photolysis of N-Alkyl-4-(carboalkoxy)pyridinyls[1]

Katsuhiko Takagi and Yoshiro Ogata*

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Photoinduced decomposition of N-benzyl-4-carbethoxypyridinyl (**1a**), N-methyl- (**1b**) and N-benzyl-4-(carbomethoxy)pyridinyl (**1c**), and their mixture was studied in degassed acetonitrile. N-Benzyl homologues (**1a** and **1c**) were smoothly photolyzed to ethyl (or methyl) isonicotinate by loss of a benzyl group, whereas the N-methyl homologue (**1b**) was comparatively stable toward UV light; the rate of disappearance of **1c** relative to that of **1b** was 11:1. A mechanism is postulated, which involves the formation of an alkyl radical by C–N bond homolysis followed by attack on the pyridinyl radical to form dihydropyridines. This is supported by a plot of the yield of ethyl isonicotinate vs. the ratio of initial concentrations [**1b**]₀/[**1a**]₀. Pyridinyl radicals **1** possess their absorption maxima at around 300, 395, and 630 nm; those at 300 and 395 nm maxima participate in this reaction.

Pyridinium ions in general act as excellent electron acceptors. For example, the bis(methyl quaternary salt) of 4,4'-dipyridyl, so called methyl viologen (MV²⁺), has often

MV²⁺
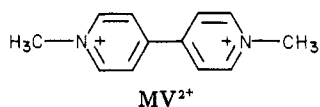
been employed as an electron trapper in order to ascertain whether visible light-induced electron transfer may occur in a certain artificial photosynthesis.[2]

The photochemical behavior of stable pyridinyl radicals is an intriguing subject, because their photostability is an essential factor for the acceptor. In our preliminary experiment, the radical cation of benzyl viologen (BV⁺·) was observed to decompose by UV light on the basis of the fact that its characteristic blue color fades on irradiation.[3] A

simpler pyridinyl radical is preferable to the study of the photochemistry of the radicals because of the formation of complex products from BV⁺·. Simple and stable pyridinyl radicals were first isolated by Kosower et al.[4] in the reduction of monopyridinium ions with zinc powder. Little data are available on the photochemistry of this stable radical except that N-ethyl-4-(carbomethoxy)pyridinyl radical induces polymerization of benzaldehyde under the influence of light.[5,6]

We disclose the photochemical behavior of this pyridinyl radical as a first step in the study of the photochemistry of these electron trappers.

(1) Contribution no. 275.

(2) (a) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974); (b) P. J. Dehaive, J. T. Lee, H. W. Sprintschnik, H. Abruna, T. J. Meyer, and D. G. Whitten, *ibid.*, **99**, 7094 (1977); (c) D. C. Bookbinder, N. S. Lewis, M. G. Bradley, A. B. Bocarsly, and M. S. Wrighton, *ibid.*, **101**, 7721 (1979).

(3) K. Takagi and Y. Ogata, Symposium on Photochemistry, Tsu, Japan, Oct 1980, Abstract of Papers, p 218.

(4) (a) E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963); (b) E. M. Kosower and E. J. Poziomek, *ibid.*, **86**, 5515 (1964).

(5) E. M. Kosower and I. Schwager, *J. Am. Chem. Soc.*, **86**, 5528 (1964).

(6) Irradiation of **1c** was independently done by Ikegami et al.[7] They obtained the spectral evidence for benzyl radical from low-temperature photolysis of **1c** at 77 K, but their attention was mainly focused on its photophysical processes.

(7) Y. Ikegami, S. Kubota, and H. Watanabe, *Bull. Chem. Soc. Jpn.*, **52**, 1563 (1979).

Irradiation of *N*-Alkyl-4-(carboalkoxy)pyridinyls (1). Irradiation of a degassed solution of *N*-benzyl-4-carbethoxypyridinyl (**1a**) in acetonitrile with a high-pressure Hg lamp through Pyrex (>290 nm) gave ethyl isonicotinate (54%). Similarly, *N*-benzyl-4-(carbomethoxy)pyridinyl (**1c**) gave methyl isonicotinate (51%) under the identical conditions. No decomposition was observed with their precursors, *N*-benzyl-4-(carboalkoxy)pyridinium bromide.

