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New Persistent Radicals: Synthesis and Electronic Spin Structure of 2,5-Di-*tert*-butyl-6-Oxophenalenoxyl Derivatives

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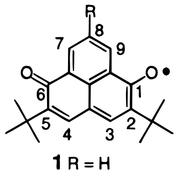
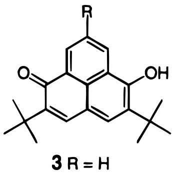
Neutral radicals such as galvinoxyl, α-nitronyl nitroxide, and verdazyl play most important roles as spin sources to prepare magnetically interesting organic materials.[1,2] In particular, it is well-known that galvinoxyl is a pilot open-shell molecule in the field of organic molecule-based magnetism. The π-spin delocalized nature of galvinoxyl contrasts with other heteroatomic radicals such as α-nitronyl nitroxide. Novel stable open-shell molecular systems not only give a testing ground for various theoretical models, but also they are materials challenges as building blocks for spin-mediated new molecular functionality.[1,3] To expand the variety of such spin sources, we have designed 3- and 6-oxophenalenoxyl radicals as new neutral radicals, which possess electronic characteristics similar to those of galvinoxyl. Although we succeeded in the generation and detection, the isolation of these radicals was unsuccessful.[4] A general strategy to isolate reactive and open-shell chemical species is the introduction of *tert*-butyl groups on appropriate positions.[5] In this contribution, we report on the synthesis and characterization of the new stable neutral radicals, 2,5-di-*tert*-butyl-6-oxophenalenoxyl derivatives **1** and **2** as studied by ESR and electron−nuclear multiple resonance (ENDOR/TRIPLE) spectroscopy.



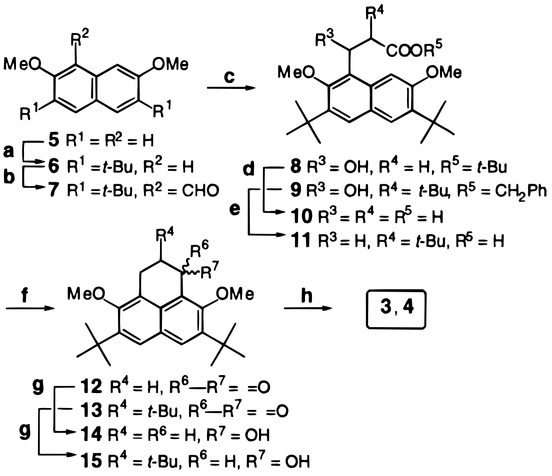
1 R = H
2 R = *t*-Bu



3 R = H
4 R = *t*-Bu

The radical precursors, 2,5-di-*tert*-butyl-6-hydroxyphenalenone derivatives **3** and **4**, were efficiently synthesized from commercially available 2,7-dimethoxynaphthalene (**5**) in nine steps (Scheme 1).[6] Although the *tert*-butylation of **5** by the conventional method (*t*-BuCl, $AlCl_3$) failed, the reaction of **5** with *t*-BuOH in CF_3COOH in the presence of concentrated H_2SO_4[7] successfully gave di-*tert*-butylated product **6** in quantitative yield, which was formylated by Vilsmeier−Haack reaction. Reaction of the aldehyde **7** with lithium enolates generated from *tert*-butyl acetate or benzyl *tert*-butylacetate with lithium diisopropylamide (LDA) gave the aldol products **8** or **9** as a mixture of diastereomers, respectively. These compounds were converted to carboxylic acid derivatives **10** and **11** by reductive removal of the hydroxyl group and de-esterification. Cyclization into the phenalanone skeletons was achieved by chlorination of **10** and **11** with $(COCl)_2$ followed by Friedel−Crafts cyclization. Reduction of **12** and **13** with $LiAlH_4$ gave the phenalanol derivatives **14** and **15**, respectively. Finally, the methyl ether-protecting groups were removed by LiI, and the resulting triol was treated with 2 M aqueous HCl, to give the desired 6-hydroxyphenalenone derivatives **3** and **4** as reddish orange powders, respectively.[8]

Scheme 1[a]



[a] Reagents: (a) cat. concd H_2SO_4, excess *t*-BuOH, CF_3COOH, 45 °C, 99%; (b) 10 equiv DMF−$POCl_3$, $(CH_2Cl)_2$, 90 °C, 99%; (c) 4.2−4.5 equiv LDA−$R^4CH_2COOR^5$, THF, 0 °C, 97% (for **8**), 86% (for **9**); (d) (i) 1.5 equiv Et_3SiH, 4.5 equiv CF_3COOH, CH_2Cl_2, rt; (ii) Pd/C, H_2, EtOH, rt; (iii) 9.5 equiv KOH, EtOH−H_2O, reflux, 82%; (e) (i) 1.5 equiv Et_3SiH, 4.5 equiv CF_3COOH, CH_2Cl_2, rt; (ii) Pd/C, H_2, EtOH, rt, 85%; (f) (i) excess $(COCl)_2$, reflux; (ii) 3.5 equiv $AlCl_3$, CH_2Cl_2, 82% (for **12**), 93% (for **13**); (g) 3.3 equiv $LiAlH_4$, THF, rt, 90% (for **14**), ∼100% (for **15**); (h) (i) 20 equiv LiI, HMPA, 170 °C; (ii) 2 M HCl aq, rt; (iii) reprecipitated from hexane−CH_2Cl_2, 40% (for **3**), 62% (for **4**).

