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THE THERMAL AND PHOTOCHEMICAL BEHAVIORS OF THE CYCLOMERS OF ETHYLENEBIS- AND TRIMETHYLENEBIS(PYRIDINYL) DIRADICALS.*

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Abstract——Pyridinyl diradicals of the type $\dot{P}y\text{-}(CH_2)_n\text{-}\dot{P}y$ ($\dot{P}y$ = pyridinyl, n = 2, 3), which possess two pyridinyl monoradicals connected through a methylene chain, exist usually in equilibrium with the meso and dl cyclomers formed by intramolecular cyclization of the diradical. The equilibrium between diradical and cyclomers tends overwhelmingly toward the cyclomers in the dark and the cyclomers photodissociate to generate the diradical. This paper concentrates our recent results on the preparation, structure, and thermal and photochemical behaviors of the diradicals and the cyclomers.

I. Introduction

Since the first preparation of 1-ethyl-4-methoxycarbonylpyridinyl radical,[1] a number of studies on pyridinyl radicals have been undertaken.[2~4] The chemistry of pyridinyl radicals has been established through systematic studies on the physical and organic properties. Pyridinyl diradicals of the type $\dot{P}y\text{-}(CH_2)_n\text{-}\dot{P}y$ ($\dot{P}y$ = 4-methoxycarbonylpyridinyl, n = 2 ~ 5), which possess two stable pyridinyl π-radicals connected through a methylene chain, were chosen as species favorable

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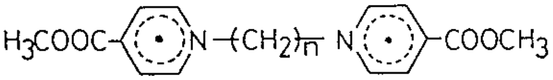
* Dedicated to the memory of the late Dr. Tetsuji Kametani.

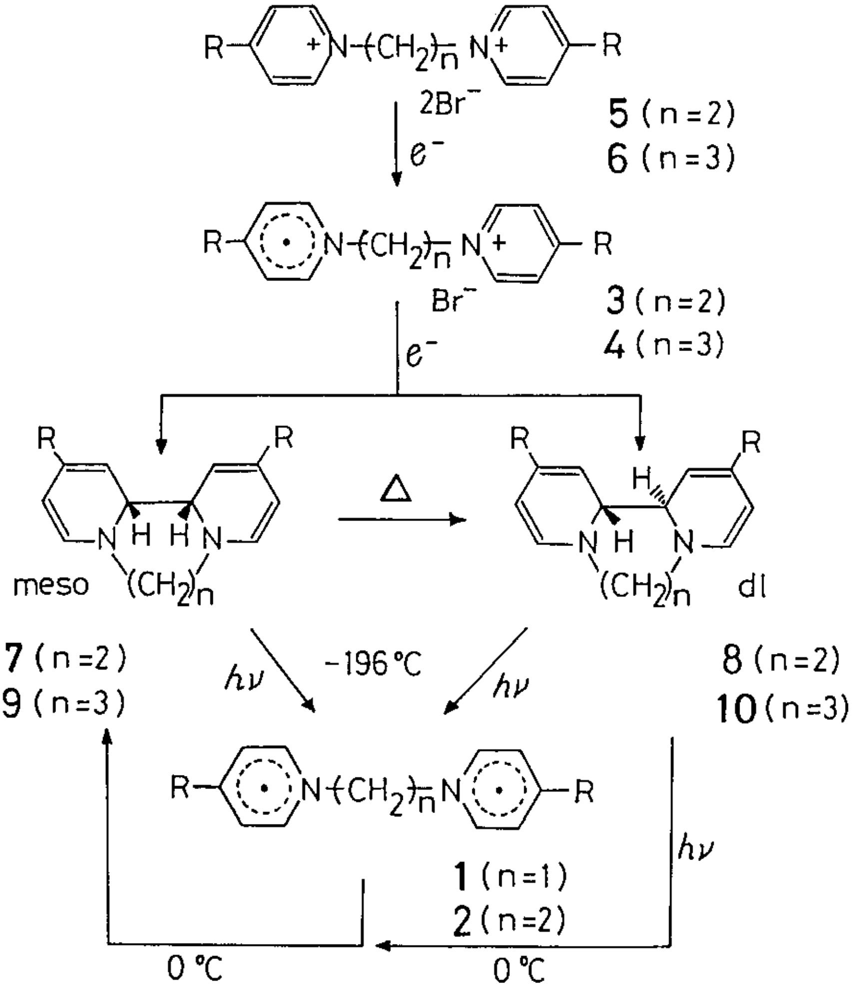
to investigate intramolecular spin-spin interactions. In the series of these diradicals, the intramolecular spin dipole interaction of **1d**[5] and the intramolecular charge transfer interaction of **2d**[6] were reported. However, the results obtained at that time involved some problems mainly caused by the limited experimental techniques. After having established the existence of an equilibrium between a pyridinyl radical and the covalently bonded dimers[7~9] and photolytic C-C cleavage of the dimers of alkylpyridinyl radicals,[4,10] a reinvestigation of the pyridinyl diradicals was carried out by us and made clear that the present diradicals usually are in the form of cyclomers. This review will concentrate the recent results[11~15] on (a) the cyclomer formation of diradicals, (b) *structure of the cyclomers, (c) thermal and photochemical behavior of the cyclomers,* and spin-spin interaction in the diradicals. The reactions of the cyclomers are summarized in Scheme 1.



