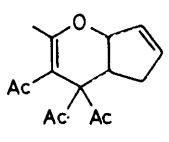
Benzoquinones and Related Compounds. Part 4.[1] Thermolysis of the Diels–Alder Adduct of 2-Acetyl-5,6-dichloro-1,4-benzoquinone and Cyclopentadiene: Evidence for a Partial Retro-diene Reaction

By Roy L. Beddoes, J. Malcolm Bruce,* Harry Finch, Leslie M. J. Heelam, Ian D. Hunt, and Owen S. Mills, Department of Chemistry, The University, Manchester M13 9PL

Addition of chlorine to (2-methyl-1,3-dioxolan-2-yl)-1,4-benzoquinone occurs at the unsubstituted double bond. Subsequent enolisation and cleavage of the acetal affords 2-acetyl-5,6-dichlorohydroquinone in 50% overall yield. Oxidation of this gives the corresponding 1,4-benzoquinone which with cyclopentadiene yields, predominantly, the 1 : 1 Diels–Alder adduct (6) by *endo*-addition to the 2,3-double bond. Thermolysis of this adduct in benzene results in disproportionation to cyclopentadiene and the spiro-acetal (13); thermolysis in acetic acid also yields (13), but the major product is the dihydrobenzofuran (14), an isomer of the Diels–Alder adduct. Mechanisms for the formation of these products are discussed.

FORMATION of the cyclopentapyran (1) on heating a mixture of 3,4-diacetylhex-3-ene-2,5-dione and cyclopentadiene in chloroform has been accounted for [2] by a [3,3] sigmatropic shift, as shown, in the transient Diels–Alder adduct (2), and this mechanism satisfactorily accounts for the facile rearrangement of other, similarly substituted, Diels–Alder adducts,[3] some of which have been isolated.[4] However, an alternative route, involving heterolysis of one of the two bonds formed between the dienophile and the diene, has also been suggested,[5] and this mechanism, as (3), has recently been invoked [6] to account for the formation of 2-(2-nitroethyl)furan from nitroethylene and furan.

The acid-catalysed isomerisation of Diels–Alder adducts of 1-methoxycyclohexa-1,3-diene with αβ-unsaturated ketones [7] and with 1,4-benzoquinones [8] has been similarly explained. Thus (4) yields (5), as shown [the product isolated was the ketone resulting from cleavage of the enol ether moiety of (5)]. Analogous products result,[9] but with greater facility, from 1,3-dimethoxycyclohexa-1,3-diene: the second methoxy-group can complement the first in stabilising the incipient cation resulting from heterolysis of the 4a,5 carbon–carbon bond in the adduct [as (4)], although in these examples the products can also be accounted for by nucleophilic addition of the diene to the quinone.



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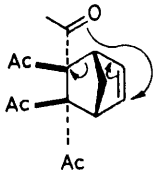

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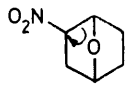

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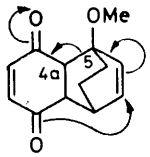

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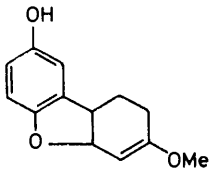

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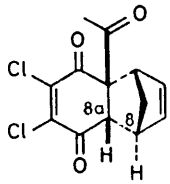


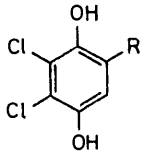
(6)

We now present evidence for heterolysis of the corresponding carbon–carbon bond in the Diels–Alder adduct (6) † of 2-acetyl-5,6-dichloro-1,4-benzoquinone and cyclopentadiene, which can be rationalised in terms of stabilisation of the incipient anion.