In contrast, *N*-methyl-4-(carbomethoxy)pyridinyl (**1b**) was stable toward UV light, but prolonged irradiation of **1b** gave methyl isonicotinate to some extent along with decomposition of **1b** to unknown products.

1

a, R' = CH₂Ph; R'' = Et
b, R' = Me; R'' = Me
c, R' = CH₂Ph; R'' = Me
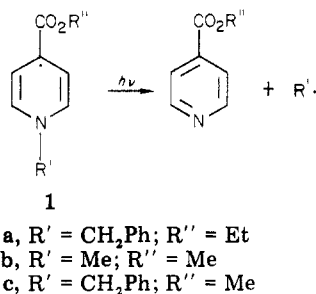
A solution immediately after complete photolysis of radical **1c** shows absorption maxima at 268 and 373 nm as well as 272 nm which is assigned to the absorption of methyl isonicotinate.[8] The solution is air sensitive, decomposing to a dark brown material. These characteristics imply the formation of 1,2- and/or 1,4-dihydropyridines (A and B, respectively) by attack of the resulting alkyl radical on another pyridinyl radical.
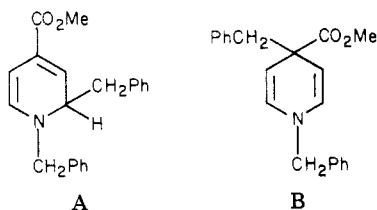
In fact, the dihydropyridine derived from methyl isonicotinate was reported to be sensitive to air and nonisolable in contrast to that from methyl nicotinate.[9] In spite of careful GLC analysis, the products contain neither bibenzyl nor 2-benzyl-4-(carbomethoxy)pyridine, although a trace of 2-methyl-4-(carbomethoxy)pyridine was detected in the photolysate of **1b**. Additionally, analysis of the reaction mixture immediately after exposure to air by means of high-performance LC techniques shows the formation of two products (R_f 10.2 and 15 min) as well as methyl isonicotinate (R_f 4 min). Our efforts to isolate and characterize them failed.

Figure 1 shows the plots of the conversion of **1b**, **1c**, and their equimolar mixture against the irradiation times. From the initial slope of the plot, the ratio of their initial rates for consumption of **1c** vs. **1b** was estimated to be 11:1. At an initial stage, an equimolar mixture of **1b** and **1c** decomposed at a rate analogous to that of **1c** alone. Moreover, decomposition of photoinert **1b** proceeds during consumption of **1c**. The conversion of **1b** + **1c** reaches ca. 80% after 90 s of irradiation. Benzyl radical was spec-
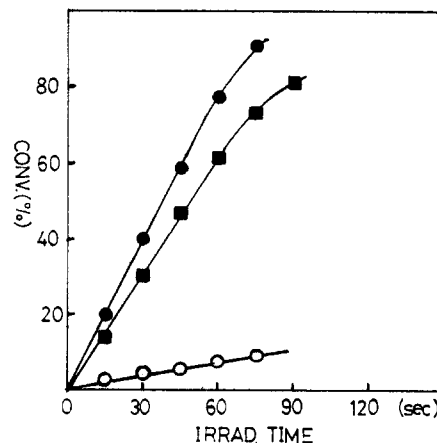
Figure 1. Plots of irradiation time vs. % conversion for pyridinyl radicals: (O) **1b**, (●) **1c**, (■) equimolar mixture of **1b** and **1c**.

Table I. Quantum Yield of Disappearance of Radical 1c in Acetonitrile

wavelength, nm	% conversion of 1c	photons adsorbed by 1c, photons/h	Φ_{dec}
254	1.8–3.6	0.49 × 10¹⁸	1.6 ± 0.4
310–430	2.1–12.6	14.6 × 10¹⁸	0.63 ± 0.02
>450	1.2–2.4	3.7 × 10¹⁹	(9 ± 0.4) × 10⁻³

trophotometrically confirmed to survive in a matrix glass at 77 K after being irradiated by UV light, but it was not observed in the room-temperature photolysis of **1c**.[7] These facts strongly suggest that the benzyl radical formed attacks exclusively another radical to give coupling products, dihydropyridines.

Effect of Light Source. The pyridinyl radicals (**1a–c**) have their absorption bands in the visible region (near 630 nm) as well as in the ultraviolet (at 395 and 302 nm) in acetonitrile. Photodecomposition of **1c** was used to examine whether all these absorption bands induce the reaction.