1d (n=2)
2d (n=3)

II. Preparation of Cyclomers

The cyclomers can be prepared by two procedures as follows. (P-1) Reduction of bispyridinium dibromides (**5**, **6**) with 3% sodium amalgam in degassed acetonitrile at 0 ℃. (P-2) Reduction of **5** or **6** with 3% sodium amalgam in H_2O-cyclohexane (or n-hexane) in nitrogen atmosphere. The reduction products by P-1 and P-2 were extracted with 2-methyltetrahydrofuran (MTHF) in vacuo, and then the solvent was replaced by CD_3CN or CH_3CN. Care was taken in handling the products to maintain the temperature lower than 25 ℃ in the dark. In the course of reduction of **5** and **6** by P-1, esr signals of the cation radicals (**3b**, **3c**, and **3d**) produced by one electron reduction of the corresponding dications could be detected, though the esr signals disappeared by further reduction. The finally obtained products from **5** and **6** were each a mixture of the meso and dl cyclomers formed by intramolecular cyclization of the corresponding diradical.



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

Scheme 1

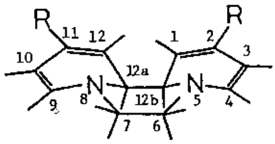
III. Structure and Properties of the Cyclomers

Reduction products of **5a**, **5b**, and **5c** by P-1 and P-2 were usually composed of the two diamagnetic isomers (**7** and **8**) in solution. These isomers were identified independently by nmr measurements as follows. When a reduction product was warmed in CD_3CN at 80 °C, the ^1H nmr spectrum changed gradually, showing thermal conversion, and finally gave only the spectrum of one isomer **8**. In contrast to the thermal conversion, light irradiation to a solution of **8** at 0 °C caused conversion in the reverse direction and the ^1H nmr spectrum showed the almost pure solution of **7**. Analysis of the spectra by the aid of ^1H nmr simulation with the first-order approximation and by comparing them with the spectra of 1,2-dihydropyridines[16~19] substantiated that **7** and **8** have a structure of 6,7,12a,12b-tetrahydro[1,2-a:2',1'-c]pyrazine. This structural assignement corroborated by the ^{13}C nmr and mass spectral measurements of **7** and **8**. By reference to the lower stability of cis cyclomer of **2d** than the trans cyclomer,[20] the unstable isomer was assigned to meso(cis)-form (**7**) and another isomer to dl(trans)-form (**8**).

The reduction of **5d** (R = $COOCH_3$) by the P-1 procedure also afforded the diamagnetic product, but the ^1H nmr spectrum of the product was more complicated than those of the products from **5a**, **5b**, and **5c**. This complexity would be mainly caused by the coexistence of meso and dl cyclomers and these nitrogen-interconverted forms. The thermal and photochemical conversions to either side of meso and dl form were unsuccessful for the cyclomers of **1d**.

