Tetrahedron Letters, Vol.22, No.20, pp 1903 - 1904, 1981
Printed in Great Britain

0040-4039/81/201903-02$02.00/0

ESR STUDIES OF A NEW PHENOXYL-NITROXIDE HETERO BIRADICAL

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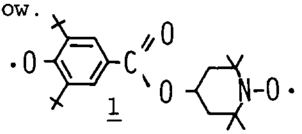
A new phenoxyl-nitroxide hetero biradical was prepared, and the nitrogen hyperfine splitting and g_{iso}-value of the biradical in toluene have been determined from its solution ESR spectrum.

In recent years, many stable phenoxyl[1)] or nitroxide[2)] biradicals have been reported. The existence of the triplet state in the biradicals has been confirmed by ESR measurements in rigid media at 77 K. Zero-field splitting parameters and hyperfine splitting constants of the biradicals have been determined from their frozen and fluid solution ESR spectra, respectively. On the basis of these data, the conformation and electronic structure of the biradicals have been discussed. However, the hetero biradical, which has two kinds of different radical groups in a molecule, has not been reported, as far as we know.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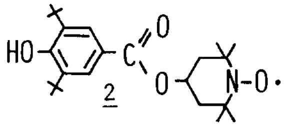
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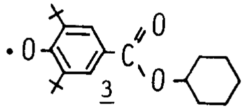
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In the present work, we have succeeded in the preparation of the hetero biradical (1) by oxidizing the phenol-nitroxide precursor (2) of the biradical with PbO_2 in toluene.

3,5-Di-t-butyl-4-hydroxybenzoic acid (5) and 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (6) are commercially available. 5 was condensed with 6 via the acid chloride[3)] of 5 to yield the nitroxide monoradical (2).[4)] The crude product was recrystallized first from methanol, and then from n-hexane. Mp 174~176°C. The phenol precursor (4) of the phenoxyl monoradical (3) was similarly prepared by condensation of 5 with cyclohexanol. The crude product was recrystallized first from ethanol, and then from n-hexane. Mp 121~123°C.

When the phenol precursor (4) of the phenoxyl monoradical (3) was oxidized with PbO_2 in toluene under vacuum, the color of the phenol solution immediately became green. The ESR spectrum of this solution showed three line hyperfine splittings due to the equivalent two meta-ring protons in the phenoxyl ring (a^H= 2.1 G and g_{iso}(3)=2.0047), as shown in Fig. 1(c). The nitroxide monoradical precursor (2) of the hetero biradical (1) shows a three-line hyperfine pattern (a^N=15.2 G, g_{iso}(2)=2.0060) in toluene, as shown in Fig. 1(b). By oxidizing 2

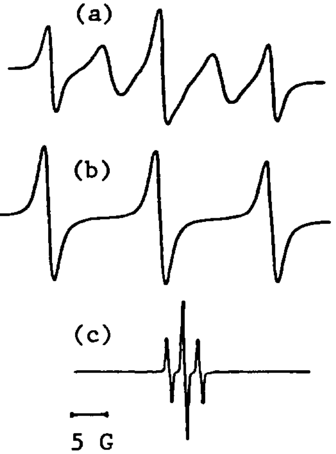

Fig. 1. ESR spectra of (a) 1, (b) 2 and (c) 3 in toluene at 20°C.

with PbO_2, the orange color of the solution changed to green, a broad three-line absorption being superposed on the hyperfine spectrum of the monoradical. The broad absorption is thought to be attributable to the hetero biradical. As this biradical is not so stable, ESR measurements were performed on several samples, under slightly different conditions of oxidation, in order to obtain a better ESR spectrum. The best spectrum obtained is shown in Fig. 1(a). However, the spectrum indicates that a considerable amount of the parent nitroxide monoradical still remains in the solution. The ESR spectrum of the hetero biradical (1) shows three lines from coupling of the electron spins to a nitrogen nucleus. The hyperfine splitting (a^N=7.6 G) which is observed is one half of the splitting (a^N=15.2 G) which is observed from nitrogen in the parent nitroxide monoradical (2), indicating a strong exchange interaction (J) between two spins in a molecule. Splittings from the two meta-ring protons in the phenoxyl radical part were not resolved in the spectrum of the biradical. The coupling should be one half the value of the hydrogen coupling constant (a^H=2.1 G) of the parent phenoxyl radical and are probably not resolved because of line broadening by the incompletely averaged electron-electron dipolar interaction. The g value ($g_{iso}(1)=2.0053$) of the biradical is shifted to an averaged position between that ($g_{iso}(2)=2.0060$) of the starting nitroxide and that ($g_{iso}(3)=2.0047$) of the phenoxyl. The observed nitrogen hyperfine splitting and g value of the biradical correspond to what is predicted for a two-spin molecule in which J>>a and $\Delta g=g_{iso}(2)-g_{iso}(3)$.$^{5)}$

Usually, by freezing the solution containing the biradical into a rigid glass (77 K), one can observe dipolar splittings. However, because of the small dipolar interaction in the hetero biradical (1), we could not observe the zero-field splitting; only a broad absorption due to 1 was superposed on the anisotropic three-line hyperfine pattern of the nitroxide monoradical (2). On the other hand, the weak $\Delta m=\pm 2$ transition spectrum was observed at 1650 G, indicating the existence of the triplet state in the hetero biradical.

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(Received in Japan 27 January 1981)