RESULTS AND DISCUSSION

Preparation of Materials.—2,3-Dichlorohydroquinone (7; R = H) was conveniently prepared by addition [10] of chlorine to 1,4-benzoquinone followed by enolisation of the enedione (8; R = H) with hydrogen chloride in dry ether; treatment of (8; R = H) with hydrochloric acid in acetone gave 2,5-dichlorohydroquinone, probably *via* an elimination–addition mechanism.[11]

Attempts to prepare the acetophenone (7; R = Ac) by treatment [12] of the hydroquinone (7; R = H) with



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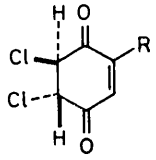

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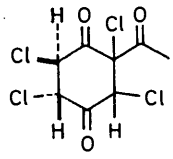

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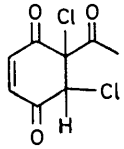


(10)

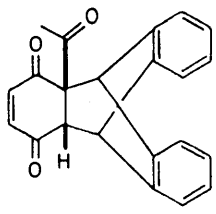
acetic acid and boron trifluoride afforded only the diacetate of the starting material, but this did undergo a Fries rearrangement [13] with aluminium chloride at at 165 °C to give, after hydrolysis, the required compound, although the yield was poor. Scaling-up of the light-induced reaction [14] between 2,3-dichloro-1,4-benzoquinone and acetaldehyde was also unsatisfactory.

Acetyl-1,4-benzoquinone reacted rapidly with an excess of chlorine in chloroform to give the adduct (9),

† All compounds were racemic, but only one enantiomer is shown.

the stereochemistry of which was not determined; when treated with hydrogen chloride in ether this afforded 2-acetyl-3,5,6-trichlorohydroquinone. Addition of chlorine (1 mol) to the quinone gave (10), possibly by nucleophilic attack of the halogen. Whilst the addition of nucleophiles to the 3-position of acetyl-1,4-benzoquinone has been well documented,[15] the addition of halogens has not previously been reported, although nucleophilic addition of chlorine to electron-poor double bonds has been described.[16]

In order to direct the addition of chlorine to the unsubstituted double bond of acetyl-1,4-benzoquinone, protection of the other double bond was necessary. Treatment of the quinone with anthracene in boiling benzene gave the adduct (11) which readily added chlorine at the enedione moiety, but attempts to effect enolisation and loss [17] of anthracene met with very limited success: treatment with hydrogen chloride in acetic anhydride gave a low yield of 2-acetyl-5,6-dichlorohydroquinone diacetate.



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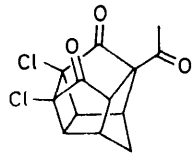
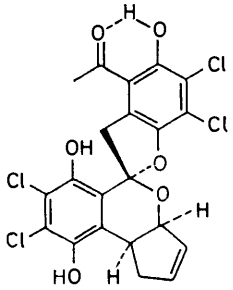


(12)

The best route involved conversion of acetylhydroquinone into its ethylene acetal, oxidation to the quinone with silver oxide, addition of chlorine in acetic acid [18] to give (8; R = 2-methyl-1,3-dioxolan-2-yl), and enolisation and cleavage of the acetal with, successively, hydrogen chloride in dry ether, and aqueous ethanolic sulphuric acid to give the hydroquinone (7; R = Ac) in an overall yield of 50%. The dioxolanyl substituent in the quinone protects the substituted double bond both sterically and electronically,[10] and addition of chlorine then occurs as required.

Oxidation of (7; R = Ac) with silver oxide gave the corresponding 1,4-benzoquinone which with cyclopentadiene in benzene at 20 °C afforded a 23 : 2 mixture of the *endo* (6) and *exo* mono-adducts,[19] the former being isolated by crystallisation from cyclohexane. Its configuration was established by ^{1}H n.m.r. spectroscopy [8a-H, δ 3.63(C_6D_6), δ 3.96($CDCl_3$), both doublets] which gave $J_{8,8a}$ 4.0 Hz, typical [20] of an *endo* system ($J_{8,8a\text{-}exo}$ *ca.* 0 Hz), and by cyclisation [21] with visible light [15] to yield the cage compound (12).