The reduction products of **6a**, **6b**, and **6c** by the P-1 procedure were each a mixture of the meso(**9**) and dl(**10**) cyclomers. The meso cyclomers thermally converted into the dl cyclomers and, inversely, light irradiation caused conversion in the reverse direction. Thus, the conversions of **9** and **10** well resembled those of **7** and **8**. The structures of **9** and **10** were readily determined by ^1H, ^{13}C nmr and mass spectral measurements and by comparing them to the spectra of **7** and **8** to be a skeleton of 7,8,13a,13b-tetrahydro-6H-dipyrido[1,2-a:2',1'-c]diazepin. The thermal and photochemical conversions of $\mathbf{7} \rightleftharpoons \mathbf{8}$ and $\mathbf{9} \rightleftharpoons \mathbf{10}$ were completely reversible to each other in degassed sealed solutions. In the two possible structures for meso(**7**, **9**) and dl(**8**, **10**) cyclomers, the later would be more stable conformation than the former. The most stable conformations for these cyclomers are depicted.

meso



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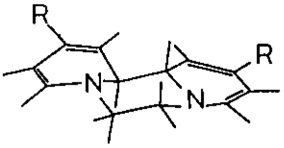

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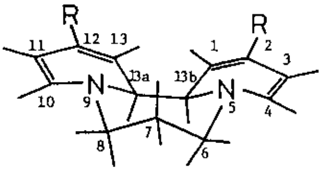
dl



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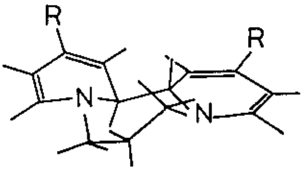

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It is considered that the meso and dl cyclomers form an equilibrium system with the diradical, though the equilibrium tends overwhelmingly toward the cyclomers in solution. The meso and dl cyclomers of **1** and **2** possess thermal and photochemical sensitivities and form the diradicals by C-C bond cleavage. This implies that the covalent bonds between two dihydropyridine moieties of the cyclomers have a character specific to these skeletons. The solutions of these cyclomers exhibit broad absorption bands in the near-ultraviolet region (300-370 nm). The shape of these bands well resembles that of the covalently bonded dimers of pyridinyl radicals.[7,8,13] This band has been assigned to a $\pi\sigma \longrightarrow \pi\sigma^*$ transition[3,4] by which both photochemical and thermal dissociations are allowed. The MINDO/3 MO calculations for **7a** and **8a** recently provided the following structural informations:[21] (1) The energy of **7a** is 1.5 kcal mol^{-1} higher than that of **8a** in ground state. (2) The bond lengths between C_{12a}-C_{12b} of **7a** and **8a** are 0.157 and 0.156 nm, respectively, suggesting that the thermal cleavage between C_{12a}-C_{12b} bond would easily occur. (3) HOMOs for **7a** and **8a** have mainly a bonding character and LUMOs an antibonding one at the C_{12a}-C_{12b} bond, and the former possesses a π-character and the later a σ^* one. The results imply that the photodissociation of **7a** and **8a** would occur in the excited states arising from the $\pi \longrightarrow \sigma^*$ transition.

IV. Properties of 1,1'-(1,2-Ethanediyl)bis(pyridinyl) Diradicals and the Cyclomers

As mentioned above, **7** thermally isomerizes to **8**, while the inverse conversion is only observed photochemically. The thermal isomerization could be followed by nmr measurements for the sealed solution in CD_3CN. The rates of isomerizations of **7a**, **7b**, and **7c** apparently obeyed a first-order kinetics. The estimated activation energies are 22-28 kcal mol^{-1}. These activation energies are comparable with those of σ-bond cleavages in which free radicals form in the transition state.[22] The thermal isomerization would proceed via a diradical intermediate. The transition state of isomerization would be somewhat restricted stereochemically (preexponential factors : 10^{10}-10^{12}). In contrast to the thermal conversion of meso cyclomer, photochemical conversion of dl cyclomer into meso cyclomer is very rapid at room temperature. Such a facile C-C bond cleavage on light irradiation is characteristic of pyridinyl radical dimers.[4,23] It can be mentioned that the activation energy to form dl cyclomer from the diradical would be considerably higher than that to form the meso cyclomer from the diradical, because the formation of dl cyclomer from the diradical, which can be generated by photodissociation of meso and dl cyclomers at low temperature, did not occur. Schematic reaction coordinate is tentatively depicted in Figure 1.

