Association and Photolysis of 1-Benzyl-4-methoxycarbonylpyridinyls

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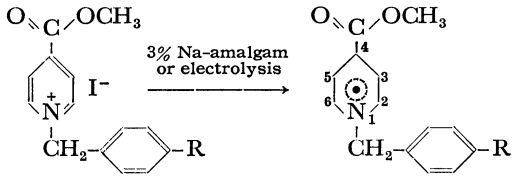
1-Benzyl- and 1-(4-methylbenzyl)-4-methoxycarbonylpyridinyl radicals have been prepared by reducing the corresponding pyridinium iodides with sodium amalgam. Hyperfine structures of the ESR spectra were analyzed. The radicals were decomposed photochemically with visible light in the region 380—440 nm in order to generate the intermediate benzyl radicals which were identified spectroscopically at 77 K. Association of each radical at low temperature forms a diamagnetic radical dimer, which is transformed by irradiating the solution with 440—470 nm light into the triplet dimer with zero-field parameters, $D=ca.$ 0.017 cm^{-1} and $E\approx 0$. Another radical, 1-(4-nitrobenzyl)-4-methoxycarbonylpyridinyl, is unstable at room temperature.

Pyridinyl radicals play an important role in studies on radical structure, radical reactions and radical association since the radicals are stable, neutral, and aromatic.[2)] One peculiar property of pyridinyls is the association to form both the diamagnetic singlet (A_S) and paramagnetic triplet (A_T) dimers at low temperature. Another triplet species (B_T) is generated from A_S by irradiating the radical solution with visible light.[3,4)] 1-Benzyl-4-methoxycarbonylpyridinyl (**1**) was prepared in order to investigate the effect of *N*-substituent on stability and association.[5)] In the course of the study, an unexpected sensitivity of the radical to light was observed. The photosensitivity as well as the association were examined for the radical and its derivatives.

Results and Discussion

Preparation. Generation of radicals **1**—**3** for preliminary study was performed by electrolytic reduction of the corresponding pyridinium iodides in degassed acetonitrile or *N*,*N*-dimethylformamide using tetrapropylammonium perchlorate as the supporting electrolyte. Each radical was generated in a stable form, exhibiting the expected ESR spectrum.

Treatment of 1-benzyl-4-methoxycarbonylpyridinium iodide with 3% sodium amalgam in degassed acetonitrile under ice-cooling in the dark afforded a green solution. Removal of the solvent gave blue crystals composed of **1** and NaI. The radical is slightly soluble



1: R=H
2: R=CH_3
3: R=NO_2

in hydrocarbons, soluble in ethereal and aprotic polar solvents, and not distillable in a vacuum. In solution it is stable for a long period at room temperature in the dark, but decomposes gradually in the light and rapidly in contact with alcohols, water, or air. Yield of the radical in preparation, based on spectroscopic titration, was over 85%. The 4-methylbenzyl derivative **2** prepared in a similar manner to the above showed