Thermolysis of Adduct (6).—A degassed 5% solution of the adduct in [$^2H_6$]benzene was heated at 80 °C, and the progress of the reaction was monitored by ^{1}H n.m.r. spectroscopy. The starting material was gradually consumed, and, after 45 min, small needles began to separate. The reaction was complete after 6 h, and the spectrum of the supernatant liquid was almost entirely due to cyclopentadiene, formed to the extent of 1 mol from 2 mol of adduct (6). On the basis of this stoicheiometry, the yellow solid, m.p. 220 °C (decomp.), was formed nearly quantitatively. Elemental analysis suggested the molecular formula $C_{21}H_{14}Cl_4O_6$, and this was confirmed by electron-impact mass spectrometry; loss of C_5H_6 from the molecular ions (Cl_4 pattern), which is characteristic of Diels–Alder adducts such as (6) and related compounds,[22] and normally provides the base peak, was not observed, and, consistently, the ^{1}H n.m.r. spectrum, in [$^2H_6$]dimethyl sulphoxide, was free from absorption in the δ 0—2 region where the methylene bridge protons of norbornenes normally resonate. The remainder of the spectrum indicated the presence of an acetyl group (δ 2.61), an isolated methylene group (AB q, δ 3.41 and 4.31, *J* 18 Hz), five mutually coupled protons (δ 2.8—6.4), two ' free ' phenolic hydroxy-groups (δ 9.26 and 9.28), and one intramolecularly hydrogen-bonded hydroxy-group (δ 11.62). In agreement with this, the compound formed a triacetate and a trimethyl ether. Both are colourless, and their ^{1}H n.m.r. spectra ($CDCl_3$ and C_6D_6) indicate retention of the non-hydroxylic proton pattern of the thermolysis product. Hydrogenation over palladium–charcoal revealed the presence of one olefinic double bond, and the ^{1}H n.m.r. spectrum of the product indicated that a –CH=CH– unit had been saturated. These data, and those of spin-decoupling experiments, are consistent, *a posteriori* (see below), with the spiro-acetal structure (13).



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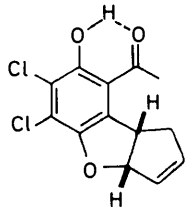

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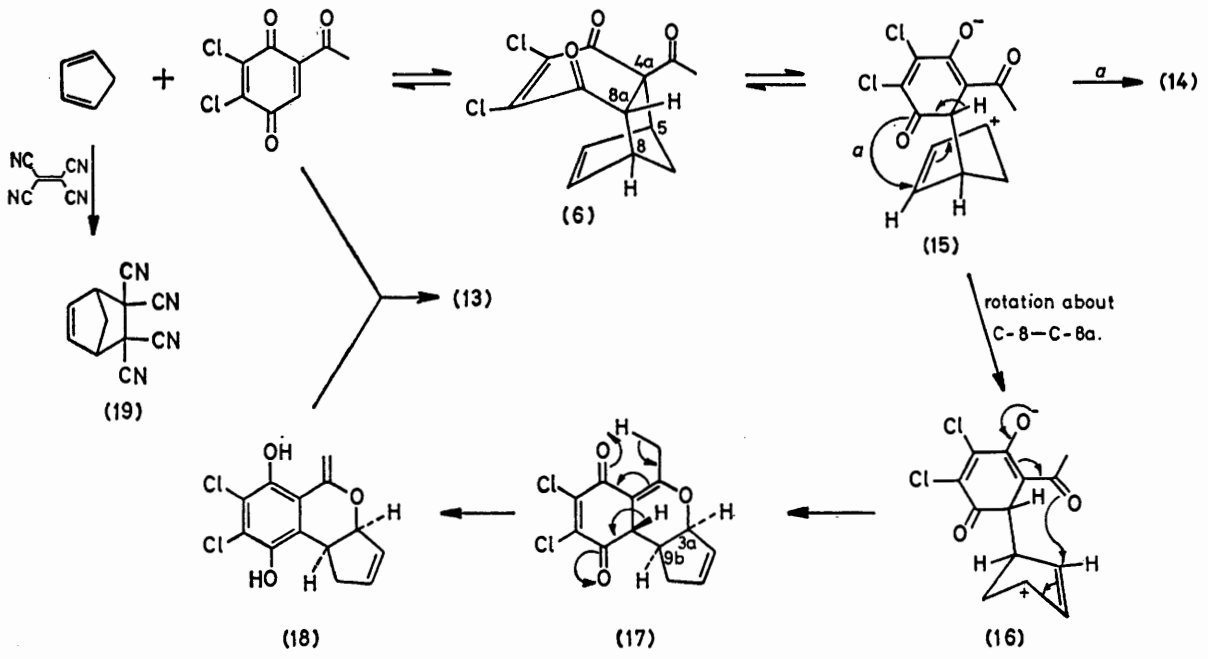
T.l.c. examination of the benzene mother-liquor from the thermolysis of the adduct (6) revealed a trace of a product having a higher R_F value than that of the spiro-compound (13). It was formed in much higher proportion [1.6 : 1 with respect to (13), total yield 88%] when the thermolysis was effected in glacial acetic acid at 80 °C for 4 h, and remained in the mother-liquor after (13) had crystallised out.

