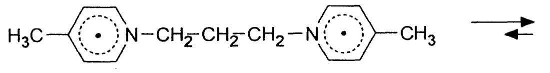
Preparation and Properties of a Novel Heterocyclic Dispiro Compound, 3,10-Diaza-*N*,*N*-dimethyldispiro[5.0.5.3]pentadeca-1,4,8,11-tetraene

Takashi Muramatsu,* Azumao Toyota,† Yusaku Ikegami,†† Shinji Onodera,††† and Hisahiro Hagiwara†††
Research Institute for Science Education, Miyagi University of Education, Sendai 980
†*Department of Chemistry, Faculty of General Education, Yamagata University, Yamagata 990*
††*The Japan Association of Chemistry, Itsutsubashi 1-4-24, Sendai 980*
†††*Institute for Chemical Reaction Science, Tohoku University, Sendai 980-77*

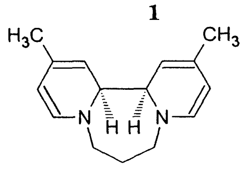
(Received October 25, 1995)

Two-electron reduction of 4,4'-(1,3-propanediyl)bis-(*N*-methylpyridinium) dibromide with sodium amalgam in degassed solvent affords the titled compound, which is characterized by means of NMR, mass, ESR, and UV-vis absorption spectroscopies. Under deoxygenated conditions, the dispiro compound is stable for a long time at room temperature, but undergoes a decomposition reaction at high temperatures above 200 ℃ to give several degradation products.

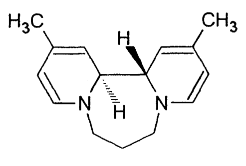
Pyridinyl diradicals in which two stable π-radicals are connected through methylene chain are interesting because they provide evidence regarding the interaction of the two-spin systems.[1-3] Experiments have shown that 1,1'-(1,3-propanediyl)bis(4-methylpyridinyl) diradical (**1**) is in equilibrium with two cyclomers of *meso* (**2a**) and *dl* (**2b**) forms formed by intramolecular cyclization in solution.[2] Interestingly, cyclomers **2a** and **2b** exhibit such high response to heat and light that the former isomerizes thermally into the latter, which converts photochemically into the former. Also, both cyclomers are photolized to generate the diradical **1** at low temperature in vacuo. It is intriguing in this connection to see whether 4,4'-(1,3-propanediyl)bis(*N*-methylpyridinyl) diradical (**3**) yields analogous cyclomers, and, if such is the case, it is essential to study thermal and photochemical behaviors of the cyclomers for understanding the chemistry of pyridinyl diradicals. In this paper, we report that the diradical **3** forms 3,10-diaza-*N*,*N*-dimethyldispiro[5.0.5.3]pentadeca-1,4,8,11-tetraene (**4**), a novel heterocyclic dispiro compound.[4] Some properties of the compound **4** is also presented.



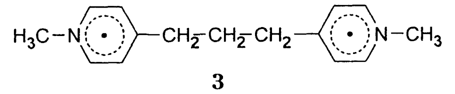
1



2a



2b



3

Reduction of 4,4'-(1,3-propanediyl)bis(*N*-methylpyridinium) dibromide (**5**) with sodium amalgam was carried out as follows. Using standard vacuum line techniques, **5** (30 mg) and 2.8% sodium amalgam (192 mg) in degassed CH_3CN were stirred at 0 ℃ for 10 h. After the amalgam changed into a liquid state, the solvent was removed and the residue was extracted with 2-methyltetrahydrofuran (MTHF), and then the solvent was replaced by CH_3CN or CD_3CN in vacuo for spectral measurements. All operations were performed under vacuum without isolation of the product.

