

Photochemical Generation of 1,1'-Ethylenebis(pyridinyl) Diradical
from Its Cyclomers

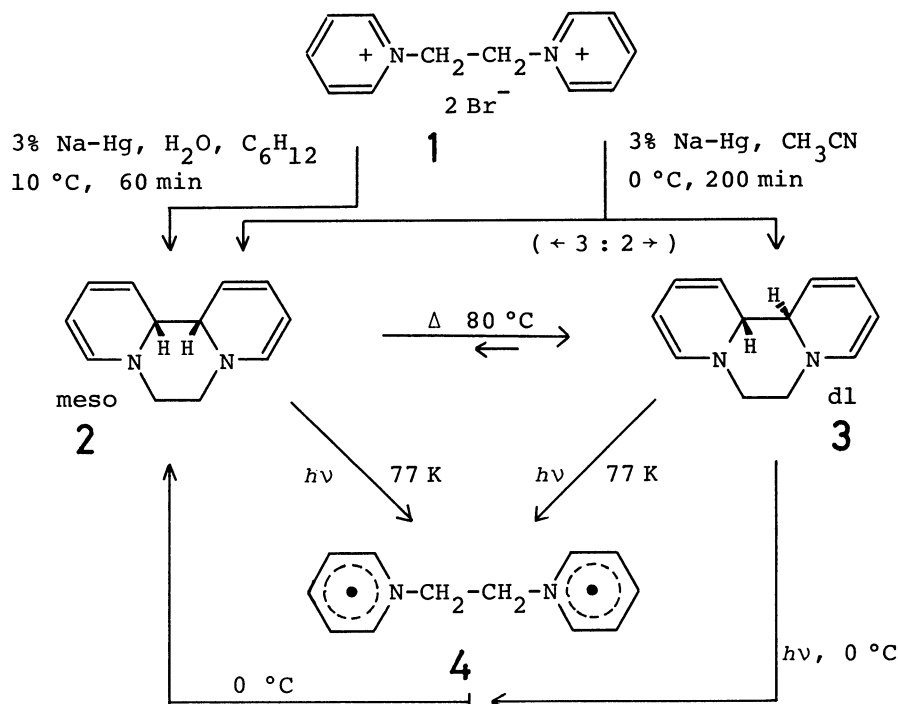
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Reduction of 1,1'-ethylenebis(pyridinium) dibromide with sodium amalgam afforded the cyclomers of 1,1'-ethylenebis(pyridinyl) diradical. Meso and dl forms of the cyclomers are convertible to each other. Photolysis of the cyclomers showed a triplet ESR spectrum characteristic of the diradical.

A recent study on the 1,1'-ethylenebis[4-(methoxycarbonyl)pyridinyl] diradical revealed that this diradical is in equilibrium with the cyclomers formed by intramolecular cyclization. The equilibrium tends overwhelmingly toward the cyclomer side in the dark and the cyclomers photodissociate to generate the diradical, which was characterized by an ESR triplet spectrum at 77 K.¹⁾ 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,^{2,3)} various pyridinyl diradicals without any electron withdrawing and delocalizing group in the pyridine rings might be generated. Accordingly, we attempted photochemical generation of 1,1'-ethylenebis(pyridinyl) diradical from the cyclomers and obtained explicit results on the structural assignments to the cyclomers with meso and dl forms, conversion of both forms to each other, and photochemical generation of the diradical from the cyclomers. Mutual relation of the substances is summarized in Scheme 1.

Reduction of 1,1'-ethylenebis(pyridinium) dibromide (1) with sodium amalgam was carried out by two procedures: (P-1) Using standard vacuum line techniques, 1 (100 mg) and 3% sodium amalgam (450 mg) in degassed acetonitrile (30 cm³) were stirred in a flask at 0 °C for 4 h. After the amalgam changed to a liquid state, the solvent was removed, residue was extracted with 2-methyltetrahydrofuran (MTHF), and then the solvent was replaced by CD₃CN or CH₃CN. (P-2) According to the procedure by Cairns and Corran,⁴⁾ a solution of 1 (100 mg) in water (5 cm³) was added dropwise to a suspension of 3% sodium amalgam (1.5 g) in cyclohexane (10 cm³) with stirring at 10 °C for 30 min. After further stirring for 30 min, the organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was replaced by CD₃CN or CH₃CN using a vacuum line. Care was taken in



Scheme 1.

