in which AH is an antioxidant (e.g., phenolic), ROO• is a peroxy radical, Z is an electron-donating substituent, and X is an electron-withdrawing substituent. In general, as Z is added to an antioxidant or becomes a better electron donor and as the electron affinity of X increases (e.g., by introduction of halogens into $\alpha$ position), a faster reaction rate is observed for inactivation of peroxy radicals, e.g., reaction 6 vs reaction 11.

The antioxidation activity of uric acid may be extended to chemical repair of oxidative damage to DNA. Uric acid repairs efficiently the guanyl radical, reaction 16, in simple guanine derivatives and DNA.[34] This type of reaction may be critical in the repair of direct effects of ionizing radiation[2] in cells.

(43) Commercial products are identified here only for technical purposes and are not meant to be an endorsement by the National Institute of Standards and Technology.

# Photosensitive Cyclomer Formation of 1,1′-(1,2-Ethanediyl)bis(pyridinyl) Diradical and Its Derivatives

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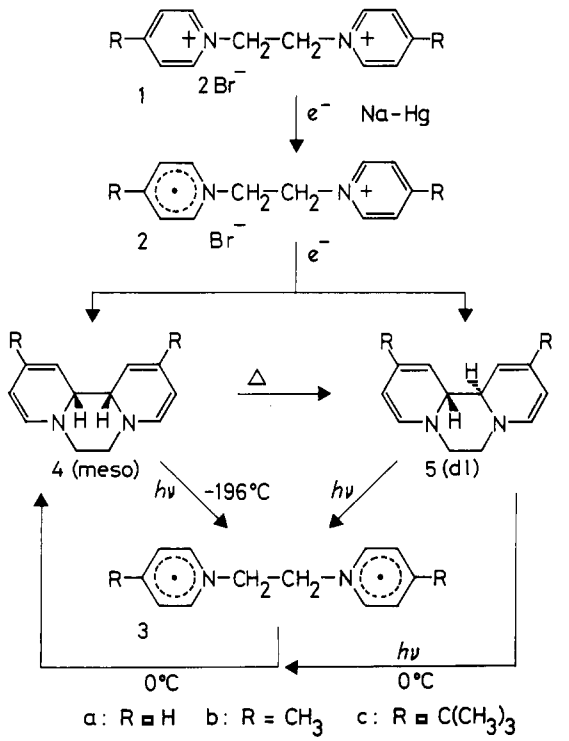
*Received November 29, 1988*

**Abstract:** Two-electron reduction of 1,1′-(1,2-ethanediyl)bis(pyridinium) dibromide (**1a**) with sodium amalgam affords the meso and *dl* cyclomers formed by intramolecular cyclization of the diradical (**3a**). The meso cyclomer (**4a**) is thermally converted into the *dl* cyclomer (**5a**), while inversely **5a** is photolytically converted into **4a**. Reduction of the 4,4′-dimethyl and 4,4′-di-*tert*-butyl derivatives (**1b** and **1c**, respectively) of **1a** similarly affords the corresponding meso (**4b** and **4c**) and *dl* (**5b** and **5c**) cyclomers, which are convertible to each other. One-electron reduction products (**2b** and **2c**) of **1b** and **1c** are detected at room temperature as shown by the ESR spectra in acetonitrile, which exhibited intramolecular rapid spin exchange between the two pyridine rings in the cation radical. The activation energy for the meso to *dl* conversion was obtained by NMR spectroscopy to be 22.4, 26.9, and 28.8 kcal·mol$^{-1}$ for **4a–c**, respectively. Photodissociation of the cyclomers gives the diradicals, which were characterized by the ESR triplet spectra at −196 °C with the zero-field parameters: $|D| = 0.0222$ and $|E| = 0.0012$ cm$^{-1}$ for **3a**, $|D| = 0.0210$ and $|E| = 0.0008$ cm$^{-1}$ for **3b**, and $|D| = 0.0219$ and $|E| = 0.0016$ cm$^{-1}$ for **3c**. Calculations of the $D$ value suggest that the dihedral angle of the $NCH_2CH_2N$ group of the diradical in a rigid glass is about 95° for these three diradicals.

Our recent study revealed that the 1,1′-(1,2-ethanediyl)bis-[4-(methoxycarbonyl)pyridinyl] diradical is substantially in equilibrium with the cyclomers formed by intramolecular cyclization of the diradical.[2] The equilibrium tends overwhelmingly toward the cyclomers in the dark, and the cyclomers photodissociate to generate the diradical, which is characterized by an ESR triplet spectrum at −196 °C. These results strongly implied a possibility that similar diradicals can be generated photochemically from the corresponding cyclomers. Since photolytic C–C bond cleavage of the dimers of alkylpyridinyl radicals has been demonstrated,[3,4] various pyridinyl diradicals without any electron-withdrawing and electron-delocalizing groups in the pyridine rings might be generated. We therefore examined the properties of the cyclomers of 1,1′-(1,2-ethanediyl)bis(pyridinyl) diradical and its 4,4′-dimethyl and 4,4′-di-*tert*-butyl derivatives and report the structural assignments to the cyclomers in their meso and *dl* forms, the conversion of both forms to each other, and the photochemical generation of the diradicals from the cyclomers. These reactions are summarized in Scheme I.