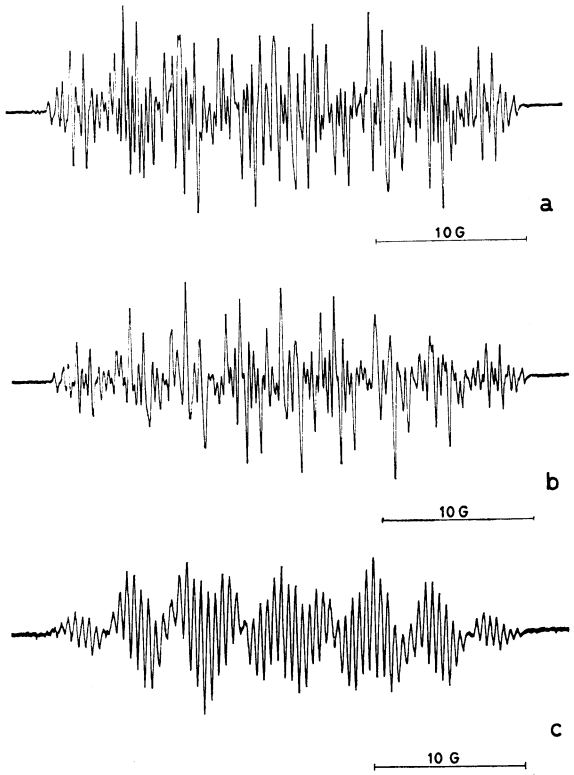


Fig. 1. ESR spectra of 1-benzyl- (a), 1-(4-methylbenzyl)- (b), and 1-(4-nitrobenzyl)-4-methoxycarbonylpyridinyls (c) in acetonitrile at room temperature. The 4-nitrobenzyl derivative was generated electrolytically.

similar properties. On the other hand, the 4-nitrobenzyl derivative **3** was not so stable as **1** and **2**. The deep blue color of **3** turned gradually yellow even in the dark. Approximate half-life for the decomposition, estimated by the ESR signal intensity, was *ca.* 15 min in acetonitrile at 20 °C. Because of the instability, spectroscopic examination of **3** was not carried out.

ESR spectra of radicals **1**—**3** in acetonitrile at room temperature are shown in Fig. 1. The hyperfine structure of each spectrum is interpreted as arising from the radical structure with six splitting constants. The constants observed in two solvents are summarized in Table 1, the assignments being given tentatively according to the type of splitting and by comparing them with the assignments to the constants of 1-methyl-4-methoxycarbonylpyridinyl.[6)] The coplanarity of the carbonyl

TABLE 1. HYPERFINE SPLITTING CONSTANTS FOR RADICALS **1**—**3** AT ROOM TEMPERATURE

Assignment	Splitting constant, *G*				
	1 (R=H)		**2** (R=CH_3)		**3** (R=NO_2)
	In CH_3CN	In MTHF	In CH_3CN	In MTHF	In CH_3CN
CH_3	0.88	0.84	0.91	0.80	0.92
3,5-H	0.56	0.42	0.58	0.40	0.54
2-H	3.73	3.95	3.70	3.98	3.95
6-H	3.83	4.05	3.80	4.08	4.07
N	6.30	6.26	6.24	6.28	6.28
$-CH_2-$	3.56	3.56	3.59	3.60	3.51

group with pyridinyl ring is clearly seen in the nonequivalence of the constants at positions 2 and 6.

The radical concentration of the solution of **1** or **2** for spectroscopic studies was determined spectroscopically by the following electron-transfer reaction.

1 (or **2**) + 1,1′-Dimethyl-4,4′-bipyridinium (MB^{2+})
$\longrightarrow$ $\mathbf{1}^+$ (or $\mathbf{2}^+$) + MB^{+}

The reaction of a dilute solution of the radical (concn$<5\times10^{-3}$ M) with an excess of solid 1,1′-dimethyl-4,4′-bipyridinium (MB^{2+}) dichloride in acetonitrile in the dark proceeded rapidly to form the corresponding radical cation (MB^{+}) (Paraquat radical cation). The absorption intensity of the resulting cation at 605 nm ($\varepsilon=10060$)[7] was used to calculate the radical concentration.

TABLE 2. ABSORPTION MAXIMA OF RADICALS **1** AND **2** IN ACETONITRILE (23 °C)

Radical	λ_{max} (ε)			
1	246(25300)	302(14900)	393(6830)	630(91)
2	241(22380)	303(14970)	393(6840)	630(104)