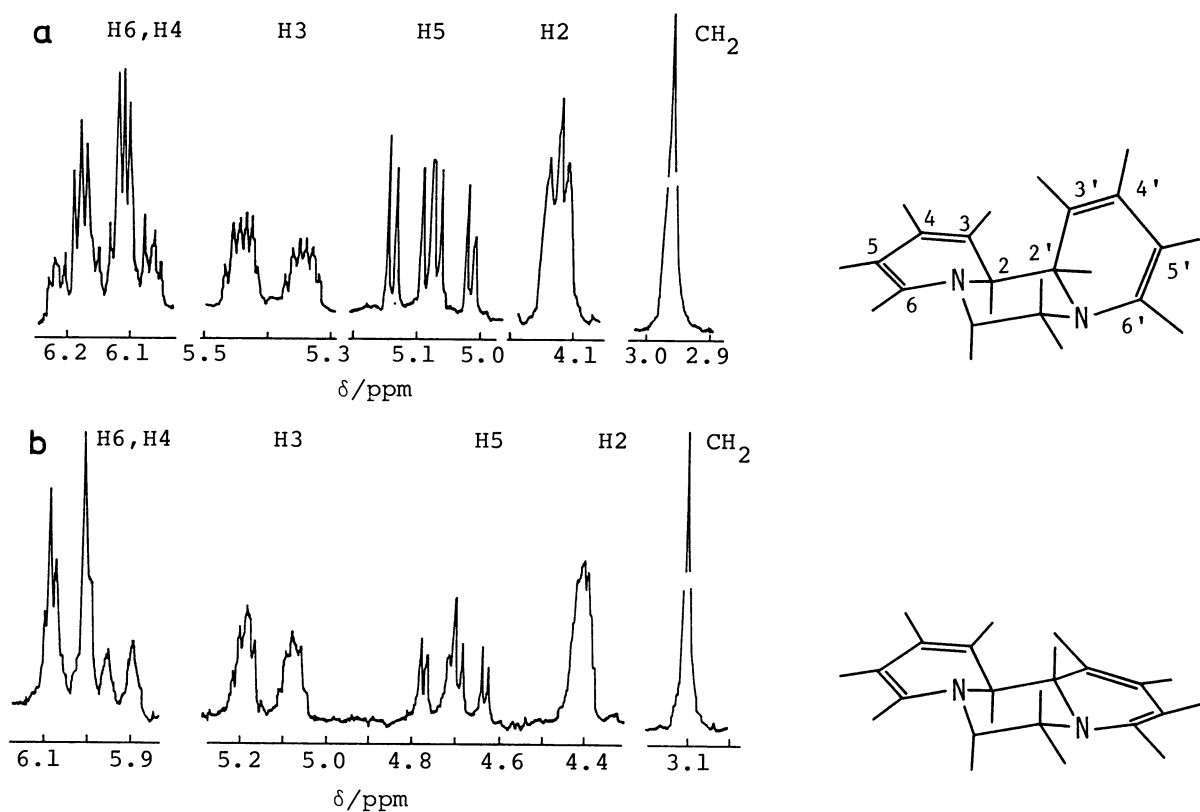


Fig. 1. ^1H NMR spectra of the meso (a) and dl (b) cyclomers in CD_3CN and their stereochemical structures.

handling the products to maintain the temperature lower than 25 °C in the gloom.

The ^1H NMR spectrum of the product in P-2 (Fig. 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 Fig. 1b after 90 min. These results mean that the product in P-2 was one isomer ($\underline{2}$) and that in P-1 was the mixture with another isomer ($\underline{3}$). Measurements of the ^{13}C NMR spectra were interpreted similarly. Analysis of these spectra by the aid of ^1H NMR simulation with the first-order approximation substantiated that both of $\underline{2}$ and $\underline{3}$ have a structure of 1,1'-ethylene-1,1'2,2'-tetrahydrobipyridine. Product ratio of $\underline{2}$ to $\underline{3}$ in P-1 was about 3/2. The thermal conversion of $\underline{2}$ into $\underline{3}$ occurred also at room temperature very slowly. Since the cis cyclomer is expected to be less stable than the trans cyclomer, in analogy with the cyclomer formation of 1,1'-trimethylenebis[4-(methoxycarbonyl)pyridinyl] diradical,⁵⁾ the stable isomer $\underline{3}$ was assigned to the dl-form and the less stable isomer $\underline{2}$ to the meso-form.

In contrast with the thermal conversion, light irradiation caused the conversion of $\underline{3}$ into $\underline{2}$. The solution of $\underline{3}$ in CD_3CN was irradiated by using a high pressure Hg-lamp (500 W) equipped with a UV-29 glass filter at 0 °C. The ^1H and ^{13}C NMR spectra after the 25 min irradiation were those of the almost pure meso isomer. The above thermal and photochemical conversions were completely reversible for the degassed solution in a sealed tube.

