The Reaction of Tetrahalogeno-o-benzoquinones with 2,3-Dimethylbut-2-ene

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Summary The reaction of tetrachloro- and tetrabromo-*o*-benzoquinones with 2,3-dimethylbut-2-ene leads to products derived from overall direct addition, as well as from dehydrogenation; tetrachloro-*o*-benzoquinone also forms a novel 2 : 1 adduct.

WHEREAS the thermal addition of dienes and phenyl-conjugated alkenes to tetrahalogeno-*o*-benzoquinones to form benzodioxans[1] is well known, the thermal addition of a simple non-conjugated olefin to such an *o*-quinone has not previously been reported.

2,3-Dimethylbut-2-ene reacts with *o*-chloranil at room temperature (benzene solution, 24 h) to form the benzodioxan (**3**)† [10% yield, m.p. 143—144°, M^+ $C_{12}H_{12}O_2{}^{35}Cl_4$ 328, n.m.r. ($CDCl_3$) one peak δ 1·37] together with the benzodioxan (**2**) (15% yield), identical to that derived[2] from 2,3-dimethylbuta-1,3-diene and *o*-chloranil, tetrachlorocatechol (15% yield) and (**5**) [38% yield, M^+ $C_{12}HO_4{}^{35}Cl_7$ 454, i.r. (Nujol) 3500, 3400, and 1685 cm^{-1}] produced[3] by a condensation of *o*-chloranil and tetrachlorocatechol with loss of hydrogen chloride. Compounds (**3**) and (**2**) were separated from each other by preparative t.l.c. (silica-gel HF 254/petrol 40—60°). There was no evidence for the formation of a dioxole as in the reaction of the *o*-halogeno-anils and 2,5-dimethylhexa-2,4-diene.[4]

Treatment of *o*-chloranil with 2,3-dimethylbut-2-ene in refluxing benzene (1¼ h) gave compounds (**2**) and (**3**), tetrachlorocatechol, and (**4**) [25% yield, m.p. 225—227°,

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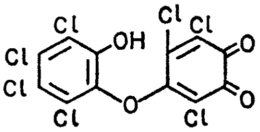
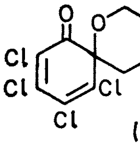
† All new compounds gave satisfactory elemental analyses.

M^+ $C_{18}H_{12}O_4{}^{35}Cl_8$ 572, i.r. (Nujol) 3380 (sharp), n.m.r. ($CDCl_3$) δ 1·48, 1·53, and 1·63 (3s, 9H), 4·55 (s, 2H), 7·53 (s, 1H, disappears on deuteriation)]. Cleavage of (**4**) with hydrogen iodide (1 mol) in acetic acid gave (**2**). *o*-Bromanil gave similar results except that no compound analogous to (**4**) was found.