The new compound, m.p. 175 °C, was yellow, and isomeric with the adduct (6) (elemental analysis and m.s. confirmed $C_{13}H_{10}Cl_2O_3$). Its electron-impact mass spectrum showed loss of a methyl group, but, again, loss of C_5H_6 was not observed, indicating that reorganisation of the norbornene moiety in the starting material had occurred. Its ^{1}H n.m.r. spectrum in [$^2H_6$]acetone revealed an acetyl group (δ 2.74), six mutually coupled protons, four attached to sp^3 carbon (δ 2.2—4.9) and two to sp^2 carbon (δ 5.8—6.2, olefinic –CH=CH–, con-

firmed by hydrogenation over palladium–charcoal), and an intramolecularly hydrogen-bonded hydroxy-group (δ 12.50). It formed a colourless mono-acetate. These data, complemented by the results of spin decoupling, are accommodated by the dihydrobenzofuran (14).

The structures of the spiro-acetal (13) and the dihydrobenzofuran (14) were obtained [23,24] by *X*-ray crystallography, for the former using the derived triacetate; the stereochemistry at the spiro-centre was not defined by the ^{1}H n.m.r. spectra.

Mechanism of Thermolysis.—The formation of compounds (13) and (14) can be rationalised in terms of concomitant partial and complete reverse Diels–Alder reactions of the adduct (6), as shown in the Scheme.



SCHEME

Thus heterolysis of the 4a,5 carbon–carbon bond generates the zwitterion (15) from which the dihydrobenzofuran (14) is formed by intramolecular attack of the 1-carbonyl oxygen on the cyclopentenyl cation, as shown. Alternatively, rotation about the 8,8a carbon–carbon bond (adduct numbering) together with re-orientation of the acetyl group gives the conformation (16) from which the dihydropyran (17) can be derived. Enolisation of both carbonyl groups, one *via* a [1,5] hydrogen shift, then affords the vinyl ether (18). Addition of this to the 3-position of 2-acetyl-5,6-dichloro-1,4-benzoquinone, formed by normal retro-diene reaction of the adduct (6), then yields the spiro-compound (13): precedent exists in the facile addition of enol ethers to the 3-position of acetyl-1,4-benzoquinone to give 2,3-dihydrobenzofurans.[15,25]

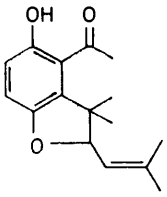
The spiro-compound (13) is formed almost exclusively when the thermolysis is effected in benzene, suggesting that conformation (16) is preferred for collapse of the zwitterion. In acetic acid, the dihydrobenzofuran becomes the major product, suggesting that the acetyl group predominantly adopts the conformation shown in (15), possibly due to solvation or to protonation of the enolate to give the internally hydrogen-bonded, and favourably conjugated, enolone; alternatively, this would be formed directly if the 4-carbonyl group of the adduct (6) were protonated on oxygen prior to cleavage of the 4a,5 bond, and the overall process would then be analogous to the proton-induced rearrangement [8] of the methoxycyclohexadiene adduct (4).

