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## An Unusual Ring Closure Reaction with Formation of Pyrrolidin-2,5-dione Derivatives

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Mild oxidation of amidine (1) bearing two sterically crowded phenol moieties leads to the formation of the dispirocyclohexadienone derivative (6) of pyrrolidin-2,5-dione *N*-arylamine through an intramolecular ring closure recombination of the intermediate biradical (4).

Two stable phenoxyl radicals (2) and (3) were found to be formed (approximately 1:1) upon addition of an alkaline solution of equimolar amounts of  $K_3Fe(CN)_6$  or PbO<sub>2</sub> to an argon degassed benzene solution of amidine (1) (Scheme 1). This is confirmed by the e.s.r. spectrum of the reaction mixture, which shows the superposed spectra of both radicals, *i.e.*, (2) whose spectrum is simulated using hyperfine coupling constants  $a(2 H_m) 2.0$ , a(N) 3.3 G and (3)  $[a(2 H_m) 1.8 G]$ .<sup>+</sup> In the presence of excess K<sub>3</sub>Fe(CN)<sub>6</sub> a further oxidative process

<sup>+</sup> The e.s.r. spectra of (2) and (3) were assigned by comparison with the spectra of the reference phenoxyl radicals obtained by oneelectron oxidation of *N*-acetyl-N,N'-di-(p-methylphenyl)-4'-hydroxy-3',5'-di-t-butylbenzamidine and *N*-(4-hydroxy-3,5-di-t-butylbenzoyl)-N,N'-di-(p-methylphenyl)benzamidine, respectively.



occurs, manifested by the complete disappearance of e.s.r. signals after stirring the solution for 8 h at ambient temperature. After drying over  $CaCl_2$  and solvent removal, the dispirocyclohexadienone derivative (6) (95%) crystallized



Figure 1. ORTEP projection of (6). Ellipsoids are at 50% probability. Important distances (Å) and angles (°): N(1)–C(1) 1.410(3), N(1)–C(4) 1.381(3), C(1)–C(2) 1.545(3), C(2)–C(3) 1.596(3), C(3)–C(4) 1.527(3), C(1)–N(2) 1.242(3), N(2)–C(3) 1.432(3), C(4)–O(1) 1.215(3); C(1)–N(1)–C(4) 112.9(2), N(1)–C(1)–C(2) 106.7(2), C(1)–C(2)–C(3) 100.1(2), C(2)–C(3)–C(4) 101.4, N(1)–C(4)–C(3) 107.3(2), N(1)–C(1)–N(2) 120.8(2), N(2)–C(1)–C(2) 132.5(2), O(1)–C(4)–N(1) 125.8(2), O(1)–C(4)–C(3) 126.8(2). Pyrrolidine ring possesses a slightly twisted conformation with C(2) and C(3) atoms extending out of the N(1)–C(1)–C(4) plane at 0.27 and 0.32 Å, respectively. The planes of the 3- and 4-cyclohexadienone moieties intersect the N(1)–C(1)–C(4) plane at 99.1 and 86.1°, respectively.

out.<sup>‡</sup> The molecular structure of compound (6) was confirmed by X-ray crystal structure analysis (Figure 1).<sup>§</sup> The formation of the dispiro compound (6) may be explained by the mechanism proposed in Scheme 1. Biradical (4), the common product of one-electron oxidation of both radicals (2) and (3), undergoes conformational isomerization to (5) which brings the atomic centres rich in spin density into close proximity, favouring the intramolecular recombination to give (6). No similar reactions have previously been reported.<sup>2</sup>

An interesting structural peculiarity of compound (6) is a significant lengthening of the endocyclic C(2)-C(3) bond. Its length [1.596(3) Å] is appreciably larger than the C(2)-C(3) distances in the parent pyrrolidin-2,5-dione<sup>3</sup> and its simple

 $\pm$  Spectral data for (6): yellow crystals (from hexane), m.p. 231–232 °C. <sup>1</sup>H n.m.r. (CCl<sub>4</sub>)  $\delta$  0.93 (18H, s, Bu<sup>1</sup>), 1.10 (18H, s, Bu<sup>1</sup>), 2.14 (3H, s, CH<sub>3</sub>), 2.36 (3H, s, CH<sub>3</sub>), 6.25–7.40 (12H, m, aromatic and cyclohexadienone H); i.r.(nujol) v1780, 1680, 1660, 1640 cm<sup>-1</sup>. Compound (6) gave satisfactory elemental analysis.

§ Crystal data for (6): C<sub>44</sub>H<sub>54</sub>N<sub>2</sub>O<sub>3</sub>, monoclinic, space group P2<sub>1</sub>/c, a = 11.149(3), b = 10.111(7), c = 36.391(19) Å, β = 90.93(2)°, U = 4103(1) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.03 g cm<sup>-3</sup>. 3175 Independent observed reflections ( $F^2 \ge 4\sigma$ ) were measured on a CAD-4 automatic four-circle diffractometer (using Mo-K<sub>α</sub> radiation, ratio of scanning velocities N: θ = 1.2: 1, θ ≤ 24°). The structure was solved by direct methods using the MULTAN program. Anisotropic refinement for the non-hydrogen atoms and isotropic for the hydrogen atoms resulted in a final value of R = 0.054 (R<sub>w</sub> = 0.069). The SPD-PLUS series of programs<sup>1</sup> has been employed in all calculations. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1988.



Scheme 2. Reagents: i, LiAlH<sub>4</sub>, ether; ii, H<sup>+</sup>, H<sub>2</sub>O, PrOH.

derivatives, ranging from 1.505—1.537 Å.<sup>4,5</sup> This stretching of the C(2)–C(3) bond in (6) occurs owing to fairly favourable steric conditions for through-bond interaction between the two cyclohexadienone  $\pi$ -systems separated by three  $\sigma$ -bonds. In similar compounds the central  $\sigma$ -bond is much weakened by a  $\pi$ - $\sigma^*$  orbital interaction, which results in a 0.1—0.25 Å lengthening.<sup>6</sup> The resultant lability of the C(2)–C(3) bond reveals itself in a smooth reduction of (6) to (1) upon treatment with LiAlH<sub>4</sub> in ether. Acid hydrolysis of (6) in propanol proceeds equally smoothly giving rise to the symmetrical dispiro derivative (7)¶ of pyrrolidin-2,5-dione in quantitative yield (Scheme 2).

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¶ Compound (7): yellow crystals (from hexane), m.p. 176–177 °C. <sup>1</sup>H N.m.r. (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.17 (36H, s, Bu<sup>1</sup>), 2.40 (3H, s, CH<sub>3</sub>), 6.60 (4H, s, cyclohexadienone H), 7.27–7.50 (4H, m aromatic H); i.r. (nujol) 1740, 1670, 1650 cm<sup>-1</sup>. A satisfactory elemental analysis was obtained.