Irradiation of **1c** with 254-nm light gave 8% conversion for 5 min and 17% for 10 min. No decomposition of **1c** occurred with a 550–680-nm light for 60 min, but **1c** was photolyzed with >350-nm light in 16% conversion for 30 min and 36% for 60 min.

The quantum yields for decomposition of **1c** in degassed acetonitrile were independently measured and summarized in Table I. The values were obtained at the lowest possible conversion in order to eliminate the possible secondary adsorption of incident light by photoproducts. The results indicate the dependence of the photoreaction on wavelength; i.e., the ultraviolet-region (300 and 395 nm) excitation participates in the decomposition, but the visible-region (630 nm) excitation has little effect. The electronic transition of radical **1c** was reported to occur at 246, 302, 393, and 630 nm in acetonitrile,[7] which correspond to 112, 95, 73, and 45 kcal/mol, respectively. On irradiation, the radical may absorb the excitation energy according to the wavelength of incident light.

The light-induced N–C bond homolysis was observed in some cases. For example, *N*-benzyl- but not *N*-methylaniline can be photolyzed to benzyl and anilino radicals.[10] Similarly, *N*-benzyl-2-pyridylacetate methide undergoes N–C bond homolysis to benzyl radical, but not the corresponding *N*-methyl analogue, in which a remarkable wavelength dependency was noted.[11]

---

(8) The absorption maxima of dihydronicotinate are as follows: the 1,2-isomer at 432 nm; the 1,6-isomer at 263 and 362 nm. No reliable data on *N*-methyldihydroisonicotinate are available on account of their instability.[9]

(9) N. Kinoshita, M. Hamana, and T. Kawasaki, *Chem. Pharm. Bull. Jpn.*, 10, 753 (1962).

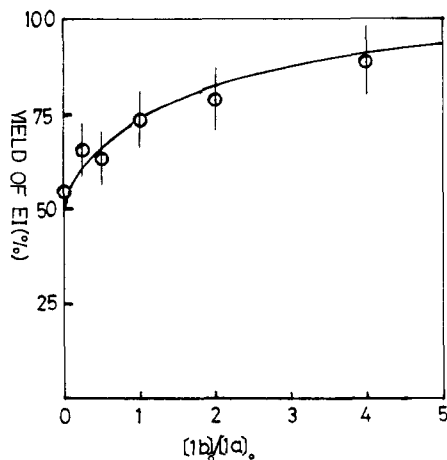(10) Y. Ogata and K. Takagi, *J. Org. Chem.*, 35, 1642 (1970).

Figure 2. Calculated plot of the % yield of EI vs. $[1b]_0/[1a]_0$ (eq 14) (solid line). Observed points are indicated by white circles.

In the present case, it seems surprising to observe the similar wavelength effect, because it seems unlikely for **1c** to require so much energy to dissociate into benzyl radical and neutral nicotinate in comparison with the cases which produce a radical pair. The excited state, which is directly responsible for the reaction, remains ambiguous, since little knowledge of the excited properties of the radical have accumulated on account of no emission between 300–600 nm.[4b]

Reaction Pathways. All these facts are explicable by eq 1–3. The resulting benzyl radical was preferentially

$$\text{(1a)*} \xrightarrow{k_d} \quad + \quad PhCH_2\cdot \qquad (2)$$

(EI)

$$PhCH_2\cdot + 1a \xrightarrow{k_{1a}} \quad (3)$$
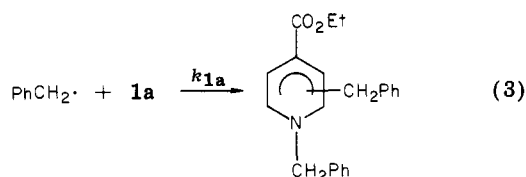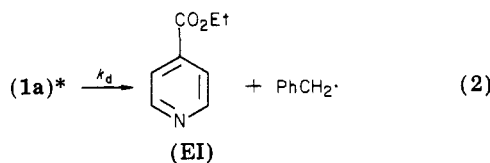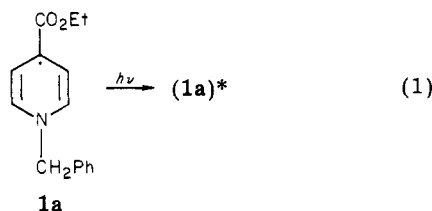
trapped by the pyridinyl radical at $[1a]_0 = 0.02$ M, since no other products derived from benzyl radical such as bibenzyl or benzyl-substituted isonicotinates were detected.