Addition of tetracyanoethylene (1 mol) to a benzene solution of the adduct (6) completely suppressed the formation of the spiro-compound (13), and gave the tetracyanonorbornene (19) quantitatively, indicating that complete reversal of the Diels–Alder reaction is fast relative to cleavage of the 4a,5 bond discussed above. The parallel experiment using acetic acid as solvent was precluded by decomposition of the tetracyanoethylene.

Facile thermolysis of the adduct (6) into its addends raises the possibility that zwitterions (15) and (16) could be formed directly by nucleophilic attack of the diene on the 3-position of the quinone (*cf.* ref. 9). However, studies [15] of the addition of cyclopentadiene to a variety of 1,4-benzoquinones do not provide a precedent; the formation [26] of the dihydrobenzofuran (20) from 2,5-dimethylhexa-2,4-diene and acetyl-1,4-benzoquinone is almost certainly due to the inability of this diene to adopt the s-*cis* conformation required for the Diels–Alder reaction. Formation of the dihydrobenzofuran (14) is therefore satisfactorily accounted for in terms of heterolysis of the 4a,5 bond in the *endo*-adduct (6).

Dissociation of systems related to (6) is not facilitated by tetracyanoethylene,[26] and it therefore follows that

reversal of the Diels–Alder step could control the formation of the spiro-compound (13): re-addition of cyclopentadiene to give the *exo*-adduct (21), a normal equilibrium-controlled process for several other acyl and related 1,4-benzoquinones,[15,22] followed by heterolysis of the 4a,5 bond would provide the necessary zwitterion; as depicted, this would be diastereoisomeric with (16), but the principle of the remaining steps would be unchanged. Alternatively, a [3,3] sigmatropic shift as



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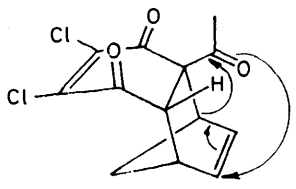

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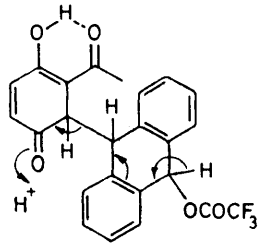

(22)

shown (*cf.* ref. 2) in the *exo*-adduct (21) would give the intermediate (17; opposite configuration at positions 3a and 9b) directly, and this represents an attractive route for thermolysis in benzene, a solvent of relatively low polarity. Precise identification of the route(s) involved awaits further investigation.

Decomposition of Adduct (11).—Because of its thermal instability, this compound was best obtained by treatment of anthracene with a *ca.* 10% excess of acetyl-1,4-benzoquinone in boiling benzene followed by cooling and extraction of the excess of quinone with cold benzene. Monitoring of the reaction between a 1 : 1 mixture of the quinone and anthracene in [$^2H_6$]benzene at 80 °C revealed equilibration at a ratio of 87 : 13 adduct : addends; the same value was obtained by thermolysis of the pure adduct.