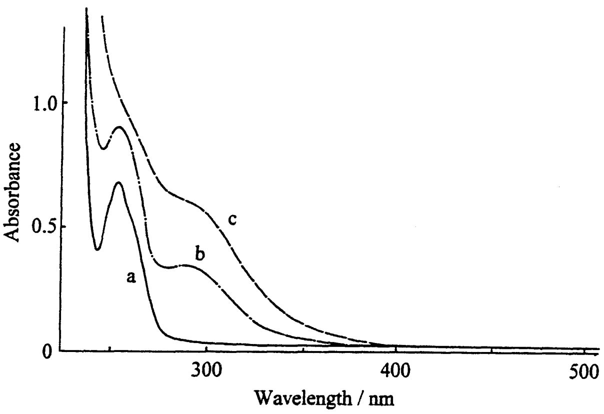


Figure 1. Absorption spectral change during the course of reduction of **5**(8.24×10^{-3} mmol) with 2.8% sodium amalgam in CH_3CN(7 ml) at 0 ℃ : (a) before reduction, (b) after 30 min, and (c) after 10 h.

Figure 1 shows the absorption spectral change during the course of reduction, where the spectrum (a) corresponds to that of **5**. After about 30 min reduction, the spectrum changed into (b) with the longest wavelength absorption band at about 290 nm. After about 10 h reduction, the spectrum changed into (c) with a broad band. No spectral change was observed upon further reduction. It is noteworthy that no ESR signal was observed at all during the reduction process. It should be noted in this connection that during electrolytic reduction of **5** in CH_3CN, using tetrabutylammonium perchlorate as supporting electrolyte, no ESR signal due to the intermediate cation radical from **5** was observed. This suggests that **5** undergoes a relatively fast two-electron reduction. In this reaction, a diamagnetic product was obtained in almost quantitative yield. The product is expected to have a highly symmetrical structure, since the ^{1}H NMR spectrum shown in Figure 2 is very simple. The NMR spectral pattern of six-memberd ring protons was very similar to that of 4,4'-bis(1,4-dihydro-1,4-dimethylpyridine),[5] the covalently bonded dimer of 1,4-dimethylpyridinyl radical. Analyses of ^1H NMR and ^{13}C NMR spectra[6] suggest that two dihydropyridine rings are magnetically equivalent with each other and, hence, the molecular structure should belong to the point group C_{2v}. The assignment of the product was also supported from the mass spectrum, which showed peaks at m/z = 120, 213, and 228 (M^+). Consequently, the reduction product is identified as the dispiro compound **4**.

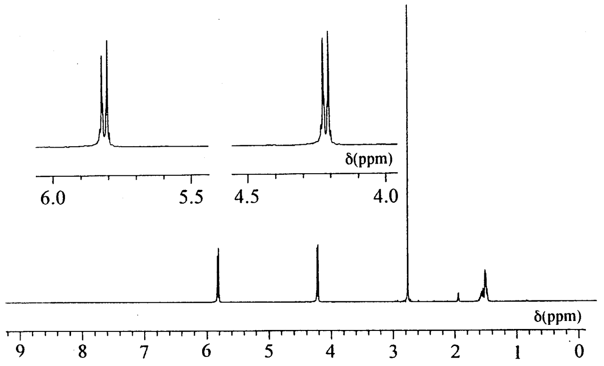
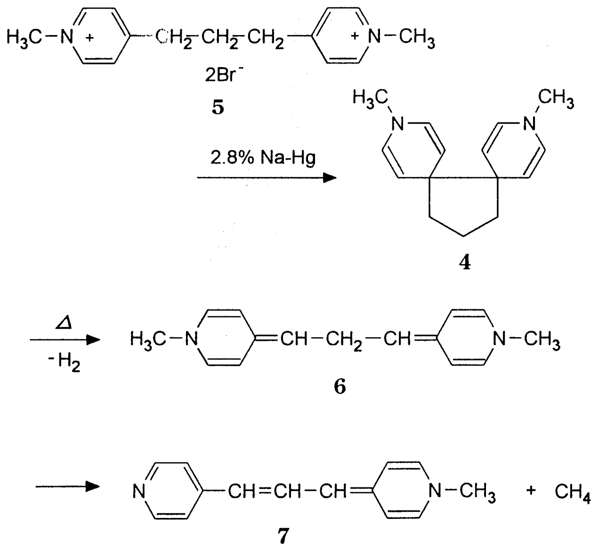


Figure 2. 400 MHz ^1H NMR spectrum of **4** in CD_3CN.