The mechanism suggests that the yield of ethyl isonicotinate (EI) cannot exceed 50%,[13] unless a benzyl radical scavenger is added. N-Methylpyridinyl (**1b**) may be a trapper for the resulting alkyl radical, because it is stable enough to neglect its decomposition compared to that of the benzyl homologue (**1a**), and also because the rate constant for the attack of benzyl radical on **1b** is

(11) K. Takagi and Y. Ogata, *J. Chem. Soc., Perkin Trans. 2*, 1410 (1977).
(12) The longest absorption band of **1c** ranges between 500 and 800 nm. The shortest wavelength (500 nm) corresponds to 57 kcal/mol.
(13) The yields of isonicotinate from photolysis of **1a** (54%) and **1c** (51%) are in accordance with the expected value (50%) within experimental error (±5%).

similar to that on **1a**, since **1a** is a homologue of **1b**; i.e., the radical coupling reaction is fast and diffusion controlled ($k_{1a} \simeq k_{1b} \simeq k$).

$$PhCH_2\cdot + 1b \xrightarrow{k_{1b}} \quad (4)$$
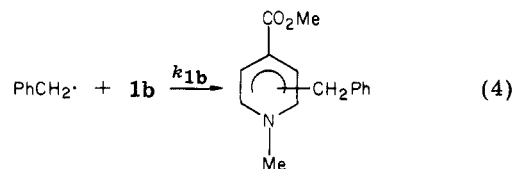
Applying the steady-state approximation to eq 2–4 gives eq 5.

$$-\frac{d[PhCH_2\cdot]}{dt} = k_d[1a] - k([1a] + [1b])\,[PhCH_2\cdot] = 0 \qquad (5)$$

Therefore,

$$[PhCH_2\cdot] = \left(\frac{k_d}{k}\right)\left(\frac{[1a]}{[1a]+[1b]}\right) \qquad (6)$$

The rate of consumption of **1a** is as shown in eq 7.

$$-\frac{d[1a]}{dt} = k_d[1a] + k[1a][PhCH_2\cdot] \qquad (7)$$

By substitution with eq 6,

$$-\frac{d[1a]}{dt} = k_d[1a]\left(\frac{2[1a] + [1b]}{[1a] + [1b]}\right) \qquad (8)$$

Similarly, the rate of consumption of **1b** is given by eq 9.

$$-\frac{d[1b]}{dt} = k_d[1a]\cdot\frac{[1b]}{[1a] + [1b]} \qquad (9)$$

Combination of eq 8 with eq 9 leads to eq 10.

$$\frac{d[1a]}{d[1b]} = \frac{2[1a]}{[1b]} + 1 \qquad (10)$$

By integration of eq 10, where [ ]₀ means initial concentrations,

$$\ln\left[\left(\frac{[1a]}{[1b]} + 1\right)\Big/\left(\frac{[1a]_0}{[1b]_0} + 1\right)\right] = \ln\frac{[1b]}{[1b]_0} \qquad (11)$$

The concentration of ethyl isonicotinate (EI) would be expressed by eq 12 from the material balance and eq 6.

$$[EI] = 0.5\left[\frac{[1a]}{[1a] + [1b]} + ([1a]_0 - [1a]) + ([1b]_0 - [1b])\right] \qquad (12)$$

The concentrations of EI may be expressed by eq 13 when

$$[EI] = 0.5([1a]_0 + [1b]_0 - [1b]) \qquad (13)$$

1a is completely consumed; i.e., $[1a] = 0$ at this moment. By substitution by eq 11,

$$[EI] = 0.5\left([1a]_0 + [1b]_0 - \frac{[1b]_0^2}{[1a]_0 + [1b]_0}\right) \qquad (14)$$

We now have the relationship between the yield of EI and $[1b]_0/[1a]_0$, using eq 15, where $X = [1b]_0/[1a]_0$. Equation

$$\text{yield of EI} = \frac{100[EI]}{[1a]_0} = 100\left(1 - \frac{1}{2(X + 1)}\right) \qquad (15)$$

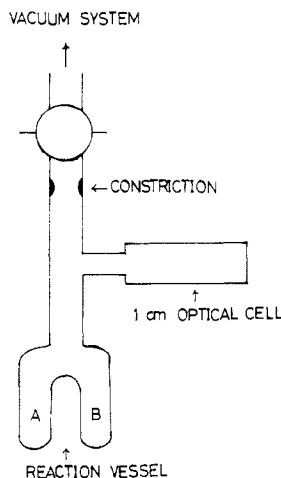15 means that the yield of ethyl isonicotinate increases

Figure 3. Reaction apparatus used for preparation of pyridinyl radicals (1).

from 50% to 100% with increasing $[1b]_0/[1a]_0$ as shown in Figure 2.