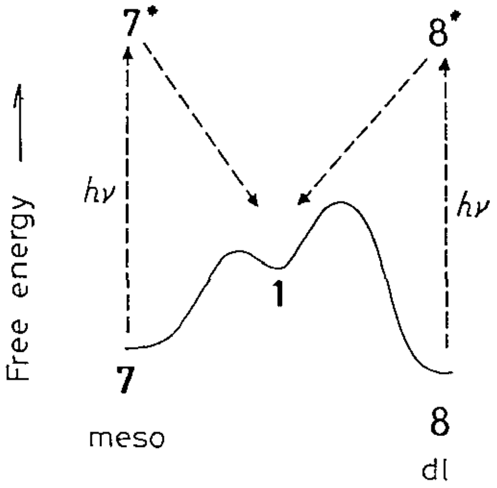


Figure. 1 Schematic reaction coordinate for the meso-dl conversions.

The diradical generation is clearly observed by the change in the absorption specta obtained after the photolyses of **7** and **8** at -196°C. Irradiation of either solution of **7** or **8** with visible light shorter than 500 nm led to an appearance of absorption band in 370-390 nm, which is assignable to the diradical **1**. The generation of the diradical is clearly proven by esr measurements. Irradiation of either solution of **7** or **8** with visible light at -196 °C led to an appearance of strong esr signal. This esr signal is due to the triplet transition of a two spin system generated by photodissociation of a cyclomer. The zero-field parameters obtained for some diradicals are listed in Table 1. The D values were consistent with a spin-spin dipolar interaction for an average separation of about 0.49 nm.

Table 1. Zero-field Splitting Parameters for **1a**, **1b**, **1c**, and **1d**

Diradical	$\lvert D\rvert$ /cm^{-1}	$\lvert E\rvert$ / cm^{-1}	r / nm^{a}
1a	0.0222	0.0012	0.49
1b	0.0210	0.0008	0.49
1c	0.0219	0.0016	0.49
1d	0.0178	0.0017	0.53

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

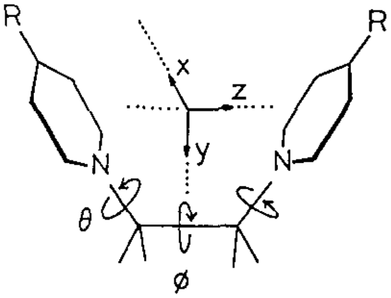


Figure. 2 Structure of the diradical **1**.

In the photolytic generation of pyridinyl radical pairs from the dimer, the E value is usually close to zero. Therefore, the above E values strongly imply that two pyridinyl moieties of the diradical are sterically restricted by bonding to the ethylene bridge. From the calculations of dipolar splitting tensors for the various conformations of diradical (Figure 2) using the following equations,

$$D = \frac{3}{4}g^2\beta^2\sum_{i,j}\frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}^5}\rho_i\rho_j$$

$$E = \frac{3}{4}g^2\beta^2\sum_{i,j}\frac{y_{ij}^2 - x_{ij}^2}{r_{ij}^5}\rho_i\rho_j$$

the agreement between the calculated and observed D values were obtained with ϕ = 90-100°. This angle corresponds to that of a possible structure in which the two pyridinyl rings slightly rotate around the central C-C bond after the breakage of C_{12a}-C_{12b} bond of the cyclomer in solvent matrix. The esr and absorption spectra due to the diradicals remained unchanged for a long period at -196 °C, indicating that the conformation of the diradical remained fixed in solvent cage. With a rise in temperature of the solution, the triplet esr signal rapidly disappeared. Light irradiation of the cyclomer solution at -50 °C did not show any esr signal, implying that the recombination of diradical to form the cyclomers is very rapid. In the case of **1d**, a characteristic behavior was observed at low temperature below -100 °C. Light irradiation of the concentrated solution of cyclomer (c > 10^{-2} M) in MTHF at -135 °C exhibited the esr spectrum shown in Figure 3,a, which has a strong central line due to the monoradical moiety, besides the triplet spectrum. With a rise in temperature, the triplet spectrum deformed (Figure 3,b) indicating a change of interspin distance caused by the restricted motion of the diradical. The subsequent lowering of the temperature led to a significant increase of the signal intensity due to the monoradical (Figure 3,c). Intensity of the monoradical signal usually increased with the cyclomer concentration. Such a change in the esr spectrum may be interpreted as arising from the association of the diradical, as shown in Figure 4. The associated species should show an esr spectrum resembling that of the monoradical.