**Scheme I**




## Results and Discussion

**Reduction of Bis(pyridinium) Salts and Conversion of Two Isomeric Products.** Reduction of 1,1′-(1,2-ethanediyl)bis(pyridinium) dibromide (**1a**) with sodium amalgam was carried out by two procedures: (P-1) When standard vacuum-line techniques are used, **1a** (100 mg) and 3% sodium amalgam (450 mg) in degassed acetonitrile (30 mL) were stirred in a flask at 0 °C for 4 h. After the amalgam changed to a liquid state the solvent was removed, the residue was extracted with 2-methyltetrahydrofuran (MTHF), and the solvent was replaced by $CD_3CN$ or $CH_3CN$.

(1) (a) Tohoku University. (b) Miyagi University of Education.
(2) Ikegami, Y.; Muramatsu, T.; Hanaya, K.; Onodera, S.; Nakayama, N.; Kosower, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 2876.
(3) Akiyama, K.; Tero-Kubota, S.; Ikegami, Y.; Ikenoue, T. *J. Phys. Chem.* **1985**, *89*, 339.
(4) Ikegami, Y. *Rev. Chem. Intermed.* **1986**, *7*, 91.

0002-7863/89/1511-5782$01.50/0 

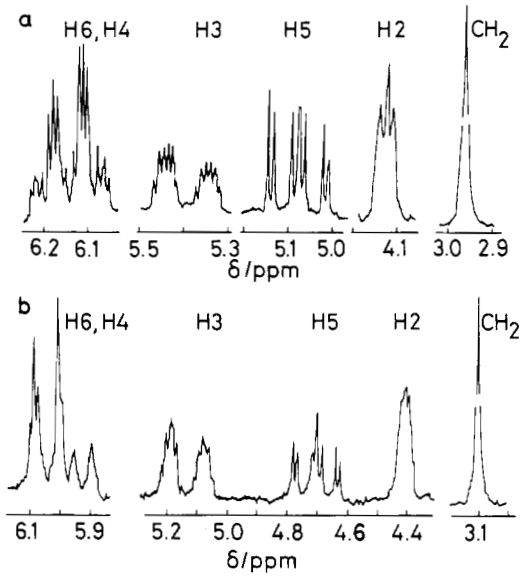



**Figure 1.** $^1$H NMR spectra of **4a** and **5a** in $CD_3CN$ at room temperature: (a) **4a**, (b) **5a**. Number indicates the position of hydrogen assigned to the NMR lines.

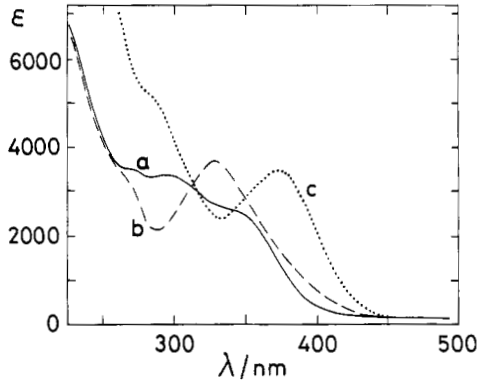



**Figure 2.** Absorption spectra of **4a**, **5a**, and **3a** in MTHF: (a) **4a**, (b) **5a** at room temperature, and (c) **3a** at −196 °C.

(P-2) According to the procedure by Cairns and Corran,[5] a solution of **1a** (100 mg) in water (5 mL) was added dropwise to a suspension of 3% sodium amalgam (1.5 g) in cyclohexane or *n*-hexane (10 mL) with stirring at 10 °C for 30 min. After further stirring for 30 min, the organic layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was replaced by $CD_3CN$ or $CH_3CN$ using a vacuum line. Care was taken in handling the products sealed in the tube to maintain the temperature lower than 25 °C in the dark.

The solutions obtained by the above two procedures showed no ESR signal but exhibited well-resolved NMR spectra. The $^1$H NMR spectrum of the product in P-2 (Figure 1a) was simpler than that obtained in P-1. When both products were warmed in acetonitrile at 80 °C, the spectra changed gradually, showing thermal conversion, and finally gave the spectrum shown in Figure 1b after 90 min. These results mean that the product in P-2 was one isomer (**4a**) and that in P-1 was the mixture with another isomer (**5a**), and the production of two isomers strongly implied the cyclomer formation of the reduction product.

In contrast with the thermal conversion, light irradiation caused conversion in the reverse direction. The solution of **5a** in $CD_3CN$ was irradiated using a high-pressure Hg lamp (500 W) equipped with a UV-29 glass filter at 0 °C. The $^1$H NMR spectrum after the 25-min irradiation was that of the almost pure solution of isomeric **4a**.

The above thermal and photochemical conversions were demonstrated by the $^{13}$C NMR measurements and also by the measurements of absorption spectra illustrated with Figure 2. The spectrum of **5a** (Figure 2b) changed on irradiation into that of **4a** (Figure 2a). The resulting solution, on warming at 80 °C, showed the spectrum of Figure 2b. The conversions were completely reversible for the degassed solution in a sealed tube.

(5) Cairns, J. F.; Corran, J. A. *Chem. Abstr.* **1969**, *71*, 8142g.

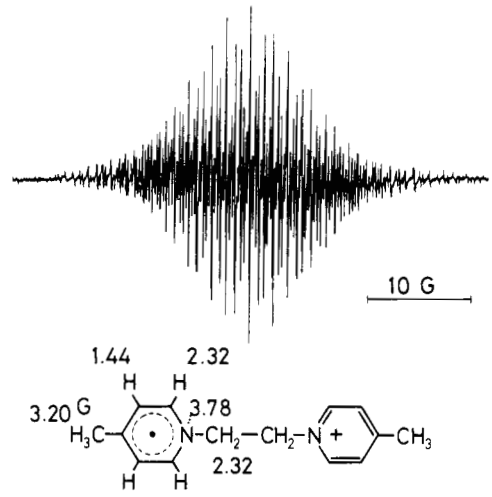



**Figure 3.** ESR spectrum of **2b** in $CH_3CN$ at room temperature and the hyperfine splitting (hfs) constants in Gauss.