The radicals **1** and **2** were obtained as brownish black powder or deep green-colored needles by treatment of the corresponding hydroxyl compounds **3** and **4** with a large excess of active PbO_2[9]

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(1) For recent overviews, see: Proceedings of the 5th International Conference on Molecule-Based Magnets, Osaka, Japan, 1996; Itoh, K., Miller, J. S., Takui, T., Eds.; Gordon and Breach: New York, 1997: *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 1−586; *Ibid.* **1997**, *306*, 1−520 and references therein.

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(6) All new compounds described here gave correct spectroscopic data.

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(8) Selected physical data: **3**, mp 235 °C; ^1H NMR ($CDCl_3$) δ 1.57−1.65 (br, 18), 6.26 (s, 1), 7.50−7.80 (m, 3), 8.35−8.65 (br, 2); EI-MS, *m/z* 308 (M^+, 14%); Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84; N, 0.00. Found: C, 81.43; H, 7.82; N, 0.00. **4**, mp 235 °C; ^1H NMR ($CDCl_3$) δ 1.44 (s, 9), 1.48 (s, 9), 1.57 (s, 9), 6.10 (s, 1), 7.58 (s, 1), 7.67 (s, 1), 8.40 (d, 1, $J = 1.7$ Hz), 8.76 (d, 1, $J = 1.7$ Hz); EI-MS, *m/z* 364 (M^+, 20%); Anal. Calcd for $C_{25}H_{32}O_2$: C, 82.37; H, 8.85; N, 0.00. Found: C, 82.32; H, 8.87; N, 0.00.

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10.1021/ja000298t CCC: $19.00

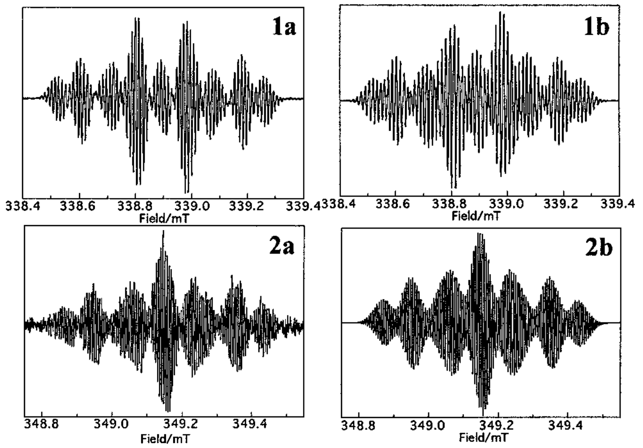

Figure 1. Hyperfine ESR spectra observed for **1** and **2** in toluene at 290 K; microwave frequency used was 9.5192840 for **1** and 9.7799000 for **2** GHz, respectively (a) and simulated one (b).

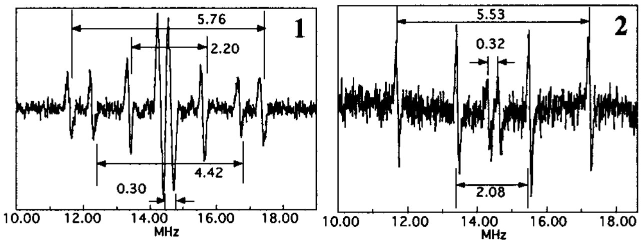

Figure 2. ^{1}H ENDOR spectra observed for **1** (at 290 K) and **2** (at 210 K) in toluene.

in benzene at room temperature in quantitative yields.[10] The two radicals in the crystal form are stable in the absence of air. Most of radical **1** decomposes for in a few weeks in air in the solid state. The radical **2** also decomposes slowly in air in the solid state, but most of the radical remains unchanged in the air for a few weeks. Both radicals are stable for a long period of time in degassed toluene but decompose in the presence of atmospheric oxygen.[11]

Figure 1 shows well-resolved hyperfine ESR spectra (a) observed for **1** and **2** in degassed toluene at 290 K, versus the simulated ones (b). The ESR measurements were carried out on a Bruker ESR 300/350 X-band spectrometer at 12.5 kHz field modulation in order to avoid line shape distortion due to sideband formation. The spectral simulations were made based on a set of isotropic hyperfine coupling constants (hfcc's) obtained by ^{1}H ENDOR/TRIPLE spectroscopies (see Figure 2). Relative signs of the hfcc's were determined by invoking ^{1}H electron−nuclear−nuclear TRIPLE resonance measurements.[12] All of the spin Hamiltonian parameters and proton assignments for **1** and **2** are summarized in Table 1. Theoretically calculated values for the hfcc's in Table 1 were made in terms of the McLachlan method.[13] Agreements between the experimental and theoretical values are satisfactory.

