Diels–Alder Reaction of *o*-Benzoquinones with Acyclic Dienes

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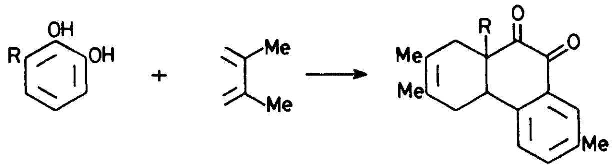
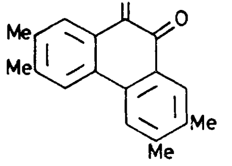
Summary Treatment of mono-substituted *o*-benzoquinones with an excess of 2,3-dimethylbutadiene, and an oxidising agent, gives the novel bis-Diels-Alder adducts, tetrahydrophenanthrenequinones.

THE formation of normal bis-Diels–Alder adducts from *o*-benzoquinones and acyclic dienes has not been recorded although abnormal 1:2 additions involving a carbonyl group are known.[1] We report the formation of the normal bis-adducts (**2**) in the reaction of the 3-substituted catechols (**1**) with 2,3-dimethylbutadiene in the presence of an oxidising agent (Table).



(**1**) (**2**)



(**3**)

2,3-Dimethylbutadiene reacts with 2,3-dihydroxybenzophenone (**1c**) in the presence of silver oxide and boiling benzene (4·5 h) to give the phenanthrenequinone (**2c**) [65% yield, m.p. 138—140 °C, M^+, *m/e* 372·3, ν_{max} (Nujol) 1730 (C=O), 1685 (conj. C=O), and 1670 (conj. C=O) cm^{-1}; δ (CDCl$_3$, Me$_4$Si reference) 7·76—7·38 (5H, m, Ph), 7·73 (1H, s, 8-H), 7·21 (1H, s, 5-H), 3·98 (1H, q, 4a-H), 3·41—1·52 (4H, m, 1- and 4-H$_2$), 2·32 (3H, s, 7-Me), 2·24 (3H, s, 6-Me), 1·8 (3H, s, 2-Me), and 1·65 (3H, s, 3-Me)].

TABLE. Addition products of quinones with 2,3-dimethylbutadiene[a]

Adduct	R	Oxid. agent	M.p./°C	Yield/%
(**2a**)	CHO	Ag$_2$O	136—138	25
(**2b**)	COMe	Ag$_2$O	85—87	51
(**2c**)	COPh	Ag$_2$O	138—140	65
(**2d**)	CO$_2$Me	MnO$_2$	169—171	78
(**2e**)	CN	NiO$_2$	98—100	43

[a] Reactions were carried out in boiling benzene for 4—5 h. All new compounds gave satisfactory elemental analyses.

Further structural proof for (**2d**) and (**2e**) was provided by hydrolysis, which gave the acid (**2**; R = CO$_2$H) [54% yield, m.p. 126—129 °C, M^+, *m/e* $C_{19}H_{20}O_4$ 312, $\nu_{max.}$ (CHCl$_3$) 3100 (OH), 1725 (C=O), 1700 (C=O), and 1680 (conj. C=O) cm^{-1}; n.m.r. δ (CDCl$_3$) 8·33br (1H, s, exchangeable, OH), 7·18 (1H, s, 8-H), 7·04 (1H, s, 5-H), 4·02 (1H, q, 4a-H), 3·73—1·29 (4H, m, 1- and 4-H$_2$), 2·27br (6H, s, 6- and 7-Me), 1·69 (3H, s, 2-Me), and 1·57 (3H, s, 3-Me)]. This acid was then decarboxylated and aromatised (refluxing toluene; Ag$_2$O; 4 h) to give 2,3,6,7-tetramethylphenanthrenequinone (**3**) as a pale red powder [57% yield, m.p. 178—180 °C, $\nu_{max.}$ (CHCl$_3$) 1690 (C=O) cm^{-1}; δ (CDCl$_3$) 7·28 (4H, s, ArH) and 2·35 (12H, s, 2-, 3-, 6- and 7-Me)].

We suggest a mechanism involving Diels–Alder addition to the quinone at the C-5—C-6 double bond, tautomerisation to a diol, oxidation to an *o*-naphthoquinone, and further addition.

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[1] M. F. Ansell and A. J. Bignold, *Chem. Comm.*, 1970, 989; L. Horner and Merz, *Annalen*, 1950, **570**, 89; M. F. Ansell and V. J. Leslie, *J. Chem. Soc.* (*C*), 1971, 1423.