

## On Phenanthrene-4,5-quinones: a Synthesis of Morphenol

Frank R. Hewgill\* and Jeffery M. Stewart

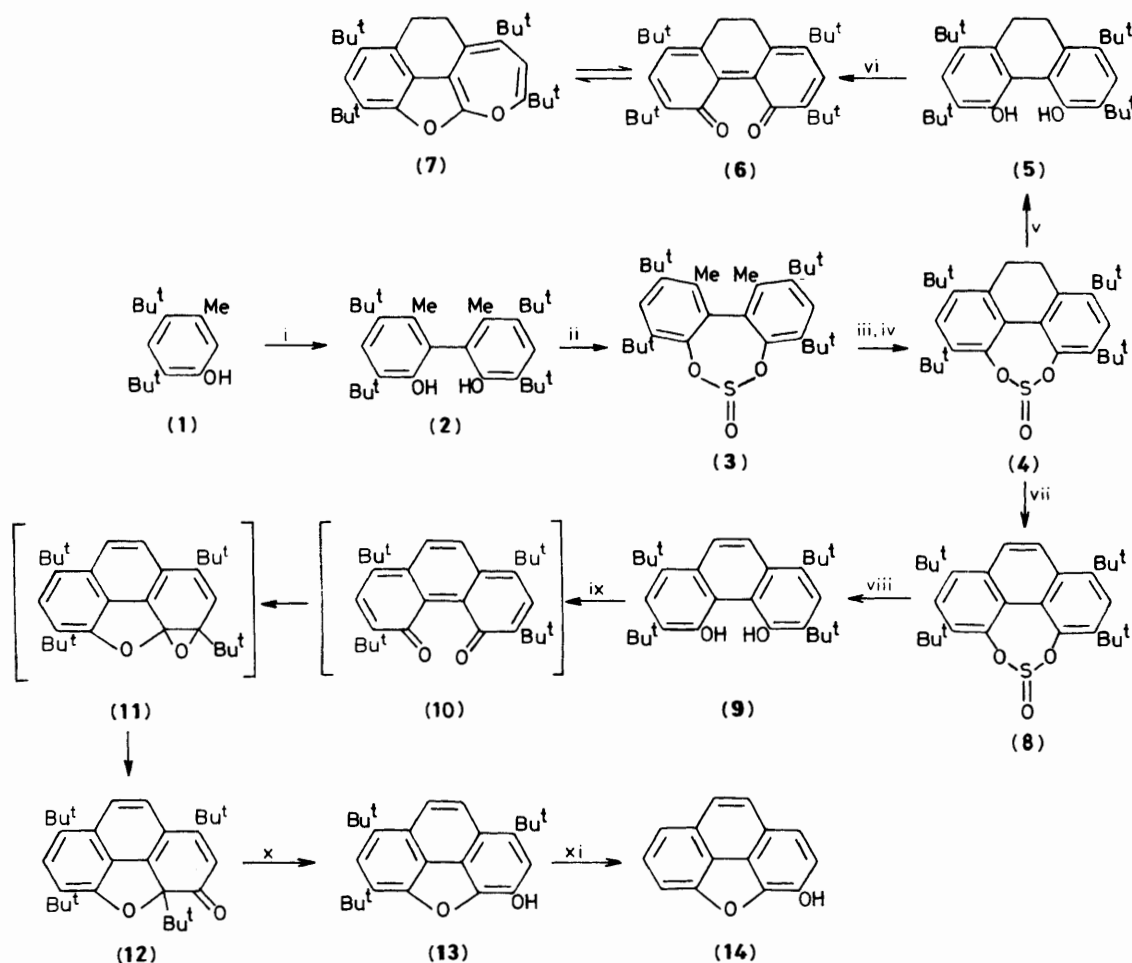
*Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia*

1,3,6,8-Tetra-*t*-butylphenanthrene-4,5-quinone (**10**) has been prepared as a short-lived species in solution, and rapidly rearranges to a dienone (**12**) which on debutylation yields morphenol (**14**): the corresponding 9,10-dihydroquinone (**6**) crystallises as its oxepine valence isomer (**7**).

Only four types of phenanthrenequinone have been described, the 1,2-, 1,4-, 3,4-, and 9,10-isomers, all of which have two Kekulé rings. Of the remaining eleven, the 4,5-isomer is of particular interest in that it could regain its full aromaticity by valence isomerisation to a cyclic peroxide. Newman and his coworkers<sup>1</sup> have synthesised and oxidised several phenanthrene-4,5-diols, most giving phenanthrene-1,4-quinones, and 1,3,6,8-tetramethylphenanthrene-4,5-diol an apparently polymeric product.<sup>2,3</sup> With these results in mind we have synthesised 1,3,6,8-tetra-*t*-butylphenanthrene-4,5-diol (**9**) both because its oxidation product may be more stable than that from the tetramethyl compound, and also because the resulting quinone may be considered as a biphen-2,2'-quinone locked in the *cis* configuration. Quinones of this type, with *t*-butyl substitution in the 3,3'-positions, undergo valence isomerisation *via* arene oxides to oxepino[2,3-*b*]-benzofurans.<sup>4,5</sup>

