4,4'-(Trimethylene)bis(2,6-di-*t*-butylphenoxy) Diradical: An Application of the Sequential Redox-Solid State Photolysis (SRSSP) Method

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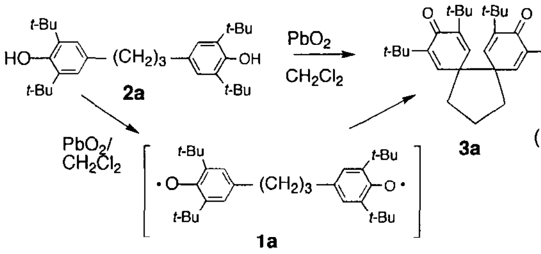
The oxidation of 4,4'-(trimethylene)bis(2,6-di-*t*-butylphenol) with lead dioxide underwent intramolecular cyclization at the 4,4'-positions to give a dispiro-compound. Irradiation of the dispiro-compound in a methylcyclohexane matrix at -150 °C produced 4,4'-(trimethylene)bis(2,6-di-*t*-butylphenoxy) diradical which has a stable triplet state.

Organic high-spin molecules have recently attracted intense attention in relation to material science as well as basic understanding of spin alignment.[1] Along with the photochemical extrusion reactions of small molecules such as nitrogen or carbon monoxide in rigid matrices,[2] oxidation and reduction of organic compounds in solution are a useful method to generate high-spin (ion) radical species. However, the generated radicals in solution sometimes dimerize and the detection of the high-spin states is unsuccessful. When the radicals are in equilibrium with the dimer, the detection of the high-spin states may be achieved by the shock-freezing method which freezes the solution equilibrium by rapid cooling. We have recently demonstrated an efficient method to generate the high-spin state by solid-state photolysis of the spin-paired dimers which are obtained by redox reactions.[3] We call this method the "sequential redox-solid state photolysis (SRSSP) method". Here, we apply this method to the generation of the titled diradical.

Hitherto, considerable studies have been accumulated on 2,6-di-*t*-butyl-4-substituted phenoxy radicals as building blocks of high-spin species.[4] These radicals have moderate stability in solution at room temperature. The titled diradical **1a** may be accessible by the oxidation of the bisphenol **2a**. However, the oxidation of **2a** with a large excess of PbO_2 in methylene chloride at room temperature gave a diamagnetic dispiro-compound, dispiro[2,6-di-*t*-butyl-2,5-cyclohexadienone)-4,1'-cyclopentane-2',4"-(2",6"-di-*t*-butyl-2",5"-cyclohexadienone)] (**3a**) in 89% yield as the sole product (eq 1).[5] The spiro-compound **3a** was stable in solution or in the solid state at room temperature and there was no indication of the bond cleavage by heating (up to ca 80 °C in benzene) or photolysis in solution in an ESR probe. Figure 1 shows an ORTEP drawing of **3a**.[6] Interestingly, the carbon (C_1)-carbon (C_2) bond is rather longer (1.62 Å) when compared with a standard C-C bond length (1.54 Å) or the other C-C bond length (1.52-1.56 Å) in the cyclopentane ring. The stability towards photolysis in solution may be due to the fast and reversible bond formation of the generated diradical **1a**.



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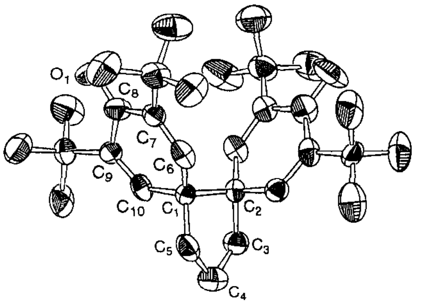


Figure 1. ORTEP view of **3a** showing 50% thermal ellipsoids: Selected bond length (Å); C_1-C_2 = 1.62, C_2-C_3 = 1.56, C_3-C_4 = 1.52, C_4-C_5 = 1.55, C_1-C_5 = 1.52, C_1-C_6 = 1.51, C_6-C_7 = 1.31, C_7-C_8 = 1.49, C_8-C_9 = 1.50, C_9-C_{10} = 1.28, C_1-C_{10} = 1.55, C_8-O_1 = 1.20.

The photolytic bond cleavage in a suitable solid media may allow the detection of **1a**. We have used methylcyclohexane as a matrix and the photolysis was carried out at -150 °C. The photolysis temperature is a little lower than the melting point (-126 °C) of methylcyclohexane. The bond cleavage would produce a triplet radical pair in equilibrium with a singlet state. The triplet diradical, if generated in such a soft matrix, undergoes geometrical relaxation leading to a local energy minimum state. Furthermore, the intramolecular dimerization of the diradical would be slow in such a relaxed state. Figure 2 shows the ESR spectrum after the photolysis (> 310 nm from 500-W Xenon lamp). After 20 s irradiation, a weak and wide spectrum was observed. Prolonged irradiation (3 min) increased the intensity.[7] The intensity did not appreciably increase by further irradiation. Importantly, similar photolysis at 77 K in the same matrix gives very slow conversion and almost no ESR in the same irradiation time. The observed ESR spectrum is interpreted by a randomly oriented triplet pattern ($D \approx 9.9$ mT, $E \approx 0.0$ mT) with overlapping hyperfine structures, indicating that the observed species have a rather fixed conformation. The above assignment is supported by the observation of $\Delta m_s = \pm 2$ signals in the half-magnetic field region at lower temperature. The relative large D-value indicates that the averaged distance between two radical centers is about 6.5 Å by the point dipole approximation. The calculated distance is considerably short, if one assumes that **1a** has a zigzag conformation (**A**) in which the distance between the oxygen atoms is almost 12 Å. Conformational analysis for the bisphenol starting from the spiro **3a** like geometry gave a conformer **B** without extra energy barrier in the conformational change. The conformer **B** has a reasonable distance (6 Å) between the two oxygen atoms and may be compatible with the observed D-value.