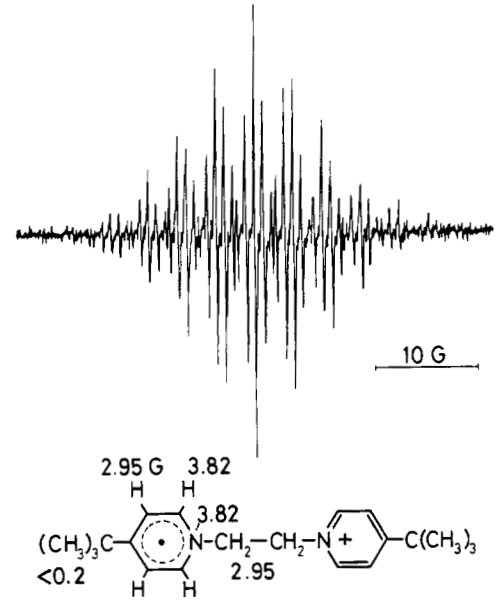



**Figure 4.** ESR spectrum of **2c** in $CH_3CN$ at room temperature and the hfs constants in Gauss.

**Cation Radicals 2b and 2c.** The above reduction of bis(pyridinium) salts would proceed through the cation radicals to reach the two-electron reduction products. In the reduction of **1a**, however, the cation radical **2a** could not be detected, indicating that **2a** rapidly changed into **1a** and **3a** by disproportionation, and then the latter was followed by cyclization to form **4a** and **5a**. On the other hand, the reduction of **1b** and **1c** exhibited ESR spectra of the cation radicals **2b** and **2c**. Hyperfine splittings (hfs) of the ESR spectra shown in Figures 3 and 4 can be simulated with the constants indicated in the figures. It is noteworthy that the

**Table I.** $^1$H NMR, $^{13}$C NMR, and Absorption Spectral Data for **4a**, **5a**, **4b**, **5b**, **4c**, and **5c**

(1) $^1$H NMR Data in $CD_3CN$[a]

| | cyclomer | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **4a** | | **5a** | | **4b** | | **5b** | | **4c** | | **5c** | |
| position | $\sigma$, ppm | $J$, Hz | $\delta$, ppm | $J$, Hz | $\delta$, ppm | $J$, Hz | $\delta$, ppm | $J$, Hz | $\delta$, ppm | $J$, Hz | $\delta$, ppm | $J$, Hz |
| 1, 12 | 5.38 (dddd)[b] | 1.0, 1.4<br>1.9, 9.5 | 5.14 (dddd) | 1.0, 1.3<br>2.0, 9.7 | 5.09 (qddd) | 1.4, 2.0<br>2.0, 2.0 | 4.90 (qddd) | 0.8, 1.0<br>2.0, 2.0 | 5.23 (ddd) | 1.1, 2.0<br>2.2 | 4.99 (ddd) | 1.0, 1.7<br>2.2 |
| 2, 11 | 6.14 (dddd) | 1.1, 1.4<br>5.5, 9.5 | 5.99 (dddd) | 1.0, 1.4<br>5.4, 9.7 | | | | | | | | |
| 3, 10 | 5.07 (ddd) | 1.4, 5.5<br>7.0 | 4.71 (ddd) | 1.3, 5.4<br>7.0 | 4.98 (dd) | 2.0, 7.0 | 4.63 (dd) | 2.0, 7.3 | 5.28 (dd) | 2.0, 6.9 | 4.94 (dd) | 2.2, 6.8 |
| 4, 9 | 6.14 (ddd) | 1.0, 1.0<br>7.0 | 6.03 (ddd) | 1.0, 1.4<br>7.0 | 6.12 (dd) | 1.0, 7.0 | 6.03 (dd) | 1.0, 7.3 | 6.15 (ddd) | <0.5, 1.1<br>6.9 | 6.08 (ddd) | <0.5, 1.0<br>6.9 |
| 6, 7 | 2.97 (s) | | 3.11 (s) | | 2.91 (s) | | 3.08 (s) | | 2.89 (s) | | 3.08 (s) | |
| 12a, 12b | 4.12 (dd) | 1.1, 1.9 | 4.42 (dd) | 1.0, 2.0 | 4.02 (qd) | 1.4, 2.0 | 4.24 (qd) | 0.8, 2.0 | 3.97 (dd) | <0.5, 2.2 | 4.13 (dd) | <0.5, 1.7 |
| $CH_3$ | | | | | 1.84 (dd) | 1.4, 1.4 | 1.74 (dd) | 0.8, 0.8 | | | | |
| $C(CH_3)_3$ | | | | | | | | | 1.19 (s) | | 1.14 (s) | |