The adduct (11) slowly decomposed when dissolved in trifluoroacetic acid at room temperature. The products, isolated by p.l.c., were acetylhydroquinone and 9-anthrone. Mass spectrometric examination of the reaction mixture revealed the presence of 9-anthrol trifluoroacetate, suggesting that proton-assisted cleavage to give (22) is followed by fragmentation, as shown; the initial cleavage is analogous to that of the 9-anthrol–maleic anhydride adduct.[27]

Conclusion.—Selective heterolytic cleavage of one diene-derived bond in Diels–Alder adducts is implicated by some of the above results. Application of the Principle of Microscopic Reversibility to these systems provides evidence that in extreme cases, involving very polar substituents, the Diels–Alder reaction occurs stepwise *via* ionic intermediates;[28] proton- and Lewis acid-mediated diene additions can fall into this category.

EXPERIMENTAL

Solvents were removed under reduced pressure. Sublimation temperatures are those of the heating bath. ^1H N.m.r. spectra were measured at 100 MHz unless stated otherwise. Tetramethylsilane was used as an internal standard. Hydroxy-resonances were removed by exchange with D_2O.

4,5-*Dichlorocyclohexene*-3,6-*dione* (8; R = H).—Dry chlorine was passed rapidly into a solution of freshly sublimed 1,4-benzoquinone (10.8 g) in dry ($CaCl_2$) chloroform (60 ml) for 1 h at −20 °C, and the excess was then removed by purging with nitrogen. The dichloro-compound which separated was collected by filtration and washed with dry chloroform (8.9 g, 50%), m.p. 144—145 °C (lit.,[10] 146 °C).

2,3-*Dichlorohydroquinone*.—Dry hydrogen chloride was passed into a solution of the foregoing enedione (15 g) in dry (Na) ether at 0 °C for 7 h, and the solution, protected from moisture, was left overnight. The solvent was then removed, and the residue was crystallised from benzene to give the hydroquinone (12 g, 80%), m.p. 143—144 °C (lit.,[29] 144—145 °C). The diacetate (excess of Ac_2O, trace Zn dust, reflux 40 min, yield 98%) had m.p. 118.5—119 °C (lit.,[30] 122—124 °C).

2,5-*Dichlorohydroquinone*.—Concentrated hydrochloric acid (0.3 ml) was added to a solution of 4,5-dichlorocyclohexene-3,6-dione (5 g) in acetone (100 ml), and the mixture was then kept at room temperature for 24 h. Removal of the solvent and crystallisation of the residue from benzene gave the hydroquinone (3.3 g, 66%) as plates, m.p. 168—169 °C (lit.,[29] 172 °C).

2-*Acetyl*-3,5,6-*trichlorohydroquinone*.—Acetyl-1,4-benzoquinone [31] (510 mg) was dissolved in dry (Al_2O_3) chloroform, and chlorine was passed in at room temperature for 1 h: the colour changed from orange to pale yellow. The solution was purged with nitrogen, the solvent was removed, and a portion (150 mg) of the residue (752 mg, m.p. 92—95 °C with loss of HCl) was dissolved in dry ether (100 ml). Hydrogen chloride was passed through the solution for 1 h at room temperature, and the solvent was then removed. Crystallisation from benzene gave the pale yellow *hydroquinone* (77 mg, 60%), m.p. 127.5—129 °C (Found: C, 37.6; H, 2.1; Cl, 40.7. $C_8H_5Cl_3O_3$ requires C, 37.6; H, 2.0; Cl, 41.7%); δ[8%, $(CD_3)_2CO$] 2.60 (s, Me), 8.75 (br s, OH), and 9.45 (br s, OH); $\nu_{max.}$ 3 350 and 1 630 cm^{-1}; *m/e* 254 (35%, $C_8H_5{}^{35}Cl_3O_3$) and 239 (50%, $C_7H_2{}^{35}Cl_3O_3$).