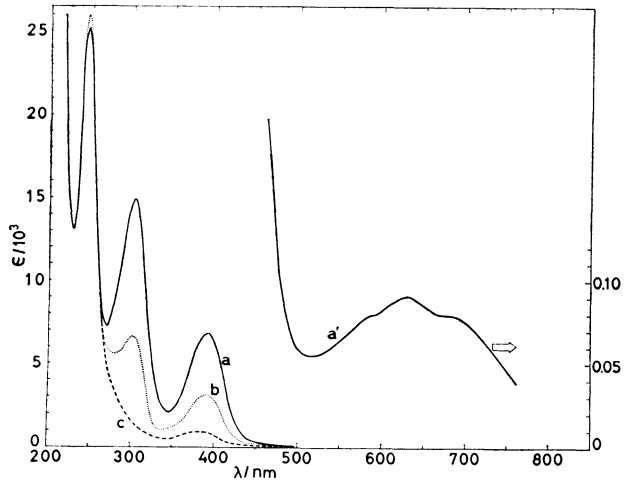


Fig. 2. Absorption spectrum of **1** in acetonitrile and the spectral change on light irradiation at room temperature: (a) 3.9×10^{-3} M and (a′) 2.6×10^{-2} M before irradiation; (b) after 100 s irradiation of (a) with visible light; (c) after 5 min irradiation. A 100 W tungsten lamp equipped with a Toshiba filter UV-39 was used for the irradiation.

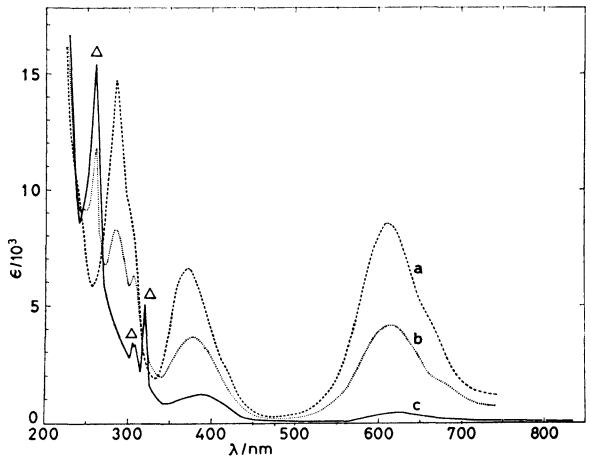


Fig. 3. Absorption spectrum of **1** in MTHF and the spectral change on light irradiation at 77 K: (a) 8.8×10^{-3} M before irradiation; (b) after 1 min irradiation; (c) after 6 min irradiation with a 100 W tungsten lamp. △: Indicates the bands due to the products.

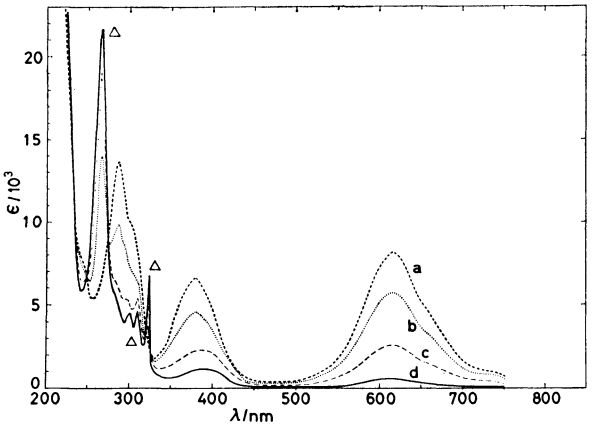
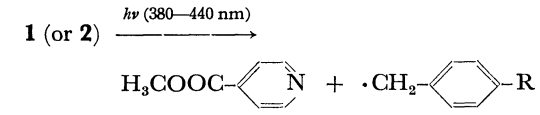


Fig. 4. Absorption spectrum of **2** in MTHF and the spectral change on light irradiation at 77 K: (a) 6.8×10^{-4} M before irradiation; (b) after 1.5 min irradiation; (c) after 6 min irradiation; (d) after 32 min irradiation. A 500 W xenon lamp equipped with a Toshiba filter UV-39 was used for the irradiation.

