

Preparation of the α -[D]Galvinoxyl Radical

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Summary

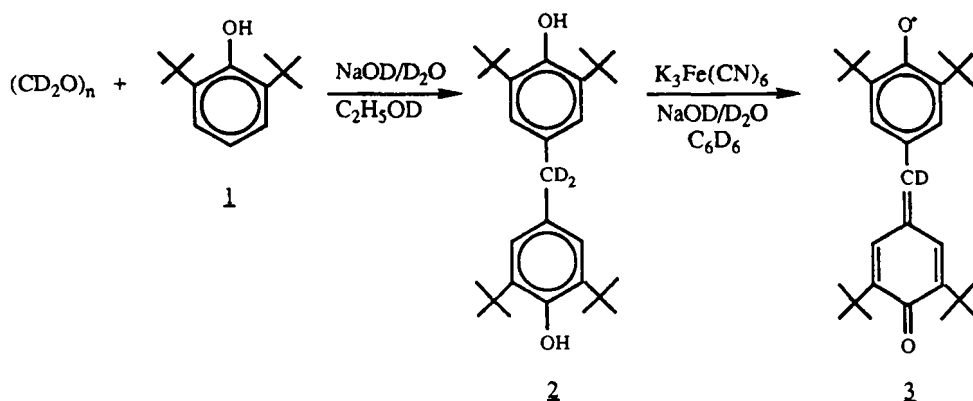
The stable galvinoxyl radical has been prepared with specific deuterium substitution at the methylene carbon bridge between the two aromatic rings. The corresponding EPR spectrum illustrates only the small residual hyperfine coupling with the aromatic ring hydrogens.

Key words: Deuterium labelled radicals, galvinoxyl, and EPR

Introduction

It is often desirable to utilize deuterium labelled radicals to simplify EPR spectra. It is also advantageous in dynamic nuclear polarization (DNP) studies to have radical samples with a single sharp EPR transition which can be readily saturated.¹⁻³ Bates has also demonstrated that solutions at low radical concentration exhibit reduced electron-electron interactions and the corresponding DNP enhancements can be significantly lower in solution studies of nitroxide radicals.⁴ For the case of nitroxide radicals, the nitrogen hyperfine triplet ($^{14}\text{N}=1$) structure is not easily saturated and represents a formidable problem in DNP studies³ at low radical concentration. The galvinoxyl radical (Coppinger's radical⁵) has long been recognized as a stable organic radical which has been utilized in a number of DNP studies. However, the galvinoxyl radical exhibits a relatively large hydrogen hyperfine coupling ($\alpha_{\text{H}}=5.1$ G) for the methylene hydrogen.⁶ Thus the availability of α -[D]galvinoxyl radical **3** should provide a single resolved EPR transition for the concentration range of 10^{-1} - 10^{-3} M which is a typical range for solution DNP studies.³

The synthetic strategy is analogous to Kharasch's procedure⁷⁻⁸ except that appropriate deuterated reagents and solvents were employed.



The isolated intermediate 4,4'-[D₂] methylenebis(2,6-di-tert-butylphenol) **2** was characterized by ¹H NMR with the methylene signal for the deuterated analog clearly absent. This intermediate was subsequently oxidized using K₃Fe(CN)₆ to the desired α-[D]-3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenylmethane (α-[D]galvinoxyl) **3**. The EPR spectrum for α-[D]galvinoxyl (in comparison with the unlabelled galvinoxyl radical) at a low radical concentration (~10⁻⁴M), clearly exhibits the reduced hyperfine coupling to the methylene deuterium with only the quintet structure due to coupling to the four aromatic hydrogens observed (Fig. 1 and 2). At higher radical concentrations (5 × 10⁻² M), the labelled α-[D]galvinoxyl sample exhibits a sharp single transition (dotted line Fig. 3). Although significant electron-electron exchange is present, the doublet structure for the unlabelled galvinoxyl radical is also still apparent at this concentration (continuous line Fig. 3).