(2) $^{13}$C NMR Data in $CD_3CN$

| | $\delta$, ppm | | | | | |
|---|---|---|---|---|---|---|
| position | **4a** | **5a** | **4b** | **5b** | **4c** | **5c** |
| 1, 12 | 99.7 | 94.7 | 103.2 | 97.8 | 101.3 | 95.9 |
| 2, 11 | 124.6 | 125.6 | 132.6 | 138.7 | 145.2 | 146.2 |
| 3, 10 | 112.6 | 110.7 | 108.8 | 106.6 | 105.8 | 103.6 |
| 4, 9 | 137.7 | 138.3 | 137.4 | 137.8 | 137.8 | 138.1 |
| 6, 7 | 46.4 | 51.2 | 46.9 | 51.1 | 46.3 | 50.7 |
| 12a, 12b | 56.6 | 58.4 | 57.2 | 59.1 | 57.1 | 58.8 |
| $CH_3$ | | | 19.3 | 19.7 | | |
| $\underline{C}(CH_3)_3$ | | | | | 33.0 | 33.0 |
| $C(\underline{C}H_3)$ | | | | | 28.2 | 27.9 |

(3) Absorption Maximum in $CH_3CN$, nm

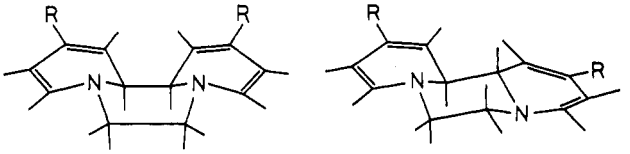
| $\lambda_{max}$ ($\epsilon$) | | | | | |
|---|---|---|---|---|---|
| **4a** | **5b** | **4b** | **5b** | **4c** | **5c** |
| 335 (2800) | 330 (3900) | 350 (3500) | 330 (6000) | 335 (4400) | 328 (7000) |

[a] $J$ values were obtained by simulation. [b] d = doublet, s = singlet, and q = quartet.

unpaired electron is delocalized in both pyridine rings in the cation radicals, while spin localization has been observed in the 1,1′-(1,2-ethanediyl)bis[4-(methoxycarbonyl)pyridinium] cation radical.[2] The hfs constants in Figures 3 and 4 were assigned by comparing them with the spin density distribution in 1,4-dimethyl- and 1-methyl-4-*tert*-butylpyridinyl radicals,[3,6] respectively, though the constants are reduced nearly to half compared with those of the 1-methyl monoradicals. The spin delocalization to both pyridine rings may be ascribed to a rapid transfer of the counterion ($Br^-$) between the two pyridines in the cation radical. Observation of spin localization in the one pyridine ring for the 4,4′-dimethoxycarbonyl derivative[2] implies a slow rate of the anion transfer; i.e. the anion stays long around the one pyridine ring of the cation radical.

**Structure of Cyclomers.** The $^1$H NMR spectra of cyclomers were analyzed through double-resonance experiments and by the aid of NMR simulation with the first-order approximation. The proton chemical shifts were reasonable compared with those of 1,2-dihydropyridine derivatives.[7,8] Appearance of five $^{13}$C NMR lines for each compound in the range of 56–139 ppm (Table I) could be interpreted as arising from two asymmetric dihydropyridine rings, and the lines in the 56–59 ppm range are characteristic of the methylene carbons in 1,2-dihydropyridine derivatives. Thus the structure of 6,7,12a,12b-tetrahydrodipyrido-[1,2-*a*:2′,1′-*c*]pyrazine and its derivatives was given to the diamagnetic products. The structures were supported by careful measurements of mass spectra, which showed the following $m/z$ ($M^+$) peaks: 186 for **4a** and **5a**; 214 for **4b** and **5b**; 298 for **4c** and **5c**.

Two possible structures are readily assigned to the meso and *dl* cyclomers, the latter being more stable than the former. Since the $^1$H NMR lines due to the methylene protons appeared as a singlet for each cyclomer, the four hydrogens in the ethylene moiety are equivalent, indicating a mobile structure of the central piperazine ring. The most stable conformations for the meso and *dl* cyclomers are depicted below.




4 5

a: R = H b: R = $CH_3$ c: R = $C(CH_3)_3$

**Thermal Conversion of the Meso Cyclomer into the *dl* Form.** As mentioned above, the meso cyclomers thermally isomerize to the *dl* cyclomers, while the inverse *dl* → meso conversion is only observed photochemically. The meso → *dl* conversion is clearly observed in the NMR measurements for the degassed-sealed solutions of **4a–c** in $CD_3CN$. The rate constants for the conversions were determined as a function of temperature. Plots of ln $k$ vs $1/T$ were linear, and rate constants, $A$ factors, activation energies, enthalpies, and entropies of activation are summarized in Table II. The enthalpies of activation are comparable with those for the $\sigma$-bond cleavages in which free radicals form in the transition state, such as the cases of the homolysis to form triphenylmethyl radical from the dimer[9] and the homolysis of meso and *dl* dimers of 3,5,5-trimethyl-2-morpholinon-3-yl radical.[10]

(6) Akiyama, K.; Tero-Kubota, S.; Ikenoue, T.; Ikegami, Y. *Chem. Lett.* **1984**, 903.
(7) Saunders, M.; Gold, E. H. *J. Org. Chem.* **1962**, *27*, 1439. Fowler, F. W. *Ibid.* **1972**, *37*, 1321.
(8) Cook, N. C.; Lyons, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 3396. Mitchell, T. N. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1149.
(9) Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429.
(10) Bennett, R. W.; Wharry, D. L.; Koch, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 2345.

