A Novel Mode of Dimerisation of a 1,2-Benzoquinone

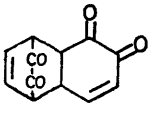
By M. F. ANSELL* and A. J. BIGNOLD

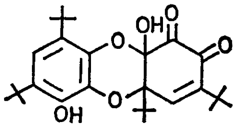
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary 3,4,6-Trimethyl-1,2-benzoquinone has been found to dimerise *via* the 4-methyl group.

SIMPLE 1,2-benzoquinones have been reported[1] to dimerise by a Diels–Alder reaction, thus *o*-benzoquinone itself gives (1). In contrast 3-hydroxy-1,2-benzoquinone dimerises[2] by an aldol-type condensation to give (2), but 3-hydroxy-4,6-di-t-butyl-1,2-benzoquinone forms[3] the dimer (3).

We now report that 3,4,6-trimethyl-1,2-benzoquinone dimerises when a solution of the quinone in chloroform is left for 24 h at room temperature. The dimer obtained had m.p. 180—184°; M^+ 300; ν_{max} 3500—3380 (several peaks), 1635, and 1615 cm^{-1}; λ (95% EtOH) 240 nm infl (ϵ 11,800) and 280 infl (7650); δ [$(CD_3)_2CO$] 1·68 s (3H), 1·75 s (3H), 1·89 d *J* 1·5 Hz (3H), 2·16 s (3H), 2·25 t *J* 7 Hz (2H), 2·98 t *J* 7 Hz (2H), *ca.* 3·2 bs exchangeable (OH), 6·85 q *J* 1·5 Hz (1H), and *ca.* 7·1 bs exchangeable (2OH). The triacetate, obtained by treatment of the dimer with acetyl chloride in benzene–pyridine, had m.p. 192—195°, λ_{max} (95% EtOH) 250 nm (ϵ 17,400). The two structures (4a) and (5a) are consistent with the spectroscopic properties of the dimer.


(1)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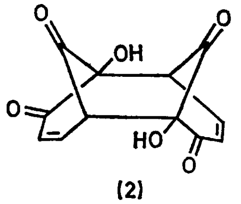
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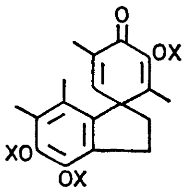
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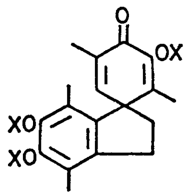
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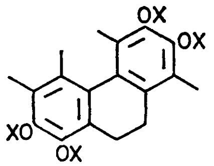
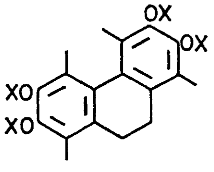
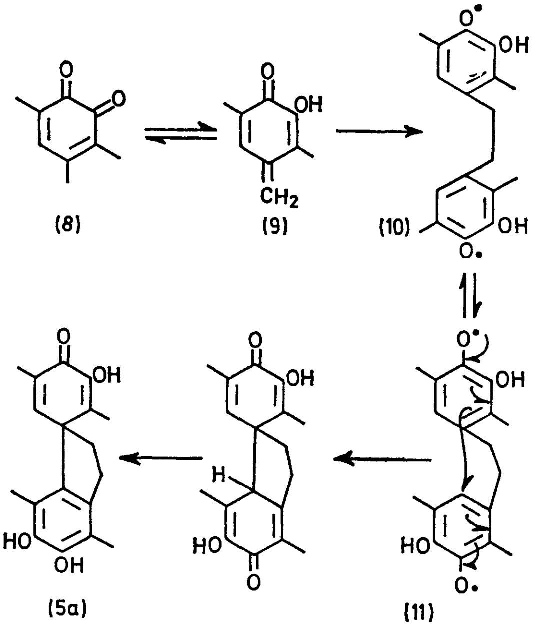

(6)

a; X = H


(7)

b; X = Ac

On treatment with acetic anhydride and concentrated sulphuric acid, the dimer underwent a dienone–phenol rearrangement to give a dihydrophenanthrene m.p. 239—241°, δ ($CDCl_3$) 2·00 s and 2·18 s (each 2 × *Me*-Ar), 2·30 and 2·33 (each 2 × MeO_2C–), and 2·5—3·0 m (CH_2–CH_2). Since the n.m.r. spectrum of this compound exhibited only two aromatic methyl signals and two acetate methyl signals, we consider it has the symmetrical structure (7b) and the dimer must therefore have structure (5a). The alternative structure for the dimer (4a) would give rise to the unsymmetrical dihydrophenanthrene (6b).



The mechanism of the dimerisation can be envisaged as involving the quinone methide tautomer (9) of the parent quinone (8). Such methides are known to dimerise[4] probably *via* biradical intermediates. In our reaction the biradical (10) would be involved which after isomerisation (to 11) could ring-close to the observed dimer (5a). Such a mode of dimerisation of an *o*-benzoquinone has not previously been reported. This type of dimerisation is not observed with 4-methyl- or 4,5-dimethyl-*o*-benzoquinone. It is probably restricted to 4-methyl-*o*-benzoquinones substituted at positions 3 and 6 so as to reduce their dienophilic properties. The weak dienophilic properties of 3,4,6-trimethyl-*o*-benzoquinone were reported by Ansell *et al.*[5] who first reported the formation of the dimer.

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