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

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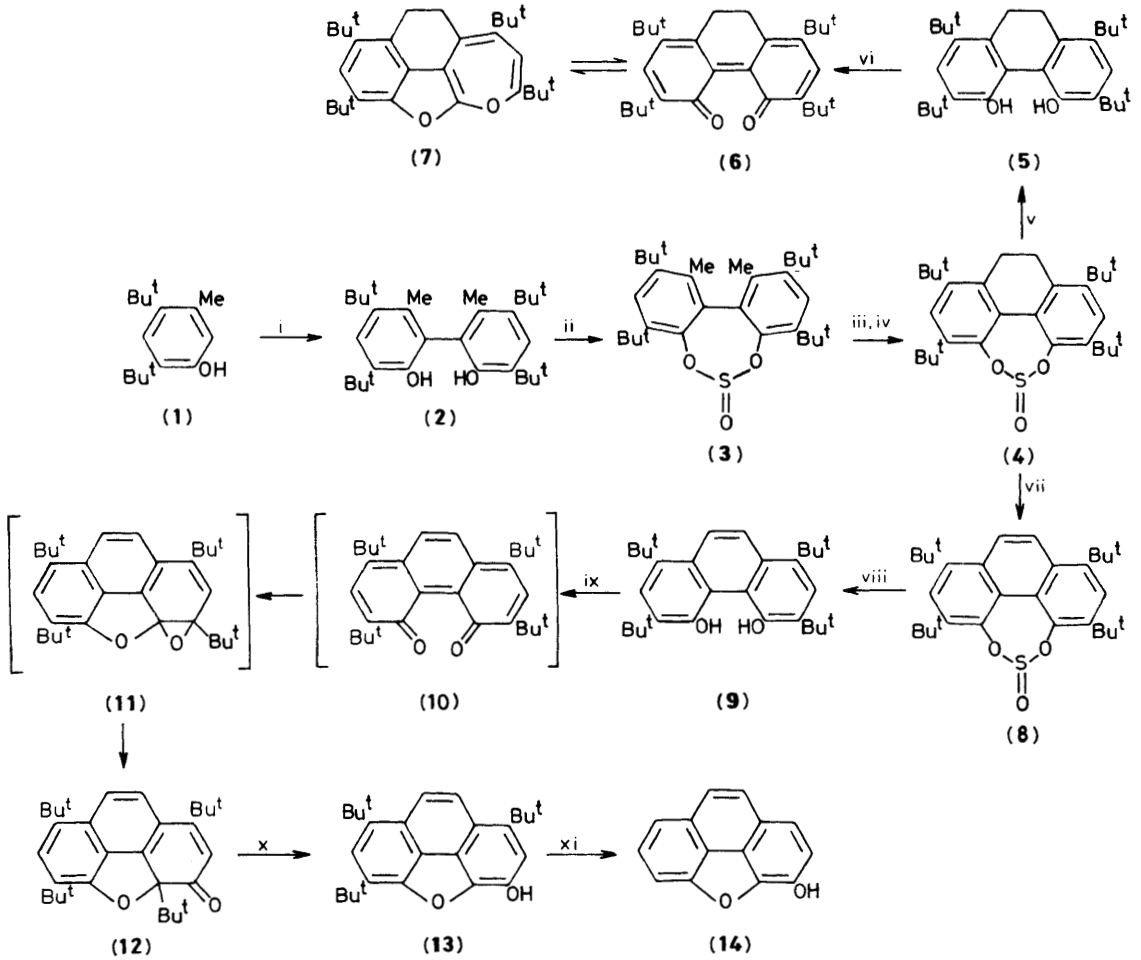
1,3,6,8-Tetra-t-butylphenanthrene-4,5-quinone (**10**) has been prepared as a short-lived species in solution, and rapidly rearranges to a dienone (**12**) which on debutylation yields morphenol (**14**): the corresponding 9,10-dihydroquinone (**6**) crystallises as its oxepine valence isomer (**7**).

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[1] 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.[2,3] 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 bipheno-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.[4,5]

We first synthesised the 9,10-dihydrophenanthrene diol (**5**); m.p. 235—237 °C, ^{1}H n.m.r. (80 MHz, $CDCl_3$): δ1.44 (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**); ^{1}H n.m.r. (80 MHz, C_6D_6): 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 bipheno-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, *hν*; 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, ^{1}H n.m.r. (80 MHz, $CDCl_3$): δ 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 bipheno-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**), ^{1}H n.m.r. (80 MHz, C_6D_6): δ 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 ^{1}H n.m.r. spectrum of the quinone (**10**) were unsuccessful. Concentration of the solution gave the dienone (**12**); m.p. 166—168 °C (decomp.), ^{1}H n.m.r. (80 MHz, C_6D_6): δ 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[6] 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.[7] The route to (**14**) described in Scheme 1 thus fortuitously constitutes a second synthesis of morphenol,[8] the overall yield from di-t-butyl-*m*-cresol (**1**) being 3.6%.

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