Spectra and Photolysis. Radical **1** shows absorption maxima given in Table 2 with features similar to 1-alkyl homologs.[8–10] Irradiation of the solution with visible light caused the disappearance of the three longer bands as a result of photolysis; the dispersed weak light in the spectrometer caused no photolysis. The effect of irradiation on the spectrum is shown in Fig. 2; the same phenomenon is observed in MTHF at room temperature. The photolysis occurred also in MTHF glass at 77 K, leading to the spectral change shown in Fig. 3, in which the disappearance of strong bands at 286, 372, and 616 nm on irradiation is accompanied by the appearance of new bands at 260, 306, and 319 nm. The new bands coincide in their wavelengths with those of the benzyl radical generated in 2-methylpentane at 77 K.[11] Irradiation of radical **2** also led to its substantial loss. The absorption bands at 267, 300, 311, and 323 nm

(Fig. 4) correspond to those of the 4-methylbenzyl radical.[11] Thus, the photolysis is interpreted to be the following C–N bond cleavage.



The photolysis occurred with 380—440 nm wavelengths. Strong irradiation of the solution with light of wavelength shorter than 350 nm from a 500 W mercury lamp led to further photoreaction showing a complex spectral change with time. Photolytic change was also observed in the ESR spectrum of a dilute solution at 77 K, an example of which is shown in Fig. 5 for radical **2**. The hyperfine structure appearing on irradiation is ascribed to the 4-methylbenzyl radical. Irradiation of **1** in a similar way resulted in appearance of hyperfine structure in the ESR spectrum differing from that in Fig. 5.

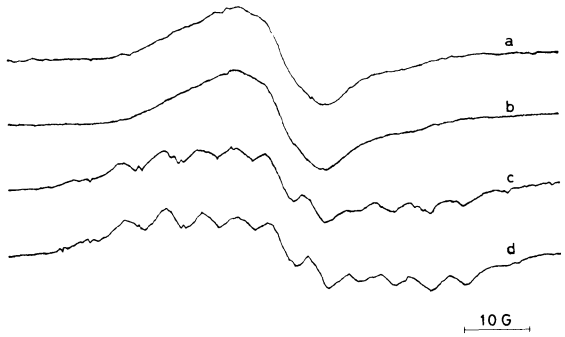


Fig. 5. The ESR spectral change observed by irradiating the dilute solution of **2** in MTHF at 77 K: (a) 1.2×10^{-4} M before irradiation; (b) after 10 min irradiation of (a) with a 500 W xenon lamp using a Toshiba filter VY-50; (c) after 1 min irradiation of (b) using a Toshiba filter VY-42; (d) after further 9 min irradiation of (c).

Since 1-alkylpyridinyls are not sensitive to visible light, the photolysis should be interpreted in terms of a photochemical interaction between the arene ring and the pyridinyl ring. One possible explanation is that excitation of the pyridinyl radical leads to the formation of an intramolecular exciplex *via* electron transfer to the aryl ring, followed by dissociation to an unstable free radical and a stable molecule, methyl isonicotinate.[12] If this is the case, the instability of the 4-nitrobenzyl derivative (**3**) can be explained by a thermal mechanism analogous to the photochemical one, as Mochida *et al.*[13] recently substantiated a general formulation, originally put forth by Kosower,[14] that electron-transfer processes resulting from charge-transfer interaction can share common photochemical and thermal pathways.

Radical Association and Associated Triplet State. The absorption spectrum of **1** at low temperature (Fig. 3a) has an intense band at 616 nm, while the absorption in this region at room temperature (Fig. 2a′) is very weak. The strong absorption is due to the radical dimer denoted by π-mer.[15] Since the solution contains a considerable amount of sodium iodide, the strong intensity might be partially due to the complex formation of the radical with sodium iodide. Complex formation can account for the hypsochromic shifts of the bands at 300 and 391 nm to 286 and 372 nm, respectively, on lowering the temperature in MTHF.[16] The spectrum of **2** can be interpreted similarly (Fig. 4a).

The radical association is also observed as conspicuous decrease in the ESR signal intensity with fall in temperature. The decrease in intensity for the solution of **1** at −150 °C is less than 2% of that at room temperature. (Fig. 6). This can be ascribed to the formation of the diamagnetic radical dimer at low temperature.