The yield of EI was measured at various values of $[1b]_0/[1a]_0$ and the observed good agreement with eq 15 indicates that the sequences 1–4 are reasonable.

Experimental Section

Materials. *N*-Alkylpyridinium salts were prepared by the reaction of alkyl isonicotinate with alkyl halides. Purification was done by recrystallization from ethanol. *N*-Benzyl-4-(carbomethoxy)pyridinium bromide: NMR (D_2O) δ 9.23 (d, 2 H, *J* = 7 Hz), 8.60 (d, 2 H, *J* = 7 Hz), 7.60 (s, 5 H, Ph), 6.0 (s, 2 H, CH_2), 4.15 (s, 3 H, OMe). *N*-Benzyl-4-carbethoxypyridinium bromide: NMR (D_2O) δ 9.2 (d, 2 H, *J* = 6.4 Hz), 8.6 (d, 2 H, *J* = 6.4 Hz), 7.6 (s, 5 H, Ph), 5.95 (s, 2 H, CH_2), 4.55 (q, 2 H, CH_2), 1.45 (t, 3 H, CH_3). *N*-Methyl-4-(carbomethoxy)pyridinium iodide: NMR (D_2O) δ 9.03 (d, 2 H, *J* = 6–7 Hz), 8.57 (d, 2 H, *J* = 6–7 Hz), 4.50 (s, 3 H, NMe), 4.07 (s, 3 H, OMe). 2-Methyl-4-(carbomethoxy)pyridine was synthesized by the reaction of methyl isonicotinate with acetic acid in the presence of silver nitrate and ammonium persulfate according to the literature;[14] NMR (CCl_4) δ 7.8–8.8 (m, 3 H), 3.93 (s, 3 H, OMe), 2.6 (s, 3 H, Me). Analogously, 2-benzyl-4-(carbomethoxy)pyridine was obtained by the reaction of the pyridine with phenylacetic acid under the identical conditions (16% yield); NMR (CCl_4) δ 7.8–8.8 (m, 3 H), 7.25 (s, 5 H, Ph), 4.17 (s, 2 H, CH_2), 3.96 (s, 3 H, OMe).

Acetonitrile was distilled over phosphorus pentoxide and then redistilled over potassium carbonate (bp 82–84 °C).

Preparation of the Pyridinyl Radicals. A solution of pyridinium halide (~0.1 mmol) in acetonitrile (2 mL) and a suspension of zinc powder (0.1 g) in acetonitrile (2 mL) were separately put in A and B of the reaction vessel equipped with a 1-cm optical cell linked to a vacuum system as shown in Figure 3.

The samples were sealed at liquid nitrogen temperature after evacuation by three freeze–thaw cycles at 10^{-3} torr and then mixed with each other by shaking. The well-mixed samples were kept overnight standing in the dark at 0–5 °C and then transferred to the quartz optical cell by either distillation or careful decantation.

The concentration of the resulting pyridinyl radical was measured spectrophotometrically, using the 630-nm peak.[15] The

spectra of **1a** and **1c** were the same as that of **1b** in the range of 300–700 nm. The concentrations of **1a** and **1b** in the mixture were assumed to be proportional to their initial concentration, since the equal amounts of pyridinium salts gave equal amounts of the corresponding radicals; e.g., 0.26 mmol of *N*-methyl-4-(carbomethoxy)pyridinium iodide gave 0.092 mmol of **1b** and 0.26 mmol of *N*-benzyl-4-(carbomethoxy)pyridinium bromide gave 0.096 mmol of **1c**.