4-*Acetyl*-4,5-*dichlorocyclohexene*-3,6-*dione* (10).—Dry chlorine was passed through a solution of acetyl-1,4-benzoquinone [31] (251 mg) in dry (Al_2O_3) chloroform at 0 °C for 2 min: the orange solution became almost colourless. It was then thoroughly purged with dry nitrogen, and kept at −15 °C for 1 h. The *dione* (257 mg, 69%) separated (Found: C, 42.7; H, 2.5. $C_8H_6Cl_2O_3$ requires C, 43.4; H, 2.7%); δ(10% $CDCl_3$, 60 MHz) 2.43 (s, Me), 4.91 (s, 5-H), 6.91 (d, *J* 9.5 Hz, 1-H or 2-H), and 7.15 (d, *J* 9.5 Hz, 2-H or 1-H); *m/e* 220 (30%, $C_8H_6{}^{35}Cl_2O_3$) and 205 (20%, $C_7H_3{}^{35}Cl_2O_3$).

4a-*Acetyl*-1,4,4a,9,9a,10-*hexahydro*-9,10-o-*benzenoanthracene* 1,4-*dione* (11).—A solution of acetyl-1,4-benzoquinone (145 mg) and anthracene (231 mg) in dry benzene (10 ml) was refluxed for 7 h, the solvent removed, and the residue

washed with cold benzene to remove the excess of quinone. Crystallisation from chloroform–cyclohexane (1 : 20) gave the *dione* (297 mg, 70%), m.p. 145 °C (Found: C, 80.2; H, 5.1. $C_{22}H_{16}O_3$ requires C, 80.5; H, 4.9%); δ(12%, $CDCl_3$) 2.40 (s, Me), 3.88 (d, *J* 3 Hz, 9a-H), 4.90 (d, *J* 3 Hz, 9-H), 5.30 (s, 10-H), 6.26 (d, *J* 10 Hz, 2-H or 3-H), 6.40 (d, *J* 10 Hz, 3-H or 2-H), and 7.0—7.4 (m, 8 × Ar-H); $\nu_{max.}$ (Nujol) 1 765s and 1 670m cm^{-1}; *m/e* 328 (25%, M^+), 286 (25), 178 (100), and 150 (30).

4a-*Acetyl*-2,3-*dichloro*-1,2,3,4,4a,9,9a,10-*octahydro*-9,10-o-*benzenoanthracene*-1,4-*dione*.—Dry chlorine was passed into a solution of the foregoing enedione (399 mg) in dry (Al_2O_3) chloroform until the starting material had been consumed (t.l.c., 4 h). Purging with nitrogen and removal of the solvent gave the *dione* (430 mg, 88%) as a cream solid, m.p. 100—105 °C (decomp.); δ(12%, $CDCl_3$), 2.35 (s, Me), 3.90 (d, *J* 6 Hz, 1 H), 4.33 (d, *J* 3 Hz, 1 H), 4.40 (d, *J* 6 Hz, 1 H), 4.98 (d, *J* 3 Hz, 1 H), 5.30 (s, 1 H), and 7.0—7.6 (m, 8 × Ar-H); $\nu_{max.}$ (Nujol) 1 710br cm^{-1}; *m/e* 398 ($C_{22}H_{16}{}^{35}Cl_2O_3$).

(2-*Methyl*-1,3-*dioxolan*-2-*yl*)-1,4-*benzoquinone*.—A mixture of acetylhydroquinone (10 g), ethylene glycol (4.1 g) and toluene-4-sulphonic acid (340 mg) in benzene (800 ml) was refluxed (Dean–Stark) for 24 h. Ether (800 ml) and triethylamine (8 ml) were then added and the ethereal phase was separated, combined with the ether (7 × 400 ml) extracts of the residue, washed (aqueous $NaHCO_3$, then H_2O), dried ($MgSO_4$), and evaporated to give crude acetylhydroquinone ethylene acetal (12.2 g, 95%) as a blue-green solid, m.p. 87—92 °C. A mixture of this material (11.9 g), silver oxide (24 g), and anhydrous magnesium sulphate (24 g) in benzene (150 ml) was shaken in the dark for 4 h, and then filtered through Celite. Removal of the solvent and distillation of the residue at 100—105 °C/0.05 mmHg gave the quinone (7.5 g, 64%) as an orange oil identical (i.r., n.m.r.) with authentic [32] material.