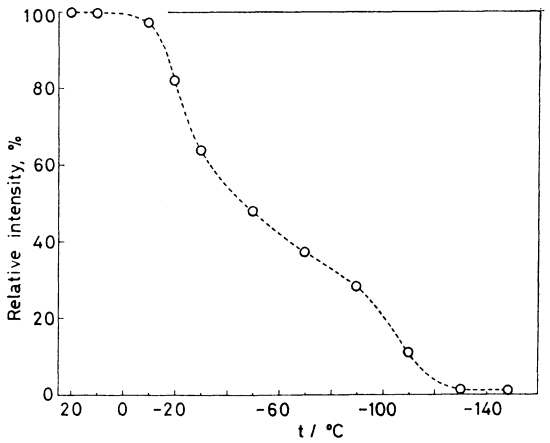


Fig. 6. Decrease of the ESR signal intensity with lowering temperature for the radical **1** in MTHF at the concentration, 4.0×10^{-2} M.

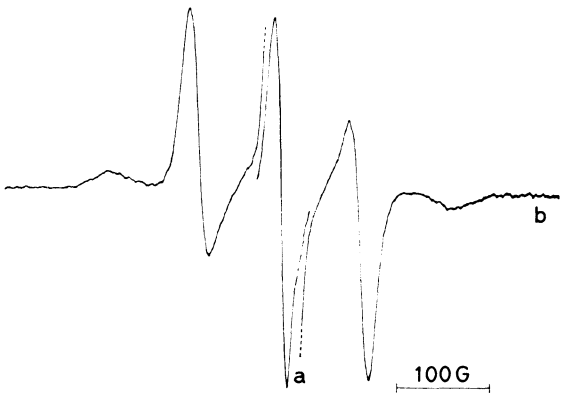


Fig. 7. ESR spectrum of **1** in MTHF at 77 K. 2.5×10^{-2} M. (a) Before irradiation; (b) after 20 min irradiation with a 500 W xenon lamp using a Toshiba filter VY-46. (a) was recorded with 1/2.5 gain amplitude of that for (b).

It has been demonstrated for 1-alkyl-4-methoxycarbonylpyridinyls that the diamagnetic dimer (A_S) is convertible into the triplet dimer (B_T) by light irradiation.[3,4] The same phenomenon is observed for the radicals. Radicals **1** in MTHF at 77 K shows a very weak signal corresponding to the central line in Fig. 7. Irradiation of the solution with light of wavelength longer than 440 nm added a new triplet signal to the ESR spectrum, with no significant change in the central

line. Appearance of the $\Delta M=2$ transition in the ESR spectrum at around 1650 G confirms the triplet. The zero-field parameters estimated roughly are $D=0.0174$ cm^{-1} and $E\approx 0$, with $2D=372$ G. The D value is consistent with a spin-spin dipolar interaction for an average separation of 5.3 Å, using the relation $D=-(3/2)g^2\beta^2r^{-3}$.[17] A similar triplet spectrum was obtained for radical **2**, the zero-field parameters, $D=0.0166$ cm^{-1} and $E\approx 0$ with $2D=356$ G, corresponding to the spin-spin interaction for an average separation of 5.4 Å. These D values for the association of **1** and **2** are close to those of 1-methyl- and 1-ethyl-4-methoxycarbonylpyridinyls. This indicates that the *N*-substituent has no significant influence upon the structure of the triplet dimer formed by an access of pyridinyl rings.

No spectral change was observed by irradiation with light of wavelength longer 470 nm. The singlet-triplet transformation occurred with visible light in the region 440—470 nm, which differs from both the light specific to the photolysis and the light corresponding to the long-wavelength charge-transfer absorption of π-mer at *ca.* 620 nm. Since no strong absorption was observed in the 440—470 nm region (Figs. 3 and 4), excitation expected in this region, corresponding to the band at 437 nm observed before irradiation for pure 1-methyl-4-methoxycarbonylpyridinyl in MTHF at 77 K,[4] might cause the dynamic reorientation of the radicals in a dimer to the positions capable of triplet transition.