Light Sources. A 1-kW high-pressure Hg lamp was used generally as a light source, which emits >290-nm light through Pyrex. The lamp and the reaction vessel were both immersed in a bath of running water at 15 °C, and the distance between the lamp and the sample was ca. 5 cm. Another type of light source was also employed for the measurement of the effect of the light source. A 150-W halogen lamp (Iwasaki Electric Co.) was selected for a visible light source of over 350-nm wavelength. The lamp was combined with some filters: a Pyrex filter for the light over 350 nm and two combined chemical filters (1 cm of $CuSO_4 \cdot 5H_2O$ and 10 cm of $K_2Cr_2O_7$) for the light of 550–680 nm.[16]

Quantum Yields. The quantum yields for the consumption of radical **1c** were measured by irradiating 3 mL of a (0.5–2.2) × 10^{-2} M solution in a quartz optical cell (10-mm thickness) with light concentrated through quartz lenses. The light used here was obtained from the following light sources combined with some glass filters: (a) 254-nm light with a low-pressure Hg lamp (Halos HIL 30) without filter; (b) 310–430-nm light with a 300-W high-pressure Hg lamp (Halos HIP 300) together with a Corning filter (7-51); (c) over 460-nm light with the above halogen lamp together with a Corning filter (3-71). Light intensities were measured with a potassium ferrioxalate actinometer.[17] Data for the individual runs are given as wavelength of emission, concentration of **1c** used, energy absorbed by solution, quantity of **1c** decomposed, quantum yield: 254 nm, 0.02 M, 0.98 × 10^{-6} einstein, 1.26 × 10^{-6} mol, 1.26; 254, 0.02, 1.29 × 10^{-6}, 2.52 × 10^{-5}, 1.96; 310–430, 0.011, 1.21 × 10^{-6}, 7.22 × 10^{-7}, 0.59; 310–430, 0.011, 6.07 × 10^{-6}, 3.98 × 10^{-6}; >450, 5.0 × 10^{-3}, 6.1 × 10^{-5}, 5.1 × 10^{-7}, 8.4 × 10^{-3}; >450, 5.0 × 10^{-3}, 9.3 × 10^{-5}, 8.7 × 10^{-7}, 9.3 × 10^{-3}.

Typical Photolysis of 1c in CH_3CN. *N*-Benzyl-4-(carbomethoxy)pyridinium bromide, 0.19 mmol in acetonitrile, and 0.3 mmol of zinc powder suspended in acetonitrile were separately put in the reaction vessel and then sealed after deaeration by three freeze–thaw cycles. The pyridinium salt mixed with zinc yielded 0.077 mmol of **1c** (40%). After 66% of the starting **1c** was decomposed by the light, the reaction mixture contained methyl isonicotinate (51% based on the consumed radical; high-performance LC analysis using isonicotinonitrile as an internal standard). The chromatography was carried out on a Yanapak DMS (30-cm length) with a 269-nm spectroscopic detector, using 20% aqueous methanol at a pressure of 15 kg/cm^2.

Effect of the Ratio ($[1b]_0/[1a]_0$) on the Yield of Ethyl Isonicotinate. A mixture of *N*-benzyl-4-carbethoxypyridinium bromide and *N*-methyl-4-(carbomethoxy)pyridinium iodide was sealed in a degassed acetonitrile. The concentration of radicals (the sum of **1a** and **1b**) was determined by using the 630-nm peak. The ratio $[1b]_0/[1a]_0$ was assumed to be proportional to the ratio of the initial concentration of the pyridinium salts used.

The yield of ethyl isonicotinate were based on the initial amount of **1a**. The results are given as the ratio $[1b]_0/[1a]_0$, the yield of ethyl isonicotinate: 1/4, 65.3%; 1/2, 61.0%; 1/1, 73.4%; 2/1, 79.4%; 4/1, 89.8%.

(14) F. Minisci, R. Bernardi, F. Bertini, R. Galli, and M. Perchinummo, *Tetrahedron*, **27**, 3575 (1971).

(15) The extinction coefficient of **1c** is reported to be 91 at 630 nm in CH_3CN.[7] The 630-nm peaks of all pyridinyl radicals (**1a–c**) with a moderately resolved structure (583 (s), 630, and 691 (s) nm) in acetonitrile were superimposed with each other, which means an N-substituent on 1 (e.g., methyl, ethyl, or benzyl) would not give any effect on the peaks.

(16) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1967, p 740.

(17) C. H. Hatchard and C. A. Parker, *Proc. R. Soc. A*, **234**, 518 (1956).