

## Synthesis and Induced Antiaromaticity of a Naphtho[9]annulenone

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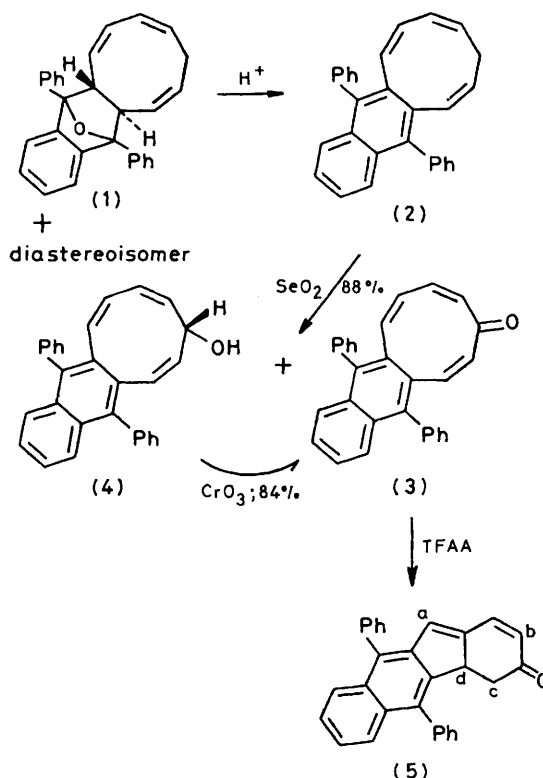
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**Summary** The synthesis and acid-induced rearrangement of the first monoannulated cyclononatetraenone (a naphtho[9]annulenone) are described.

WHILE singly annulated cyclononatetraenes<sup>1</sup> and their corresponding anions<sup>2</sup> have become available in recent years, their ketonic counterparts are so far unknown.† To examine such systems' potential antiaromaticity we have synthesized and studied the naphthannulated derivative (3).

The hydrocarbon precursor (2)‡ (white solid, m.p. 150–151 °C) was prepared in good yield (70%) by dehydration of the previously described cycloadduct(s) (1).<sup>3</sup> Exposure of (2) to SeO<sub>2</sub> in buffered dioxan at 80–90 °C produced a 25:75 mixture (by isolation) of the desired ketone (3) [white crystals, m.p. 240 °C (decomp.);  $\nu_{\text{CO}}$  (KBr) 1601 cm<sup>-1</sup>;  $\lambda_{\text{max}}$  (MeCN) 288 ( $\epsilon$  11,900) and 235 (51,300) nm; <sup>1</sup>H n.m.r. (80 MHz; C<sub>6</sub>D<sub>6</sub>)  $\tau$  2.3–3.0 (14H, m) 3.5–4.2 (5H, m), and 4.45 (1H, dd, *J* 12.0 and 3.0 Hz); § <sup>13</sup>C n.m.r. (20 MHz; CDCl<sub>3</sub>;  $\delta$  Me<sub>4</sub>Si) 195 (s, CO) and 139–126 p.p.m. (m); and the corresponding alcohol (4)‡ in 88% yield. The stability of (3) and its spectroscopic data (i.r., <sup>1</sup>H n.m.r.) show that it is neither antiaromatic nor is it associated with any paratropicity. This is not surprising since the skeleton's 9-membered ketonic unit is sufficiently large so as to resist planarization which would reduce the extent of  $\pi$ -delocalization.