These results were supported by the measurements of absorption spectra, which are illustrated with Figs. 2 and 3. The concentration of each cyclomer solution was determined in acetonitrile by following spectroscopically the slow formation of methylviologen cation radical ($\epsilon = 13000$ at 605 nm)⁶⁾ from methylviologen dichloride. The spectrum of Fig. 3a changed on light irradiation into that of Fig. 3c, which is identical with Fig. 2a. The resulting solution, on warming at 80 °C, showed the spectrum of Fig. 3a. At 77 K, light irradiation of

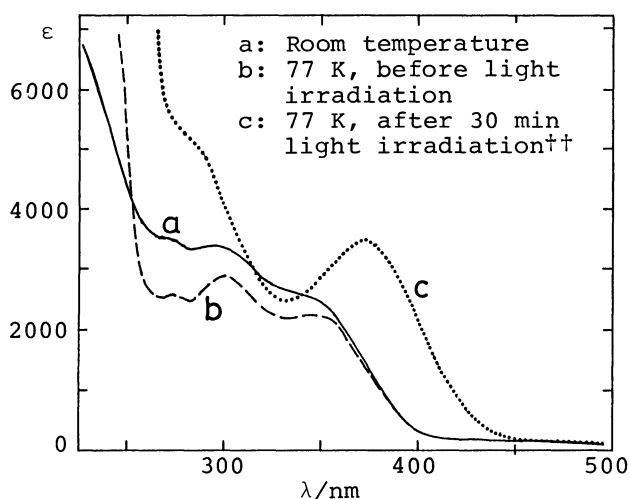


Fig. 2. Absorption spectrum of $\underline{2}$ and its change on light irradiation in MTHF. ††Intensity is inaccurate because of incomplete photolysis.

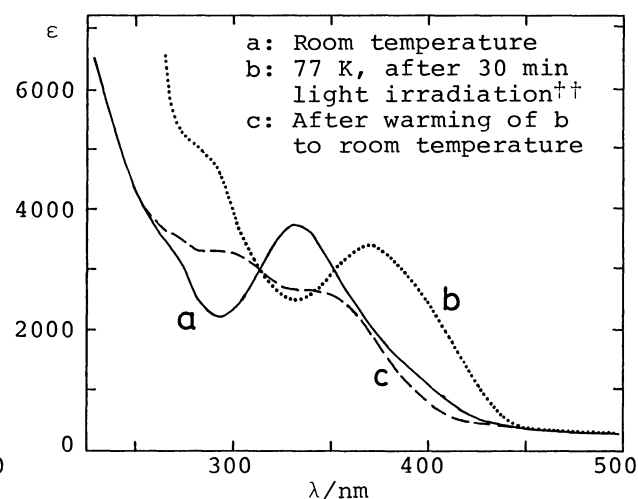


Fig. 3. Absorption spectrum of $\underline{3}$ and its change on light irradiation in MTHF. ††See the ††-note of Fig. 2.

the solutions of 2 and 3 exhibited the identical spectra of Figs. 2c and 3b. The shape of the spectrum is quite different from those of 2 and 3 and is ascribed to the diradical (4) produced by the photodissociation of 2 and 3, as it was demonstrated by the following ESR measurements.

The solutions of 2 and 3 in MTHF showed no ESR signal at 77 K. Irradiation of either solution of 2 or 3 with visible light shorter than 500 nm led to an appearance of strong ESR signal as shown in Fig. 4. This spectrum is certainly due to the triplet transition of a two spin system generated by photodissociation. The zero-field parameters are $|D| = 0.0222$ and $|E| = 0.0012 \text{ cm}^{-1}$.

In the photolytic generation of pyridinyl radical pairs from their dimers, the E value is usually close to zero. Therefore, the above E value strongly implies that the species is 4 in which two pyridinyl moieties are sterically restricted by bonding of the ethylene bridge. The D value is consistent with a spin-spin dipolar interaction for an average separation of 0.49 nm, using the relation of $D = -(3/2)g^2\beta^2r^{-3}$.

In conclusion, the diradical 4 is regarded as a component in the equilibrium system with the cyclomers. Photodissociation of the cyclomers probably occurs through the $\pi\sigma-\pi\sigma^*$ transition in the 350 nm region and involves rotation around the ring nitrogen-CH₂ bond followed by rotation around the CH₂-CH₂ bond to arrive at the stable form of 4 in a rigid matrix at low temperature.⁷⁾

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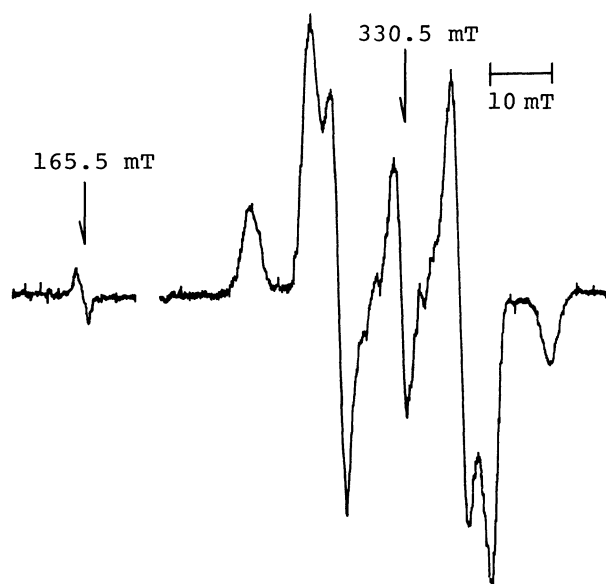


Fig. 4. Triplet ESR spectrum of the diradical 4 in MTHF at 77 K.

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