Experimental

Solvents. Acetonitrile (guaranteed reagent, Kanto Chemical Co.) was passed through an alumina (Woelm, neutral) column and distilled. After being degassed by at least five freezing-pumping cycles, the solvent was treated with 1-methyl-4-methoxycarbonylpyridinyl radical, prepared by the reaction of the pyridinium iodide with sodium amalgam, to remove radical-reactive impurities. The solvent was distilled again in a vacuum system at low temperature and left to stand over previously degassed molecular sieves (4A) in a storage vessel. 2-Methyltetrahydrofuran (MTHF) (Eastman Organic) was refluxed over sodium for 3 days and then distilled. The solvent was degassed and then distilled onto sodium and anthracene in a storage vessel. Solvents were transferred, when needed, by distillation into the apparatus using a vacuum system.

Salts. 1-Benzyl-4-methoxycarbonylpyridinium iodide was prepared by the method of Craig *et al.* through the chloride.[18] Mp 163—164 °C. 1-(4-Methylbenzyl)-4-methoxycarbonylpyridinium iodide was prepared as follows. A solution of 4-methylbenzyl chloride (0.04 mol) in acetone (50 ml) was refluxed with an excess of sodium iodide (0.05 mol) under nitrogen for 2 h. The sodium chloride produced was filtered off. Methyl isonicotinate was added to the solution, the temperature being maintained at 50 °C for 2 h, the solution allowed to cool overnight, then left at 0 °C for 40 h. The yellow crystals were filtered off and recrystallized from ethanol and then from methanol. Mp 151—152 °C. Found: C, 49.12; H, 4.34; N, 3.97%. Calcd for $C_{15}H_{16}NO_2I$: C, 48.80; H, 4.37, N, 3.79%. 1-(4-Nitrobenzyl)-4-methoxycarbonylpyridinium iodide was prepared by the method of Kosower *et al.*[19] as orange red crystals, mp 152 °C. 1,1′-Dimethyl-4,4′-bipyridinium dichloride (Wako Chemical Co.) was recrystallized from ethanol, and then dried thoroughly.

Radicals. Pyridinyl radicals were prepared using the apparatus shown in Fig. 8. A pyridinium iodide (0.001 mol), 3 % sodium amalgam, and a magnetic stirrer were put into A and the apparatus was evacuated with an oil diffusion pump to 2×10^{-6} Torr. After the addition of solvent acetonitrile into A by distillation, the mixture was stirred under ice-cooling (1—2 h) until a clear green color was obtained. The solution was filtered in order to remove insoluble substance and the filtrate was put into three tubes (B, C, and D), which were subjected to determination of radical concentration and spectral measurements.

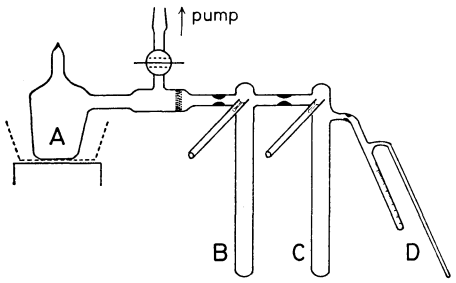


Fig. 8. Apparatus for radical preparation.

Spectral Measurements. A Cary 14 spectrophotometer was used to record absorption spectra. A specially constructed glass Dewar vessel[20] was used to measure the spectra at 77 K. ESR spectra were measured with a Varian E-4 ESR spectrometer. Electrolytic generation of radicals was carried out in the cavity of the spectrometer using acetonitrile or *N,N*-dimethylformamide as the solvent and tetrapropylammonium perchlorate as the supporting electrolyte. A JEOL spectrum computer, JEC-5, was used for spectral simulation.

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