The Reactions of Tetrahalogeno-o-benzoquinones with Hexadienes

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

(*Department of Chemistry, Queen Mary College, Mile End Road, London, E.*1)

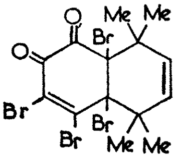
Summary Both *o*-chloranil and *o*-bromanil react with hexa-2,4-diene to give a benzodioxan and with 2,5-dimethylhexa-2,4-diene to give a dioxole.

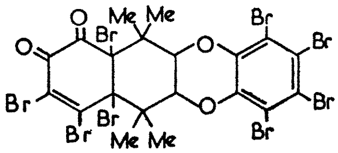
THE reaction of tetrabromo-*o*-benzoquinone and 2,5-dimethylhexa-2,4-diene has been reported by von Euler and Hasselquist[1] to give (in the warm) a 1 : 1-adduct assigned structure (I) and (in the cold) a 2 : 1-adduct assigned structure (II). We have repeated these reactions and have found no evidence for the formation of a 2 : 1-adduct, obtaining under either of the specified conditions only a compound having the same melting point as the reported 1 : 1-adduct. This compound is most conveniently prepared (80% yield) by the slow addition of the diene to a benzene solution of the bromo-quinone maintained at 0°. From its analysis and mass spectrum (*M^+*, quintet centred on *m/e* 532) the product was found to have the molecular formula $C_{14}H_{12}Br_4O_2$ and was therefore a 1 : 1-adduct less two hydrogen atoms. The product [λ_{max} (ether) 248 (ϵ 49,000), 295 (ϵ 3400), 306 (ϵ 3400) nm.] retained the diene system of the hexadiene, but exhibited no hydroxylic or carbonyl absorption in its i.r. spectrum, and is therefore formulated as the dioxole (IIIa). This structure was confirmed by its n.m.r. spectrum ($CDCl_3$) which showed the presence of three vinyl-methyl groups δ 1·81 singlet (2 × Me), δ 1·88 singlet (1 × Me), two vinyl protons as an AB-quartet (broad) δ 6·04 and 6·53, *J* 11 Hz., and a methylenedioxy-proton as a singlet at δ 6·57. Tetrabromocatechol has also been isolated from the reaction. In the analogous reaction with *o*-chloranil we have isolated (in 83% yield) the previously unreported dioxole (IIIb) m.p. 151—151·5° whose spectroscopic properties were essentially identical with those of the compound (IIIa). These structures were substantiated by the quantitative hydrolysis (dilute hydrochloric acid in aqueous acetone) of each dioxole to the corresponding tetrahalocatechol and the aldehyde (IV) [M^+ 124; λ_{max} (95% EtOH) 291 nm. (ϵ 58,000); ν_{max} 1680 (conj. C = O) and 1630 (conj. C = C) cm.$^{-1}$; n.m.r. ($CDCl_3$) δ 1·82 singlet (Me), 1·95 singlet (2 × Me), δ 6·32 and 7·08 AB quartet (broad) *J* 11·5 Hz. (2 × vinyl-H), δ 9·45 singlet (CHO)].

The formation of dioxoles has been reported to occur photochemically between phenanthraquinone and both di-t-butylethylene[2] and substituted isobenzofuran;[3] thermally between *o*-chloranil and either a substituted isobenzofuran[4] or 6-methoxy-1-tetralone.[5]

o-Quinones also react with diazoalkanes or their precursors to form dioxoles.[4] In the reaction reported here, although the exact mechanism is not yet known, the reaction is purely thermal and occurs under conditions much milder than those previously reported for thermal reactions. It appears to proceed *via* a paramagnetic molecular complex[6] as an e.s.r. signal was obtained from the brown solution formed when benzene solutions of the chloroquinone and the diene were mixed. The signal decayed to zero as the reaction proceeded to completion.

The exact structural requirement necessary for the diene component to have in order to undergo dioxole formation is not at present known, but the reaction is not given by hexa-2,4-diene. This diene was reported[1] to react with *o*-bromanil to give a 1 : 1-adduct formulated as (V). We have prepared this adduct (84% yield) and have shown that it cannot have the structure (V) as it exhibits no carbonyl or hydroxylic absorption in its i.r. spectrum. We therefore formulate it as the benzodioxan (VI) which is consistent with its n.m.r. spectrum: ($CDCl_3$, 100 MHz.), δ 1·42 doublet *J* 6 Hz. (saturated Me), δ 1·80 doublet of doublets *J* 6·5 and 1 Hz (vinyl-Me), δ 3·96 doublet of quartets *J* 7 and 6 Hz. (H_a), δ 4·22 triplet *J* 7 Hz. (H_b), δ5·49 doublet of doublets of quartets *J* 15·5, 7, and 1 Hz. (H_c), δ 6·01 doublet of quarters *J* 15·5 and 6·5 Hz. (H_d). An analogous adduct has been obtained[7] between *o*-chloranil and hexa-2,4-diene.


(I)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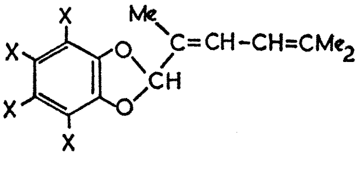
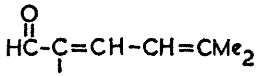

(III) a , X = Br
b , X = Cl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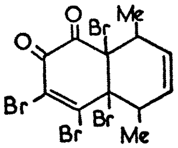
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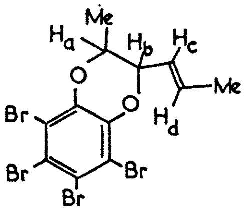
(VI)

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[1] H. von Euler and H. Hasselquist, *Arkiv Kemi*, 1953, **6**, 139.
[2] S. Farid, D. Hess, G. Pfundt, K. H. Scholz, and G. Stefan, *Chem. Comm.*, 1968, 638.
[3] W. Friedrichsen, *Tetrahedron Letters*, 1969, 1219.
[4] W. M. Horspool, *Quart. Rev.*, 1969, **23**, 204.
[5] T. R. Kasturi and T. Arunachalen, *Canad. J. Chem.*, 1968, **46**, 3625.
[6] J. W. Eastman, G. Engelsma, and M. Calvin, *J. Amer. Chem. Soc.*, 1962, **84**, 1339.
[7] M. F. Ansell and V. J. Leslie, unpublished results.