**Table II.** First-Order Rate Constants and Activation Parameters for the Thermal Conversion of Meso Cyclomers

| conversn | temp, K | rate constant, $\times 10^6$ $s^{-1}$ | $A$, $s^{-1}$ | $E_a$, kcal/mol | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, cal·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|---|---|
| | 334.7 | 21.4 ± 0.75 | | | | |
| **4a** → **5a** | 344.8 | 53.3 ± 2.13 | $1.00 \times 10^{10}$ | 22.4 ± 0.3 | 21.7 ± 0.3 | −15.0 ± 0.4 |
| | 353.6 | 125 ± 4.1 | | | | |
| | 334.5 | 1.33 ± 0.06 | | | | |
| **4b** → **5b** | 344.7 | 4.44 ± 0.16 | $3.98 \times 10^{11}$ | 26.9 ± 0.3 | 26.2 ± 0.3 | −7.7 ± 0.3 |
| | 354.0 | 12.8 ± 0.41 | | | | |
| | 334.7 | 0.16 ± 0.01 | | | | |
| **4c** → **5c** | 344.9 | 0.59 ± 0.02 | $1.00 \times 10^{12}$ | 28.8 ± 0.4 | 28.1 ± 0.4 | −5.9 ± 0.4 |
| | 355.2 | 2.01 ± 0.06 | | | | |

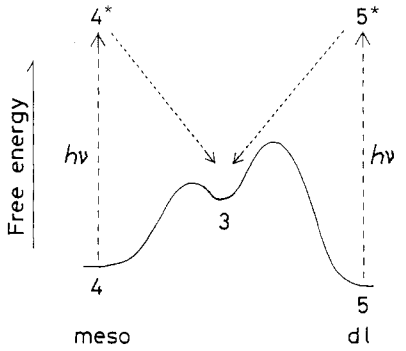



**Figure 5.** Schematic reaction coordinate for the meso (**4**) → *dl* (**5**) conversions.

The negative entropies of activation obtained may be ascribed to the fact that the transition state in the thermal conversion through a homolytic C–C bond cleavage is restricted stereochemically by the ethylene bridge.[11]

The thermal conversion was also followed by absorption spectroscopy: The spectrum of Figure 2a changed gradually by heating the solution of **4a** at around 80 °C to that of Figure 2b. Heating of the solutions of **4b** and **4c** showed similar spectral change.

Reaction mechanism of the present thermal and photochemical conversions has been unsolved. However, it can be mentioned that the activation energy to form **5** from the intermediate diradical **3** would be considerably higher than that to form **4** from **3**, because the formation of **5** from **3**, which was generated by photodissociation of **4** or **5** at low temperature, did not occur. The schematic reaction coordinate is tentatively depicted in Figure 5. Less stability of **4** than **5** at ground state has been pointed out by the calculations of the MINDO/3 method.[12]

**Photolytic Cleavage of Cyclomers.** It has been made clear that some pyridinyl radical dimers are dissociated by light irradiation at the C–C bond formed in the radical dimerization, as demonstrated for the dimers of 1-methyl-2-(methoxycarbonyl)pyridinyl,[13] 1-alkyl-4-phenylpyridinyl,[14,15] and various alkylpyridinyl radicals.[3,6,16] A similar photodissociation was observed for the present cyclomers. Light irradiation of the solutions of **4a** and **5a** at −196 °C produced the spectrum shown in Figure 2c. Although this species was stable for a long period at −196 °C, raising the temperature led to a spectral change to that of Figure 2a. The shape of this spectrum ($\lambda_{max}$ 370 nm) is quite different from those of Figures 2a and 2b and is assigned to the diradical **3a**. The dimethyl (**4b** and **5b**) and di-*tert*-butyl (**4c** and **5c**) derivatives also showed the diradical generation ($\lambda_{max}$: 376 nm for **3b**; 355 nm for **3c**). The diradical generation was clearly demonstrated by the following ESR measurements.

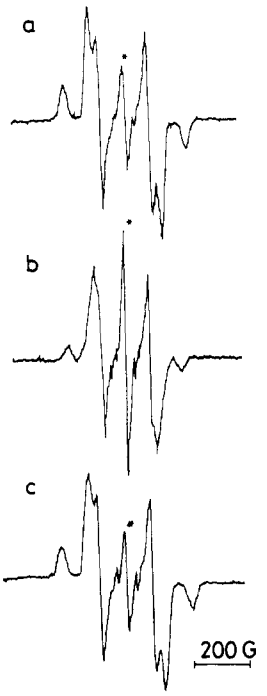



**Figure 6.** Triplet ESR spectra of the diradical **3** generated by photodissociation of cyclomers in MTHF at −196 °C: (a) **3a** from **4a** or **5a**; (b) **3b** from **4b** or **5b**; (c) **3c** from **4c** or **5d**. Concentration of cyclomer in MTHF: $10^{-2}$–$10^{-3}$ M. An asterisk denotes the line due to monoradical at 3320 G.

**Table III.** Zero-Field Splitting Parameters for Diradicals

| param | 3a | 3b | 3c |
|---|---|---|---|
| $\|D\|$, $cm^{-1}$ | 0.0222 | 0.0210 | 0.0219 |
| $\|E\|$, $cm^{-1}$ | 0.0012 | 0.0008 | 0.0016 |
| $r$,[a] nm | 0.49 | 0.49 | 0.49 |

[a] Average separation of two spins estimated from the relation, $D = (-3/2)g^2\beta^2 r^{-3}$.