In Figure 3 are depicted SOMOs (a) for phenalenyl neutral radical (**A**)[5] and 3-oxophenalenoxyl radical (**C**) as well as nonsubstituted 6-oxophenalenoxyl radical (**B**) and the corresponding π-spin density distributions (b). The introduction of oxygen atoms at 6- or 3-position gives remarkable change in topological symmetry of π-electron network. This is due to the robust heteroatomic perturbation which is attributable to π-spin delocalization from the oxygen atom. The spin structure of 6-oxophenalenoxyl in (b) well agrees with the π-electron spin network in terms of the π-spin density distribution ρ obtained from the observed hfcc's ($A_{\alpha-H}$) and McConnell's relationship $A_{\alpha-H} = \rho Q$ ($Q < 0$).

Table 1. Proton hfcc's and *g*-Values for **1** and **2**[a]

	A_H/mT					
compd	3, 4	7, 9	8	2,5-*t*-Bu	8-*t*-Bu	*g*-value
1	+0.206 (+0.210)	+0.078 (+0.076)	−0.159 (−0.119)	+0.012		2.0046
2	+0.200 (+0.206)	+0.077 (+0.075)		+0.012	±0.006[b]	2.0049

[a] hfcc's were determined by ^{1}H ENDOR spectra in toluene at 290 or 210 K and simulation successfully reproducing the ESR hyperfine spectra. The relative signs of the hfcc's were determined in terms of ^{1}H TRIPLE spectroscopy. Values in parentheses were calculated by HMO-McLachlan method[13] using the following parameters: $\lambda = 1.2$, $Q = -2.6$ mT. [b] The sign was experimentally unknown.

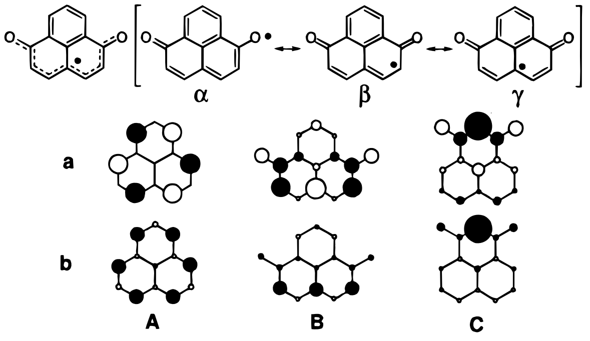

Figure 3. Canonical resonance structures for 6-oxophenalenoxyl radical in parentheses, SOMOs (a) of **A**,[5] **B**, and **C**, and the corresponding π-spin density distributions (b) calculated by HMO-McLachlan method.[13]

The effect of the spin delocalization can be understood in terms of classical canonical resonance structures as shown in Figure 3 (top), in which only representative ones with galvinoxyl features of spin structure are depicted. To validate the classical picture in a more quantitative fashion, we calculated contributing weights of any possible and desired resonance structures in terms of MO calculations.[14] We decomposed the MO-based Slater determinant corresponding to a ground-state electron configuration ($S = {}^1/_2$) into desired AO-based Slater determinants with the help of the Moffitt theorem,[15] giving contributing weights of any AO-based determinants which correspond to local spin structures, that is, resonance ones in terms of a VB picture. The representative resonance structures, α−γ in parentheses depicted in Figure 3 (top), give dominant contributing weights.

A remarkable change in topological symmetry of the π-electron network in oxophenalenoxyl radicals is established via heteroatomic perturbation such as the delocalization nature of the introduced oxygen atoms. In this context, new stable radicals under study possess electronic characteristics similar to those of galvinoxyl, which is a pilot open-shell molecule in organic magnetics and spin chemistry.

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Supporting Information Available: Experimental procedures and data for new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Selected physical data: **1**, mp 70−71 °C dec; TLC R_f 0.41 (5:1 hexane/ethyl acetate); Anal. Calcd for $C_{21}H_{23}O_2(H_2O)_{0.7}$: C, 78.81; H, 7.68; N, 0.00. Found: C, 78.64; H, 7.51; N, 0.00. **2**, mp 253−255 °C dec; TLC R_f 0.75 (5:1 hexane/ethyl acetate); Anal. Calcd for $C_{25}H_{31}O_2(H_2O)_{0.4}$: C, 81.00; H, 8.64; N, 0.00. Found: 81.13; H, 8.48; N, 0.00.

(11) TLC spectroscopy showed no spots from impurities after the radical is kept for many days in degassed toluene.

(12) ^{1}H TRIPLE spectroscopic results are shown in Supporting Information.

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