(5)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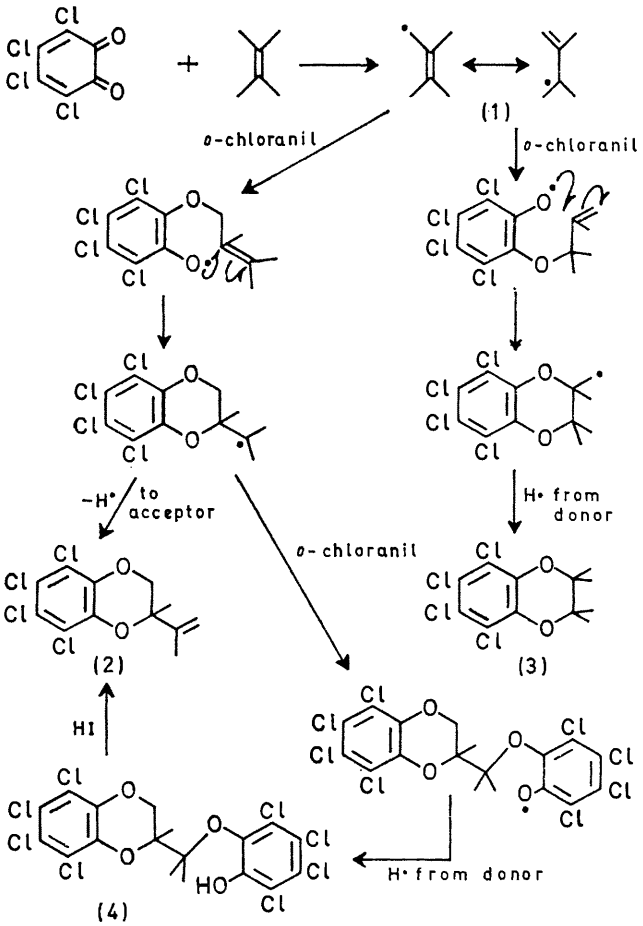
The volatile material from the reaction at room temperature was found, by g.l.c. analysis, to contain small amounts of 2,3-dimethylbuta-1,3-diene. Compound (**2**) might be considered to be formed *via* this diene, but *o*-chloranil and dimethylbutadiene at room temperature,[2] give the spirodihydropyran (**6**) and although the latter (**6**) does rearrange to (**2**) in refluxing benzene, it does not do so detectably during 24 h at room temperature. It therefore, seems probable that 2,3-dimethylbutadiene is not an intermediate in the formation of (**2**). A reaction sequence showing how the benzodioxan (**2**) may be formed from tetramethylethylene and *o*-chloranil without the participation of free dimethylbutadiene, is shown in the Scheme. The assumption that the initial step is the formation of the allylic radical (**1**) also rationalises the formation of the product (**4**), which could not be synthesised from (**2**) and tetramethylethylene with or without acid catalysis. Consideration of the mesomeric nature of the radical (**1**) suggests a possible route to the benzodioxan (**3**). Such a route from olefins to benzodioxans of the type (**3**) has, to our knowledge, not previously been considered. Such reactions can in principle be direct cycloaddition reactions as has been demonstrated[1b] by the addition of stilbene to *o*-chloranil: in this case, however, a reaction *via* an allylic radical is impossible.

It has been reported that *o*-chloranil with perinaphthene yields the perinapththenyl radical.[5] Although dehydrogenation reactions involving quinones have been suggested to proceed *via* carbonium ions,[6] such ions may not be the primary intermediates. The rationalisation we have considered is consistent with the radical-trapping ability of quinones. An attempt to demonstrate the presence of intermediate radicals by trapping them with 2-methyl-2-nitrosopropane[7] was unsuccessful. This we attribute to the radical-trapping ability of the quinone, for when the quinone was added to a benzene solution of di-t-butylnitroxide, the e.s.r. signal due to the nitroxide was immediately quenched.

In order to investigate whether the benzodioxan (**3**) arises *via* a radical intermediate or by direct cycloaddition, we have carried out the reaction between tetramethylethylene and tetrachloro-*o*-benzoquinone in the presence of dideuteriotetrachlorocatechol. If radical intermediates are involved then the benzodioxan (**3**) produced should be deuteriated (provided that tetramethylethylene does not become deuteriated prior to its reaction with tetrachloro-*o*-benzoquinone). The product (**3**) which we isolated was not deuteriated, and we therefore conclude that the benzodioxan is formed in a direct cycloaddition reaction.



SCHEME

We conclude that in the reaction of tetrachloro-*o*-benzoquinone with tetramethylethylene, there are two competing reactions—one leading to the benzodioxan (**3**) and the other to products in which reaction has occurred at an allylic position.

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[1] (a) L. Horner and H. Merz, *Annalen*, 1950, **570**, 89; (b) D. Bryce-Smith and A. Gilbert, *Chem. Comm.*, 1968, 1701.
[2] M. F. Ansell and V. J. Leslie, *Chem. Comm.*, 1967, 949.
[3] C. L. Jackson and P. W. Carleton, *Amer. Chem. J.*, 1908, **39**, 499.
[4] M. F. Ansell and A. J. Bignold, *Chem. Comm.*, 1969, 1096.
[5] D. H. Reid, M. Frazer, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Letters*, 1961, 530.
[6] J. Barnard and L. Jackman, *J. Chem. Soc.*, 1960, 3110.
[7] G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, 1968, **90**, 7141.