The MTHF solutions of the various cyclomers do not exhibit any ESR signals at −196 °C. Irradiation of a cyclomer solution with visible light shorter than 500 nm led to an appearance of strong ESR signal as shown in Figure 6 for three sets of cyclomers. Each spectrum is certainly due to the triplet transition of a two-spin system generated by photodissociation. The zero-field parameters are listed in Table III. In the photolytic generation of pyridinyl radical pairs from their dimers in a MTHF matrix, the $E$ values are usually close to zero.[4,13-15] Therefore, the present $E$ values strongly imply that the species are the diradical **3** in which two pyridinyl moieties are sterically restricted by bonding to the ethylene bridge. The $D$ values are smaller than that of the 1,1'-(1,2-ethanediyl)bis[4-(methoxycarbonyl)pyridinyl] diradical.[2]

(11) Rearrangement of the 2,4' dimer of 1,2,6-trimethyl-3,5-(diethoxycarbonyl)pyridinyl radical into the 4,4' dimer shows negative entropy of activation ($A = 1.1 \times 10^{12}$ $s^{-1}$): McNamara, F. T.; Nieft, J. W.; Ambrose, J. F.; Huyser, E. S. *J. Org. Chem.* **1977**, *42*, 988.

(12) Muramatsu, T.; Toyota, A.; Ikegami, Y., unpublished results. The MINDO/3 calculations for **4a** and **5a** gave the following structural informations: (1) The energy of **4a** is 1.07 kcal·mol$^{-1}$ higher than that of **5a** at ground state. (2) The bond lengths between $C_{12a}$ and $C_{12b}$ of **4a** and **5a** are 1.57 and 1.56 Å, respectively. (3) In the lowest excited singlet state, the $C_{12a}$–$C_{12b}$ bond has an antibonding character for both **4a** and **5a**.

(13) Hermolin, J.; Levin, M.; Ikegami, Y.; Sawayanagi, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4795.

(14) Akiyama, K.; Kubota, S.; Ikegami, Y. *Chem. Lett.* **1981**, 469.

(15) Akiyama, K.; Tero-Kubota, S.; Ikegami, Y. *J. Am. Chem. Soc.* **1983**, *105*, 3601.

(16) Akiyama, K.; Ishii, T.; Tero-Kubota, S.; Ikegami, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3535.

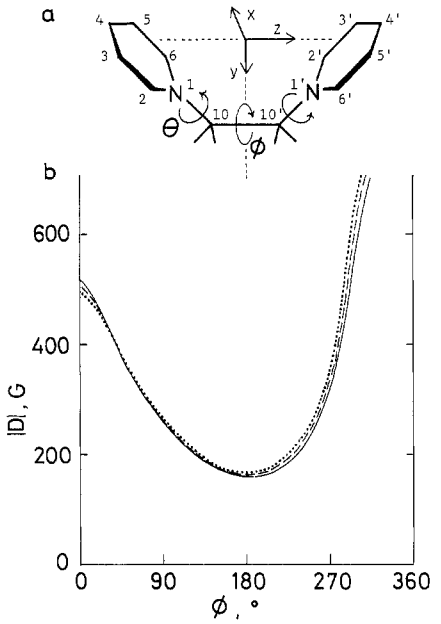



**Figure 7.** (a) Structure of the diradical **3** showing molecular axes $x$, $y$, and $z$. $\phi = 0°$ for the cis conformation, and $\theta = 0°$ when the pyridinyl ring is perpendicular to the C(10′)–C(10)–N(1) plane. (b) Calculated $D$ values as a function of $\phi$ for **3a** (—), **3b** (- - -), and **3c** (···). $\theta$ was fixed at 45°.

The above triplet spectra appear from cyclomers with a few seconds of light irradiation. Such a facile C–C bond cleavage is characteristic of pyridinyl radical dimers, which generate radicals by homolytic C–C bond breakage through a radical pair mechanism from the singlet state[4,6] and through triplet mechanism in the presence of triplet sensitizer.[17] The 12a,12b bond breakage in the present cyclomers can be interpreted similarly. Through-bond interaction between $\pi$-orbitals mediated by $\sigma$-bonds[18] accounts for an unusual, long absorption ($\pi\sigma \rightarrow \pi\sigma^*$ transition).[19] This excitation or the $\pi$–$\sigma^*$ excitation[12] induces photodissociation to form diradicals from both meso and *dl* cyclomers. The dissociation is also allowed thermally.

**Conformation of Diradicals at −196 °C.** Molecular structure of **3a–c** in MTHF at −196 °C can be clarified by calculating the dipolar splitting tensors for the assumed structures, adopting McLachlan's spin densities of the pyridinyl radical and point charge approximation. The following simplifying assumptions were made: (1) An isotropic $g$-factor is applicable. (2) Each spin is delocalized within a pyridinyl moiety. (3) The diradical has a $C_2$ symmetric structure. The molecular axes are chosen as shown in Figure 7a. The calculations were performed in a similar manner as that made for the 4,4′-di(methoxycarbonyl) derivative.[2]

There are an infinite number of ways varying $\phi$ and $\theta$ independently. However, in the range $90° > \phi > 270°$, the rotation by $\theta$ is restricted by steric repulsion of 2,2′-hydrogen atoms. The calculated $D$ values for possible conformations for **3a–c** are shown in Figure 7b for the case of $\theta = 45°$ as a function of $\phi$. By comparing the observed $D$ parameter ($|D| = 238$ G for **3a**) with the calculated ones, the agreement was best for the case of $\phi = 92$–$96°$. The observed value for **3c** ($|D| = 234$ G) also showed agreement for the angle $\phi = 94$–$115°$. For **3b**, we adopted a hyperconjugation model in the McLachlan's spin density calculation, and the resulting $D$ vs $\phi$ curves provided the agreement with the observed value ($|D| = 225$ G) for the case of $\phi = 94$–$100°$. Thus we could estimate $\phi$ to be nearly 95° for all **3a–c** in MTHF glass. This angle corresponds to that a possible structure in which the two pyridinyl rings slightly rotate around the central C–C bond after the breakage of the C–C bond of the cyclomer, in solvent matrix, regardless of the stereochemical structure of the cyclomers. However, the dependence of $D$ on $\theta$ was very small, so that the $\theta$ value could not be estimated exactly. Moreover, the calculated $E$ parameters ($|E| \sim 5$ G) are smaller than the observed ones ($|E| = 12.5$ G for **3a**, 9.0 G for **3b**, and 17.1 G for **3c**). This discrepancy may be mainly caused by the approximations in the present calculation.