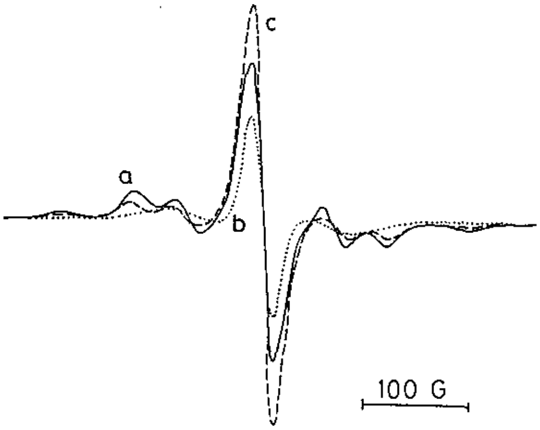


Figure. 3
Temperature dependence of the esr spectrum of **1d** generated by photodissociation of the cyclomers in MTHF (c = 1.2×10^{-2}M).
a and b were recorded at -135 °C and -100 °C, respectively with continuous irradiation. c was recorded after the solution of b was cooled down to -145 °C in the dark.

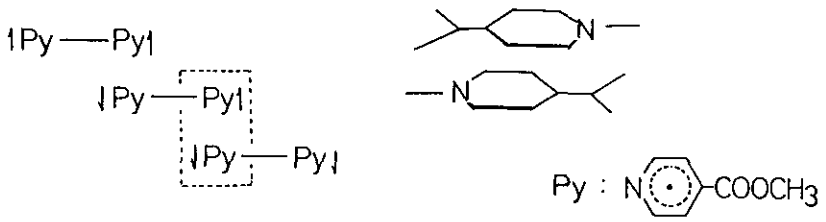


Figure. 4 Association of pyridinyl rings.

Diradical association was parallel with an appearance of the absorption band at 600 nm as well as blue color of the solution. The 600-nm band is assigned to the charge transfer transition characteristic of the intermolecular association of two pyridinyl rings.[24,25] However, intermolecular bond formation of the diradical is denied, because a typical triplet esr spectrum appeared by short irradiation of the cyclomer solution at -196 °C.

V. 1,1'-(1,3-Propanediyl)bis(pyridinyl) Diradicals and the Cyclomers

The thermal and photochemical conversions of **9** and **10** fairly resemble those of **7** and **8**. Activation parameters for the thermal isomerization of meso cyclomers (activation energies = 14-20 kcal mol^{-1}, preexponential factors = 10^5-10^9) are smaller than those of the isomerization of **7**. The difference of activation energies may be ascribed to the larger strain energies of the present meso cyclomers, because they have a seven-membered ring containing a trimethylene bridge. In general, the activation energy decreases with an increase in strain energy.[26] Further, the less preexponential factors suggest that the pyridinyl rings bonded by a trimethylene bridge would be more restricted stereochemically in the transition state as compared to the isomerization of **7**. Difference of the conformational mobility of **2** from that of **1** appeared in the triplet esr spectum of **2**. Irradiation of either solution of **9a** or **10a** with visible light exhibited the spectrum of Figure 5,a. The signal intensity increased with the time of irradiation, being accompanied by a change of the spectral shape into those of Figures 5,b and 5,c. These spectra are certainly due to the triplet transitions of two spin system of **2a**, and would be interpreted as arising from two triplet components, T(1) and T(2), both of which are stabilized in glassy matrix. A similar spectrum and change were observed for **2b**. For **2c**, triplet esr spectrum which was consistent with only one component, was observed.

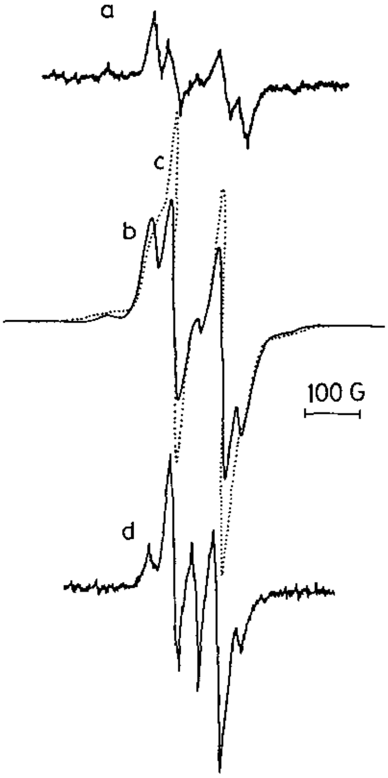


Figure. 5
Triplet esr spectra of **2a** in MTHF glass.
a, b, c were recorded after 0.5, 10, and 40 min light irradiations, respectively. d was recorded after a rise in temperature to -145 °C.