We first synthesised the 9,10-dihydrophenanthrene diol (**5**); m.p. 235–237 °C, <sup>1</sup>H n.m.r. (80 MHz, CDCl<sub>3</sub>): δ 1.44 (18H s), 1.47 (18H, s), 2.16–3.55 (4H, AA'BB', m), 5.51 (2H, s), 7.34 (2H, s); as shown in Scheme 1. † For this, it was necessary both to protect the hydroxy groups, and to lock the molecule into the *cis* configuration to prevent the formation of intramolecular cyclic ethers. Both these ends were achieved by using the cyclic sulphite ester (**3**), m.p. 293–295 °C. Alkaline hydrolysis of the cyclised ester (**4**), m.p. 300 °C, gave the diol (**5**) which was oxidised with silver oxide to the quinone (**6**); <sup>1</sup>H n.m.r. (80 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.10 (18H, s), 1.48 (18H, s), 2.28 (4H, s), 7.03 (2H, s); obtained as a deep blue solution, the colour being typical of biphen-2,2'-quinones. Within minutes most of the

† Satisfactory combustion analyses were obtained for all stable compounds, and spectroscopic data for all compounds except the quinone (**10**) and its arene oxide isomer (**11**).



**Scheme 1.** i,  $K_2Cr_2O_7$ ,  $H_2SO_4$ , AcOH (ref. 9); ii,  $SOCl_2$ , pyridine; iii,  $Br_2$ , *hv*; iv, Mg; v, NaOH, EtOH (aq.); vi,  $Ag_2O$ ,  $C_6H_6$ ; vii, NBS then KOAc, AcOH; viii,  $LiAlH_4$ ; ix,  $PbO_2$ , benzene; x, AcOH, Zn; xi, HBr, AcOH, Zn.

quinone (6) had isomerised to the oxepine (7), m.p. 150–151 °C,  $^1H$  n.m.r. (80 MHz,  $CDCl_3$ ):  $\delta$  1.23 (9H, s), 1.27 (9H, s), 1.40 (9H, s), 1.44 (9H, s), 2.77–3.35 (4H, AA'BB', m), 5.35 (1H, s), 7.02 (1H, s); although the solution retained a blue colour in accordance with the equilibrium between (6) and (7). The dihydrophenanthrene-4,5-quinone (6) thus behaves as a typical 3,3'-di-*t*-butyl substituted biphenyl-2,2'-quinone.

Dehydrogenation of the sulphite ester (4) with *N*-bromosuccinimide (NBS) gave the phenanthrene sulphite (8), m.p. 242–243 °C, but this could not be hydrolysed without extensive decomposition. Instead, the ester group was removed by reduction with lithium aluminium hydride, giving the phenanthrene diol (9),  $^1H$  n.m.r. (80 MHz,  $C_6D_6$ ):  $\delta$  1.63 (36H, s), 6.41 (2H, s), 7.84 (2H, s), 8.12 (2H, s). The unexpected sensitivity of this compound to aerial oxidation required that it be handled under an argon atmosphere. Oxidation of (9) with lead oxide in benzene gave a fleeting green solution, but attempts to obtain a  $^1H$  n.m.r. spectrum of the quinone (10) were unsuccessful. Concentration of the solution gave the dienone (12); m.p. 166–168 °C (decomp.),  $^1H$  n.m.r. (80 MHz,  $C_6D_6$ ):  $\delta$  1.04 (9H, s), 1.17 (9H, s), 1.54 (9H, s), 1.56 (9H, s), 5.55 (1H, s), 7.38 and 7.79 (2H, ABq,  $J$  9.2 Hz), 7.49 (1H, s); presumably by the N.I.H. rearrangement<sup>6</sup> of an intermediate arene oxide (11). As no evidence was obtained for the existence of a cyclic peroxide, it does not appear to be a stable alternative.

The structure of the dienone (12) was established by acid catalysed elimination of the angular *t*-butyl group to afford the phenol (13), m.p. 218–220 °C, and further debutylation to the phenol (14). This proved identical to a sample of morphenol prepared from codeine by the method of Mosettig and Meitzner.<sup>7</sup> The route to (14) described in Scheme 1 thus fortuitously constitutes a second synthesis of morphenol,<sup>8</sup> the overall yield from di-*t*-butyl-*m*-cresol (1) being 3.6%.

We thank the Australian Research Grants Scheme for financial support.

Received, 18th June 1984; Com. 853

## References

- 1 M. S. Newman and R. L. Childers, *J. Org. Chem.*, 1967, **32**, 62.
- 2 M. S. Newman and H. M. Chung, *J. Org. Chem.*, 1974, **39**, 1036.
- 3 M. S. Newman and H. M. Dali, *J. Org. Chem.*, 1977, **42**, 734.
- 4 H. Meier, H. P. Schneider, A. Rieker, and P. B. Hitchcock, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 121.
- 5 F. R. Hewgill, B. La Greca, F. Legge, and P. E. Roga, *J. Chem. Soc., Perkin Trans. 1*, 1983, 131.
- 6 G. Guroff, J. W. Daly, D. M. Jerina, J. Renson, B. Witkop, and S. Udenfriend, *Science*, 1967, **157**, 1524.
- 7 E. Mosettig and E. Meitzner, *J. Am. Chem. Soc.*, 1934, **56**, 2738.
- 8 T. Horaguchi and T. Shimizu, *Bull. Chem. Soc. Jpn*, 1974, **47**, 485.
- 9 H. E. Albert, *J. Am. Chem. Soc.*, 1954, **76**, 4983.