## Conclusion

The present paper reports the formation of photosensitive cyclomers of 1,1′-(1,2-ethanediyl)bis(pyridinyl) diradicals (**3**) produced by the reduction of the corresponding bis(pyridinum) salts (**1**). The meso cyclomers (**4**) are thermally converted into the *dl* forms (**5**), and the *dl* forms are photochemically converted into the meso forms. The intermediate, unstable diradicals are detected spectroscopically, and the possible stereochemical structures are inferred.

Although the previous paper[2] on the 4,4′-di(methoxycarbonyl) derivative of **3** could not present individual properties of the meso and *dl* cyclomers, the present study on **3a–c**, having more simple substituents, made clear the behavior of 1,1′-(1,2-ethanediyl)-bis(pyridinyl) diradicals, as mentioned above. The diradicals are substantially in equilibrium with the cyclomers. It has been briefly reported that the 1,1′-(1,3-propanediyl)bis(pyridinyl) diradical shows behavior similar to that of **3**.[20] These results promise further extension of the chemistry of pyridinyl diradical systems.

## Experimental Section

Standard vacuum-line techniques were used in the preparation and purification of the diradicals, cyclomers, and solvents.

**Materials.** 1,1′-(1,2-Ethanediyl)bis(pyridinium) dibromide (**1a**) was prepared by treating 1,2-dibromoethane with a large excess of pyridine without solvent in a sealed tube at 70 °C for about 8 h. A dark solid produced was separated by filtration and recrystallized from methanol to yield colorless crystals, dp 289–292 °C. Anal. Calcd for $C_{12}H_{14}N_2Br_2$: C, 41.64; H, 4.07; N, 8.09. Found: C, 42.01; H, 4.11; N, 8.36. 1,1′-(1,2-Ethanediyl)bis(4-methylpyridinium) dibromide (**1b**) and 1,1′-(1,2-ethanediyl)bis(4-*tert*-butylpyridinium) dibromide (**1c**) were prepared in a similar manner as above. **1b**: colorless, dp 295–298 °C. Anal. Calcd for $C_{14}H_{18}N_2Br_2$: C, 44.94; H, 4.84; N, 7.48. Found: C, 44.81; H, 4.93; N, 7.69. **1c**: colorless, mp >300 °C. Anal. Calcd for $C_{20}H_{30}N_2Br_2$: C, 52.41; H, 6.59; N, 6.11. Found: C, 52.10; H, 6.32; N, 6.21.

**Solvents.** Acetonitrile (Guaranteed Reagent) was passed through an alumina column and distilled. After degassing, the solvent was treated with 1-methyl-4-(methoxycarbonyl)pyridinyl radical to remove radical-reactive impurities. The solvent was distilled again under vacuum at low temperature and stored over previously degassed 4-Å molecular sieves in a storage vessel. 2-Methyltetrahydrofuran (MTHF) was refluxed over sodium for 3 days, degassed, and then distilled onto sodium and anthracene in a storage vessel.

**Reduction of Bis(pyridinium) Salts.** Reduction of **1a–c** was each carried out by two procedures: (P-1) A bromide (ca. 0.025 mmol), 3% sodium amalgam (0.15 mmol), and a Teflon-sealed stirring bar were placed in a reaction flask connected to a vacuum line. After 5 h of pumping at $10^{-6}$ Torr, degassed acetonitrile (5 mL) was distilled in, and the flask was sealed and stirred at 0 °C. The solution became yellowish and then almost colorless. After about 10 h, the solvent was removed and the residue was extracted with MTHF to obtain a colorless solution. The solvent was replaced by an appropriate one for spectral measurements. (P-2) The aqueous solution of a dibromide (ca. 0.3 mmol in 5 mL of water) was added dropwise to a suspension of 3% sodium amalgam in cyclohexane with stirring. The cyclohexane layer gradually turned yellow. After the solution was stirred for about 30 min, the cyclohexane layer was separated and dried over anhydrous magnesium sulfate, and then the solution was moved into a tube connected to a vacuum line. After being degassed, the solvent was replaced by MTHF or acetonitrile.

The product from **1a** in P-1 was almost pure **4a**, *cis*-6,7,12a,12b-tetrahydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazine. MS [20 eV; $m/z$ (relative intensity)]: 186 ($M^+$, 100), 185 (71), 157 (36), 91 (45). Pure **5a**, *trans*-(±)-6,7,12a,12b-tetrahydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazine, was obtained by heating the solution of **4a** in a sealed tube at 80 °C for 20 min in the dark. MS for **5a**: $m/z$ 187 ($M^+ + 1$, 2), 186 ($M^+$, 13), 108