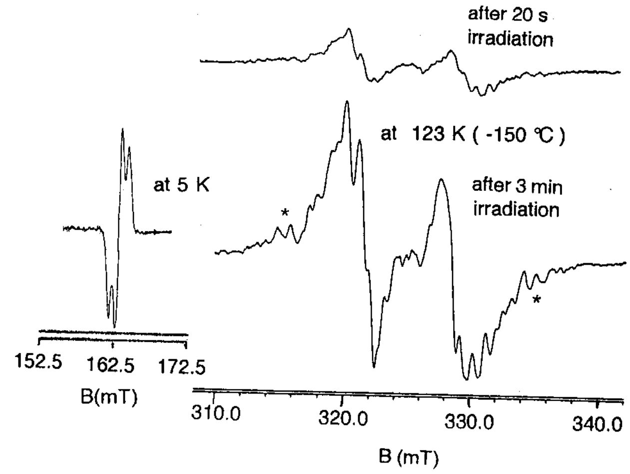
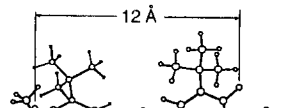
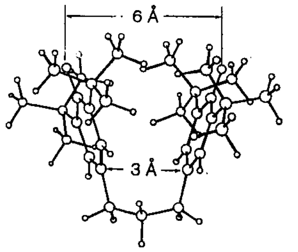


Figure 2. ESR spectra of **1a** obtained by irradiation of **3a** in methylcyclohexane matrix; top: after 20 s at 123 K (-150 °C); bottom right: after 3 min at 123 K (-150 °C); the triplet lines of the axis components are marked by asterisks, bottom left: $\Delta m_s = \pm 2$ signal measured at 5 K.



A



B

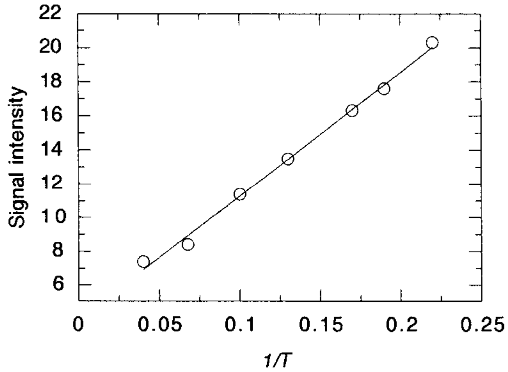
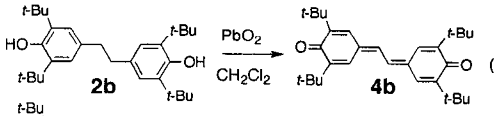


Figure 3. Temperature dependence of the signal intensity for $\Delta m_s = \pm 2$ transition of **1a**.

Figure 3 shows the Curie plots for the $\Delta m_s = \pm 2$ signals. The signal intensity linearly increases as temperature decreases, indicating a triplet ground state or a singlet ground state which degenerates with a triplet state.

The oxidation of the related bisphenol **2b** was also examined. When **2b** was similarly treated with PbO_2, the solution color turned to orange. The spiro-compound was not obtained, but the known dehydrogenated conjugated quinone methide **4b**[8] was produced in 44% yield (eq 2). In order to suppress such a dehydrogenation pathway, the methyl substituted **2c** was prepared and oxidized. However, in this case, the C-C bond cleavage occurred to give quinone methide **4c**[8] in 95% yield (eq 3).



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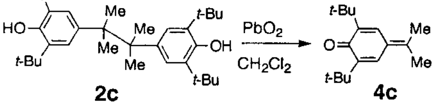

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References and Notes

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5 Spectral and physical data of **3**: pale yellow prisms, mp 153 °C; MS (FAB) *m/z* 451 (MH^+); UV (cyclohexane) λmax (log e) 239 nm (3.43), 261 nm (3.31); ^1H NMR (270 MHz, $CDCl_3$) δ 1.17 (s, 36H), 2.09 (t, $J = 7.4$ Hz, 4H), 2.31 (m, 2H), 6.43 (s, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 22.6, 29.5, 34.8, 36.1, 57.0, 141.6, 148.0, 186.2

6 Crystal data for **3**: $C_{31}H_{46}O_2$, monoclinic, space group $P2_1/n$ (No 14), $a = 9.03(9)$, $b = 12.13(8)$, $c = 26.40(7)$ Å, $\beta = 93.2(5)°$, $V = 2887.(32)$ Å^3, Z = 4, $Dc = 1.037$ g cm^{-3}; Mo-Kα radiation [λ(Kα) = 0.71069 Å]; $3° < 2\theta < 55°$; 6906 unique reflections, of which 2078 were treated as observed [$F_o^2 > 3\sigma(F_o^2)$]; $R = 0.086$, $R_w = 0.097$.

7 The conversion to the diradical **1a** was roughly estimated to be ca. 1% ([**3a**] = 1.5 x 10^4 mol dm^{-3}) by the comparison of the signal integration of **1a** using DPPH as a standard.

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