In order to test further the ability of (3) to resist the development of antiaromatic character, we examined its response to a strong acidic medium, *i.e.*, one expected to force a destabilizing positive charge on to the  $\pi$  frame. Exposure of (3) to media of differing acid strength showed that trifluoroacetic acid (TFAA) effectively destabilizes the molecule's 9-membered unit.¶ Dissolution of (3) in TFAA at 0 °C causes immediate (<sup>1</sup>H n.m.r.) rearrangement



SCHEME 1

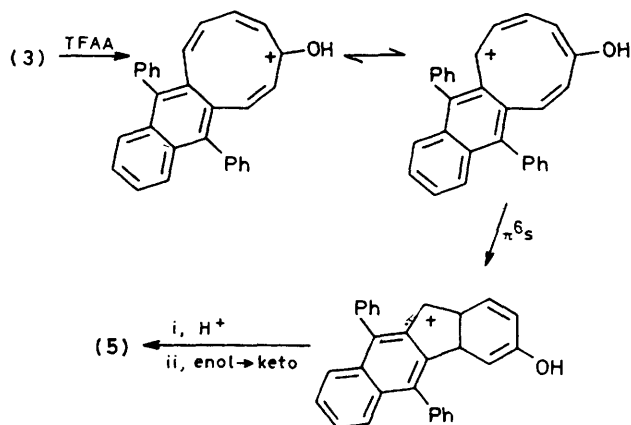
to (5), which was obtained as a yellow solid (m.p. 211–212 °C) and showed n.m.r. (<sup>1</sup>H, <sup>13</sup>C), u.v., i.r., and m.s. characteristics which are fully consistent with the assigned

† A sterically congested *bis*-annulated derivative of cyclononatetraenone was recently described; M. Rabinowitz, F. D. Bergman, and A. Gazit, *Tetrahedron Letters*, 1971, 2671.

‡ Characterized on the basis of consistent spectroscopic (<sup>1</sup>H and <sup>13</sup>C n.m.r., i.r., u.v., and mass) data.

§ The <sup>1</sup>H n.m.r. spectrum is cleanly resolved into six well separated 'olefinic' doublets ( $\tau$  4.0–6.8) when recorded in the presence of the shift reagent [<sup>2</sup>H<sub>27</sub>]-Pr(fod)<sub>3</sub>.

¶ The skeleton of (3) remains intact (<sup>1</sup>H n.m.r.) in the presence of acetic acid.



SCHEME 2

structure [ $^1\text{H}$  n.m.r.:  $\tau$  2.4—2.8 (15H, m), 3.30 (1H, d,  $J$  2 Hz,  $\text{H}_a$ ), 4.25 (1H, d,  $J$  9 Hz,  $\text{H}_b$ ), 5.90 (1H, ddd,  $J$  2.0, 7.0, and 12.7 Hz,  $\text{H}_d$ ), 7.80 (1H, dd,  $J$  7.0 and

16.0 Hz,  $\text{H}_c$  or  $\text{H}_e$ ), and 8.20 (1H, dd,  $J$  12.7 and 16.0 Hz,  $\text{H}_c$  or  $\text{H}_e$ );  $^{13}\text{C}$  n.m.r.:  $\delta$  ( $\text{Me}_4\text{Si}$ ;  $^1\text{H}$  non-decoupled) 145.6—126.0 (complex m,  $sp^2\text{-C}$ ), 189.7 (s, CO), 48.1 (d,  $J_{\text{CH}}$  126.3 Hz,  $\text{C}_d$ ), and 41.6 p.p.m. (t,  $J_{\text{CH}}$  136.2 Hz,  $\text{C}_e$ )].

The conversion of (3) into (5) may readily be rationalized by the steps in Scheme 2. The overall process [*i.e.*, (3)  $\rightarrow$  (5)] is most logically attributed to an acid-catalysed induction of antiaromatic character in (3) although it is not clear at this stage to what extent, if at all, the bond relocation is triggered as a result of the steric congestion introduced by the molecule's two phenyl substituents.

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<sup>1</sup> A. G. Anastassiou, S. S. Libsch, and R. C. Griffith, *Tetrahedron Letters*, 1973, 3103; A. G. Anastassiou and E. Reichmanis, *J.C.S. Chem. Comm.*, 1976, 313.

<sup>2</sup> A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, 1974, 96, 611; A. G. Anastassiou and E. Reichmanis, *Angew. Chem.*, 1974, 86, 784.

<sup>3</sup> T. Sasaki, K. Kanematsu, and Y. Yukimoto, *Heterocycles*, 1974, 2, 1.