Since **4** is unstable in the presence of oxygen, the chemical properties were studied under degassed conditions. Compound **4** exhibits no such response to light as cyclomers **2a** and **2b** do.[2] That is, no ESR signal due to the triplet transition of a two-spin system was observed by irradiation of light longer than 290 nm on **4** in MTHF glass at -196 ℃. Further, no NMR spectral change was observed by warming **4** in CD_3CN up to 100 ℃ for a long time. In contrast, the thermal decomposition of **4** takes place at high temperatures above 200 ℃. When the solution of **4** was heated up to 220 ℃ for 30 min, the ^1H NMR signals characteristic of **4** disappeared and new complex signals attributable to two main products appeared over the wide range of chemical shifts(δ 2.5-8.4). At the same time, the solution changed from colorless to reddish brown. A careful examination of the signals arising from the mixture of products including the 2D measurement shows that the structure of major product can be assigned to 1,3-bis(*N*-methyl-1,4-dihydropyridinylidene)propane (**6**), because the signal pattern of ring protons resembles well that of 1,2-bis(*N*-methyl-1,4-pyridyl)ethylene.[7] Further, an inspection of the NMR signals reveals the presence of aromatic[8] and olefinic protons, indicating that the structure of minor product can be assigned to 4-[3-(*N*-methyl-1,4-dihydropyridinylidene)propenyl]pyridine (**7**). Moreover, when **4** was heated to 220 ℃ in the probe of a mass spectrometer, the spectrum showed distinct peaks at m/z=211 and 226 (M^+). This gives further support for the thermal decomposition of **4** to **6**.

The formation of **6** and **7** from **4** may be rationalized as follows. If the diradical **3** is the intermediate in this reaction, disproportionated products should be produced in high yields by intramolecular hydrogen transfer. However, the observed result shows the formation of **6** as the main product. Hence, the thermal decomposition may be considered to proceed by a concerted mechanism. Namely, the elimination of two hydrogen atoms from α-methylene carbons of the trimethylene chain takes place in concert with the opening of cyclopentane ring to afford **6**. The ring opening will be supported by a result of MNDO calculations, suggesting that **4** has an extremely long CC single bond of ca. 1.61 Å connecting two dihydropyridine rings.[9] Further, **6** is considered to be partially demethylated from one of N atoms with dehydrogenation from the central methylene carbon to give **7** and methane.



We are confident that the first preparation of **4** will open a new type of dispiro chemistry, since such a compound may exhibit peculiar behavior responsible for a through-bond interaction.[10] Further studies on **4** are now in progress, and details will be discussed elsewhere in near future.

References and Notes

1 Y. Ikegami, T. Muramatsu, and K. Hanaya, *J. Am. Chem. Soc.*, **111**, 5782 (1989).
2 T. Muramatsu, Y. Ikegami, K. Hanaya, and S. Onodera, *Bull. Chem. Soc. Jpn.*, **63**, 1413 (1990).
3 T. Muramatsu, A. Toyota, and Y. Ikegami, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1481.
4 H. Dürr and R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, **17**, 559 (1978) and references cited therein.
5 4,4'-Bis(1,4-dihydro-1,4-dimethylpyridine); ^1H NMR (CD_3CN) δ 0.99(6H, s), 2.79(6H, s), 4.23(4H, d, J=8.3 Hz), 5.80(4H, d, J= 8.3 Hz).
6 4; ^1H NMR(CD_3CN) δ 1.4-1.5(4H,m), 1.5-1.6(2H,m), 2.75(6H,s), 4.21(4H, d, J=8.3 Hz), 5.81(4H, d, J=8.3 Hz); ^{13}C NMR(CD_3CN) δ 8.21(CH_2), 39.85(CH_3), 42.63(CH_2), 50.75(C), 103.47(CH), 130.42(CH).
7 T. Muramatsu, A. Toyota, and Y. Ikegami, *J. Org. Chem.*, **60**, 4925 (1995).
8 Proton signal at δ 8.42 ppm was assigned to H2 and H6, and the signal at δ 7.19 ppm to H3 and H5 of pyridine ring of 7.
9 A. Toyota, T. Muramatsu, and Y. Ikegami, *J. Mol. Struct. (Theochem)*, **310**, 239 (1994).
10 R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, **13**, 696 (1974).