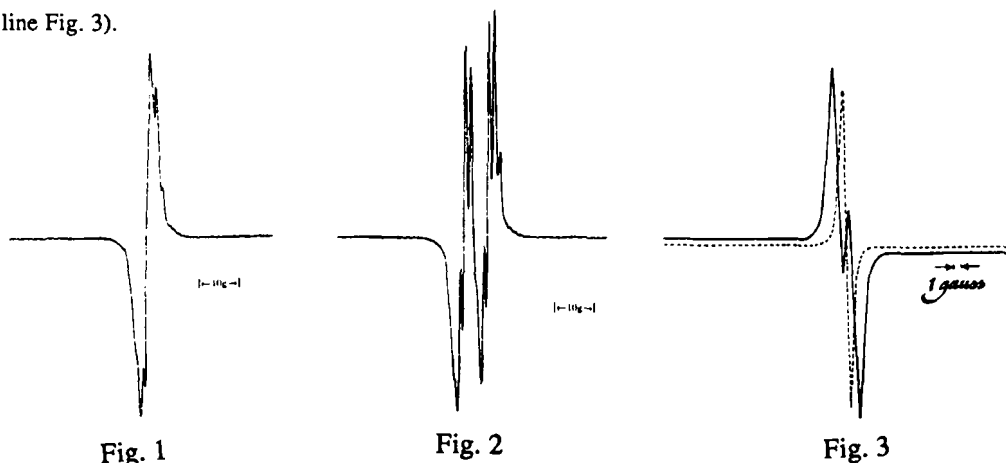


Figure Captions

1. 9.3 GHz EPR, 10⁻⁴M α-[D]galvinoxyl radical in benzene.
2. 9.3 GHz EPR, 10⁻⁴M galvinoxyl radical (unlabelled) in benzene.
3. 9.3 GHz EPR, 5 × 10⁻²M in benzene α-[D]galvinoxyl radical (dotted line) and galvinoxyl radical.

Experimental

1-[D]Ethanol. Tetraethylorthosilicate (104.2 g, 0.5 mol) and D₂O (40 g, 2 mol) were added to a 250 mL, 1-necked, round bottomed flask with a magnetic stirring bar. The flask was stoppered and stirred at room temperature for 24 hours. The resulting white mixture was vacuum distilled @ 5 mm Hg. The receiving flask was cooled with a dry ice/acetone bath and 75 mL of the product was collected.

4,4'-[D₂] Methylenebis(2,6-di-tert-butylphenol) 2. D₂-Paraformaldehyde (1.0 g) (Merck, Sharp, and Dohme), 2,6-di-tert-butylphenol (3.22 g, 0.156 mol) and 30 mL of 1-[D]ethanol were added to a 100 mL, 3 necked, round bottomed flask under an atmosphere of N₂. The flask was equipped with a water cooled condenser and an additional funnel. The reaction mixture was heated and 4 mL of 40% NaOD/D₂O was added dropwise. After the addition was complete, the reaction was heated at reflux for 10 hours. The purple mixture was filtered and the solids collected were washed twice with 5 mL of D₁-ethanol. The yellow solid weighed 2.0 g and was used without further purification. The compound afforded the following spectroscopic data. ¹H NMR (CDCl₃) δ 1.39 (s, 36 H), 5.02 (s, broad, 2 H), 7.00 (s, 4 H).

α -[D] Galvinoxyl radical 3. A mixture of K₃Fe(CN)₆ (3.09 g), NaOD/D₂O (2 mL), D₂O (10 mL) and D₆-benzene (62 mL) were combined in a 250 mL, 2 necked, round bottomed flask fitted with an addition funnel and a water cooled condenser under an atmosphere of N₂. A solution of **2** (1.09 g, 0.0026 mol) in 15 mL of D₆-benzene was added over a period of 30 minutes. During the addition, the mixture changed from a yellow to reddish brown color. The solution was stirred for 1 hour. The water layer was separated from the organic layer. The organic layer was successively washed with water until the water layer was colorless. The organic layer was dried over anhydrous MgSO₄ and the solvent removed *in vacuo*. The purple solid was recrystallized from 100% ethanol and provided 0.70 g of the product (64% yield). M.P. 155-156°C. EPR spectra are shown in Figures 1 and 2.

References

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