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(5), 107 (59), 106 (6), 93 (3), 80 (10), 79 (100), 52 (8). The product from **1a** in P-1 was a mixture of **4a** and **5a**, and the solution was heated at 80 °C to yield the solution of pure **5a**. The product from **1b** was usually a mixture of cis (meso) and trans-(±) (*dl*) isomers of 2,11-dimethyl-6,7,12a,12b-tetrahydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazine (**4b** and **5b**, respectively) in both procedures of P-1 and P-2. The pure **4b** was obtained by irradiating the solution of the mixture with a 500-W Hg lamp equipped with a UV-29 glass filter for 20 min. MS for **4b**: *m/z* 214 ($M^+$, 100), 213 (57), 120 (22), 93 (22), 91 (25). Pure **5b** was obtained by heating the solution of **4b** in a sealed tube at 80 °C for 4 h. MS for **5b**: *m/z* 214 ($M^+$, 40), 121 (28), 120 (11), 119 (14), 108 (11), 105 (3), 94 (13), 93 (100), 66 (13). The product from **1c** was also a mixture of cis and trans-(±) isomers of 2,11-di-*tert*-butyl-6,7,12a,12b-tetrahydrodipyrido[1,2-*a*:2′1′-*c*]pyrazine (**4c** and **5c**, respectively). The pure forms were yielded in a similar manner as above. MS for **4c**: *m/z* 298 ($M^+$, 9), 163 (100), 135 (68), 120 (51). MS for **5c**: *m/z* 298 ($M^+$, 11), 163 (100), 135 (64), 120 (46).

The concentration of each solution of cyclomers was determined in acetonitrile by following spectroscopically the slow formation of methylviologen cation radical ($\epsilon$ = 13000 at 605 nm)[11] from methylviologen dichloride.

**Instrumentation.** UV-vis spectra were measured on a Cary Model 14 spectrophotometer, ESR spectra were recorded on a Varian Model E-109E EPR spectrometer, and NMR spectra were recorded on a JEOL 90Q NMR spectrometer. The $^1H$ off-resonance decoupling and INEPT techniques were used to analyze $^{13}C$ NMR spectra. Irradiation was carried out with a Ushio 500-W Hg lamp and Toshiba filters. Mass spectra were obtained by using a JEOL Model LMS-DX300 mass spectrometer.

**Kinetic Treatment of Thermal Conversion.** Thermal conversions of **4** into **5** were kinetically treated by measuring the change of a $^1H$ NMR spectrum with time at various temperatures. Change of the integrated signal intensities of H-12a,12b protons of **4** and **5** were analyzed as the first-order reaction. The sample was dissolved in $CD_3CN$, degassed, and then sealed in a tube.

**Acknowledgment.** We are grateful to Associate Professor Shozo Tero-Kubota and Dr. Kimio Akiyama for their helpful discussions. The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 60430001 and 63540324 from the Ministry of Education, Science and Culture.

# Reactions of an Allylic Sulfide, Sulfoxide, and Sulfone with Singlet Oxygen. The Observation of a Remarkable Diastereoselective Oxidation

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**Abstract:** The reactions of singlet oxygen with 1-[(4-methylphenyl)sulfinyl]-2,3-dimethyl-2-butene (**6**), 1-[(4-methylphenyl)sulfonyl]-2,3-dimethyl-2-butene (**7**), and 2,3-dimethyl-2-butenyl *p*-methylphenyl sulfide (**8**) have been examined. The formation of transient intermediates and products in the reaction of **8** have been followed as a function of extent of reaction and a remarkable diastereoselective reaction has been uncovered. The implications of this discovery for the mechanism of sulfide oxidation is discussed.

The photooxidation of sulfides (eq 1), first reported by Schenck[1] more than 25 years ago, remains an active area of investigation.

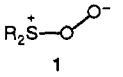
$$2R_2S + {}^1O_2 \rightarrow 2R_2SO \qquad (1)$$

The unraveling of the mechanistic complexities of this deceptively simple reaction has provided an intriguing challenge for the physical organic chemist.[2] In addition, the possibility that singlet oxygen is involved in the posttranslational modification of methionine to the sulfoxide and ultimately responsible for the loss of activity in several enzymes has attracted the interest of biochemists.[3]

Foote's group[4] in particular has extensively contributed to an understanding of dialkyl sulfide photooxidation. In aprotic solvents such as benzene or acetonitrile this reaction produces several interesting experimental observations which include the following: (1) For every mole of oxygen consumed, 2 mol of sulfoxide are produced. (2) Greater than 95% of all interactions of diethyl sulfide with singlet oxygen at room temperature are unproductive and lead to physical quenching and only 5% produce an oxidized product. (3) At lower temperatures (−78 °C) physical quenching is suppressed and product formation is accelerated. (4) The extent of physical quenching is independent of sulfide concentration. (5) Addition of diphenyl sulfoxide inhibits physical quenching. (6) The total rate of singlet-oxygen removal by the sulfide substrate is sensitive to steric bulk around the sulfur. (7) Decreasing concentrations of sulfide favors sulfone formation. (8) Increasing concentrations of sulfide favors sulfoxide formation. (9) Sulfides and sulfoxides do not compete for the same intermediate.

To explain these experimental observations, the mechanism invoking two intermediates, A and B, in Figure 1 was proposed. This mechanism satisfies the requirements that sulfide substrate and diphenyl sulfoxide do not compete for the same intermediate (experimental observation 9) and that physical quenching ($k_q$) is independent of sulfide concentration (experimental observation 4) but dependent on the concentration of added diphenyl sulfoxide (experimental observation 5).

No direct structural information is available on intermediates A or B. Diaryl sulfides, however, function as nucleophilic trapping agents[5] and diaryl sulfoxides as electrophilic trapping agents,[6] suggesting that A is best described as a persulfoxide **1** and B as



**1**

**2**

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