A New Photochemical Approach to Benzylic Polyradicals through C-N Bond Cleavage of a Pyridinyl Radical[1]

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Abstract: A new photochemical method for the generation of benzylic poly-radicals was developed using Ikegami's C-N bond cleavage reaction of a pyridinyl radical. The generation of m-xylylene and 1,8-naphthoquinodimethane was exemplified. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Methodological development for the generation of multi-radical centers at desired positions in organic compounds opens up new chemistry. Hitherto, matrix photolysis with extrusion of small molecules has enabled the generation of several unstable high-spin species. However, this method requires the preparation of the precursor such as azo- and diazocompounds.[2] We have been interested in σ-bond cleavage reactions at low temperature. In general, the cleavage of a σ-bond produces two radical centers and the detection of the desired radical may be obstructed by the presence of the concomitantly produced radical partner. However, the homolysis of the σ-bond β to the radical-center may produce a single radical-center and the spin-paired species. In 1979, Ikegami and co-workers reported an interesting photochemical reaction of pyridinyl radicals (eq 1).[1] We report an application of this reaction to high-spin species.

$$PhCH_2-N\langle\bigcirc\rangle-CO_2Me \xrightarrow[\text{77 K in MTHF}]{h\nu} PhCH_2\cdot \ + \ N\langle\bigcirc\rangle-CO_2Me \tag{1}$$
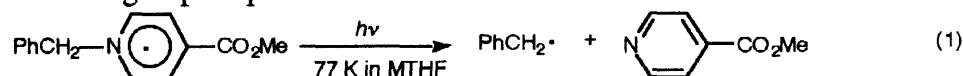
2. Results and Discussion

To demonstrate the applicability of this reaction to high-spin species, two diradicals, m-xylylene (**1a**) and 1,8-naphthoquinodimethane (**1b**) were selected. These diradicals have been well characterized by ESR spectroscopy and their zero field splitting (zfc) parameters are considerably different: $|D/hc| = 0.011$ cm^{-1}, $|E/hc| \le 0.001$ cm^{-1} for **1a** [2], $|D/hc| = 0.024 \pm 0.002$ cm^{-1}, $|E/hc| = 0.001$ cm^{-1} for **1b** [3].

Scheme 1 outlines the strategy of the generation of the diradicals **1a,b**. The pyridinium salts **2a²⁺** (X = I by anion exchange using NaI), **2b²⁺** (X = Br) were prepared in 60% and 80% yields by the reaction of **3a** or **3b** with 4-carboalkoxypyridine, respectively.[3] The reduction of these dications was achieved by shaking their acetonitrile solution with 3% Na-Hg alloy under the degassed conditions at room temperature, leading to the diradicals **2a,b**. The reduction was stopped when the dication absorption was totally replaced by the diradical absorption [λmax = 389 nm for **1a**, 387 nm for **1b**].[4]

ESR spectrum of **2a** (in MTHF after replacing the solvent) before irradiation at 10K [Figure 1 (a) for **2a**] shows a strong central signal which has no splitting. Irradiation of **2a** in ESR probe with a 500 W Xenon lamp (> 400 nm) gave new absorptions besides the central signal. The new absorption signals are assignable to a randomly oriented triplet pattern [Figure 1 (b)]. The zfc parameters ($|D/hc| = 0.010$ cm⁻¹ and $|E/hc| \approx 0.00$ cm⁻¹) are close to the reported values for **1a**. Similar irradiation of **2b** afforded a wider spectrum [Figure 1(c)] with zfs parameters ($|D/hc| = 0.021$ cm⁻¹, $|E/hc| = 0.001$ cm⁻¹) which accord with the reported values of **1b** within experimental error. These results establish the applicability of this method to various benzylic high-spin species. Such experiments are in progress.
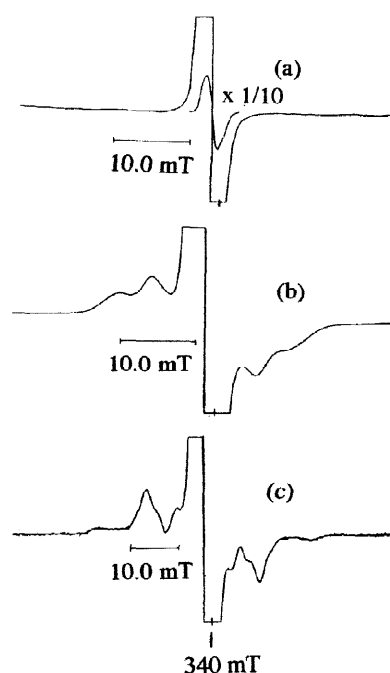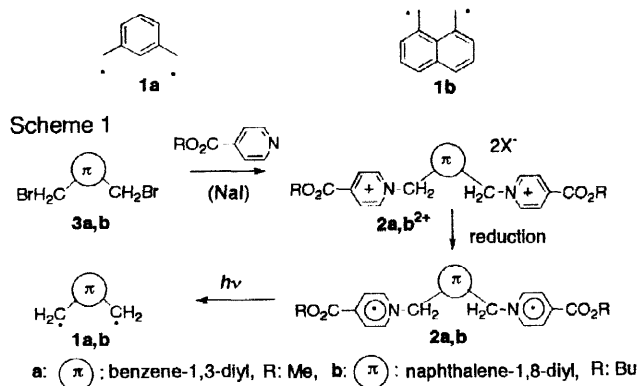

Figure 1. ESR spectra before and after irradiation of **2a** and **2b** at 10 K in MTHF; a: before irradiation of **2a**, b:after irradiation (1 h) of **2a**, c:after irradiation (30 min) of **2b**.

Scheme 1

a: $\widehat{\pi}$: benzene-1,3-diyl, R: Me, b: $\widehat{\pi}$: naphthalene-1,8-diyl, R: Bu

References

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Footnotes

1. This work was supported by a grant (No. 10146101) from the Minstry of Education, Science and Culture, Japan.

2. An alternative photochemical method utilizing benzylic halide and tetrakis(dimethylamino)ethylene has been reported by Platz et al. [4], although the generality of this method has not been reported.

3. Spectral and physical data of **1a²⁺** and **1b²⁺**; **1a²⁺**: mp 163 °C, MS (FAB) m/z 378 ([M-2I]⁺), ¹H NMR (300 MHz, CD₃CN) δ 4.00 (s, 6H), 5.98 (s, 4H), 7.55 (t-like, J = 6.8 Hz , 1H), 7.64 (d-like, J = 6.8 Hz, 2H), 7.99 (s, 1H), 8.45 (d, J = 6.5 Hz, 4H), 9.29 (d, J = 6.5 Hz, 4H), **1b²⁺**: mp 103 °C, MS (FAB) m/z 591 (M-Br)⁺, ¹H NMR (400 MHz, CDCl₃) δ 1.01 (t, J = 7.4 Hz, 6H), 1.44-1.52 (m, 4H), 1.75-1.85 (m, 4H), 4.50 (t, J = 6.6 Hz, 4H), 6.39 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.88 (s, 4H), 7.90 (d, J = 7.8 Hz, 2H), 8.58 (d, J = 6.6 Hz, 4H), 9.82 (d, J = 6.6 Hz, 4H).

4. The diradical absorption were similar to the 1-benzyl-4-carbomethoxypyridinyl monoradical (393 nm) [1] as expected.