Table 2. Zero-field Splitting Parameters for **2a**, **2b**, **2c** and **2d**

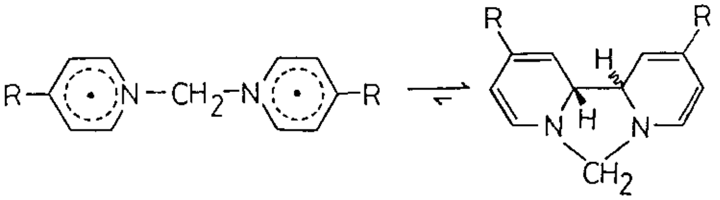
	T(1)			T(2)		
Diradical	$\|D_1\|/cm^{-1}$	$\|E_1\|/cm^{-1}$	r/nm^a	$\|D_2\|/cm^{-1}$	$\|E_2\|/cm^{-1}$	r/nm^a
2a	0.0177	0	0.53	0.0121	0	0.60
2b	0.0191	0	0.51	0.0126	0	0.59
2c	0.0194	0	0.51			
2d	0.0154	0	0.55			

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

The zero-field parameters for the triplet spectra are listed in Table 2. The T(1) spectra of **2a** and **2b** appeared strongly in the early stage of irradiation, and the spectral intensity of the T(2) component increased with the irradiation time. Upon warming to -145 °C, only the T(2) spectrum remained (Figure 5,d). The triplet esr spectrum of **2c** was no longer observed at -145 °C, implying the less stability of **2c** than **2a** and **2b**. The E values for the observed triplet species are close to zero, indicating that the structures of the present diradicals are conformationally flexible compared with those of **1a**-**1d**. Change in the separation (Table 2) from metastable T(1) to stable T(2) is attributable to conformational stabilization in the solvent matrix at low temperature, since the change occurred in the dark at -196 °C.

The 4,4'-(dimethoxycarbonyl) derivative (**2d**) exists as the cyclomers under usual conditions, as reported by Hermolin and Kosower.[20] The triplet esr signal of **2d** remained unchanged for a long period at -196 °C. With the rise in temperature to -150 °C, the signal gradually decreased accompanied by the color change from colorless to a blue solution. This blue color with the absorption at 600 nm is characteristic of the intermolecular association of two pyridinyl rings as observed for the association of **1d**.

We can expect the generation of similar diradicals by photodissociation from the corresponding cyclomers. As a preliminary examination, reduction of methylenebis(pyridinium) dibromides with 3% sodium amalgam in H_2O/n-hexane at -10 °C yielded the cyclomers(**12**). This product was only stable at temperature lower than 0 °C. Light irradiation of the solution of **12** at -196 °C exhibited the absorption of **11** (λ_{max}=360 nm), but showed no esr signal. The diradical produced by photodissociation of **11** would be singlet species, because there will be a strong spin exchange between the two pyridinyl rings through the methylene group.



11 **12**

$R = CH_3, C(CH_3)_3$

VI. Conclusion

The present paper concentrates our recent results on the chemistry of 1,1'-(1,2-ethanediyl)bis(pyridinyl) (**1**) and 1,1'-(1,3-propanediyl)bis(pyridinyl) diradicals(**2**). Radical-radical interaction between two pyridinyl radical moieties connected through two- to five-methylene chains has been a subject of investigation since 1967.[5,6,27,28] However, recent studies with careful handling of pyridinyl radicals revealed the facile cyclomer formation for **1** and **2**.[11~14] Basing upon the results obtained so far, we conclude as follows: (1) Pyridinyl diradicals of the type $\dot{Py}-(CH_2)_n-\dot{Py}$ (n = 2,3) are converted to cyclomers of meso and dl forms under ambient conditions. (2) The meso and dl cyclomers are convertible to each other through the diradical intermediate. (3) Radical-radical interactions can occur intermolecularly, as observed for **1d** and **2d** in solution at low temperature. The results presented here first established the basic chemistry of the $\dot{Py}-(CH_2)_n-\dot{Py}$ diradicals. Further extension of the chemistry of pyridinyl diradicals is promised.

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