4,5-*Dichloro*-1-(2-*methyl*-1,3-*dioxolan*-2-*yl*)*cyclohexene*-3,6-*dione*.—Dry chlorine was passed into a solution of the foregoing quinone (1.8 g) in dry (P_2O_5) acetic acid (100 ml) until the orange colour had faded to pale yellow (3 h). The solution was purged with nitrogen, and then evaporated, finally at 0.05 mmHg, to give the rather unstable enedione (2.2 g, 91%) as an off-white solid; δ(10%, $CDCl_3$) 1.70, (s, Me), 3.8—4.2 (m, CH_2CH_2), 4.62 (br s, 4-H + 5-H), and 6.92 (br s, 2-H); *m/e* 264 ($C_{10}H_{10}{}^{35}Cl_2O_4$).

2-*Acetyl*-5,6-*dichlorohydroquinone* (7; R = Ac).—The foregoing enedione (12.4 g) was suspended in dry (Na) ether (350 ml), stirred, and hydrogen chloride was passed in at room temperature for 2 h. The enedione dissolved, and a yellow precipitate was formed. The solvent was removed, and the residue was refluxed for 30 min with a mixture of 95% ethanol (200 ml) and 5% sulphuric acid (10 ml). Removal of the ethanol and filtration of the residue gave the *hydroquinone* (9.6 g, 93%) as yellow needles (from methanol), m.p. 219—220 °C (Found: C, 43.2; H, 2.5; Cl, 32.5. $C_8H_6Cl_2O_3$ requires C, 43.4; H, 2.7; Cl, 32.1%); δ[10%, $(CD_3)_2CO$] 2.65 (s, Me), 7.55 (s, 3-H), 8.75 (br s, 4-OH), and 12.50 (s, 1-OH); $\nu_{max.}$ (Nujol) 3 250br, 1 640s, and 1 610s cm^{-1}; *m/e* 220 (50%, $C_8H_6{}^{35}Cl_2O_3$) and 205 (100%, $C_7H_3{}^{35}Cl_2O_3$). The 4-*acetate* (Ac_2O, 25 °C, 10 min), pale green (sublimation, 85—90 °C/0.06 mmHg), had m.p. 126.5—127 °C (Found: C, 45.8; H, 3.1; Cl, 27.0. $C_{10}H_8Cl_2O_4$ requires C, 45.6; H, 3.1; Cl, 27.0%); δ(10%, $CDCl_3$) 2.35 (s, Me), 2.60 (s, Me), 7.36 (s, 3-H), and 12.90 (s, OH); $\nu_{max.}$ (CCl_4) 1 790s and 1 650s cm^{-1}; *m/e* 262 (8%, $C_{10}H_8{}^{35}Cl_2O_4$), 220 (100%, $C_8H_6{}^{35}Cl_2O_3$), 215 (70), and 43 (100). The *diacetate* (Ac_2O, NaOAc, reflux, 30 min), white (sublimation, 100—105 °C/0.06 mmHg), had m.p. 116—117 °C (Found: C, 47.5; H, 3.3; Cl, 23.4. $C_{12}H_{10}Cl_2O_5$ requires C, 47.2; H, 3.3; Cl, 23.3%); δ(12%, $CDCl_3$) 2.37 (s, Me), 2.40 (s, Me), 2.52 (s, Me), and 7.57 (s, 3-H); $\nu_{max.}$ (CCl_4) 1 795s and 1 700s cm^{-1}, *m/e* 304 (2%, $C_{12}H_{10}{}^{35}Cl_2O_5$), 262 (20%, $C_{10}H_8{}^{35}Cl_2O_4$), 220 (95%, $C_8H_6{}^{35}Cl_2O_3$), 205 (55), and 43 (100).

2-*Acetyl*-5,6-*dichloro*-1,4-*benzoquinone*.—A mixture of the hydroquinone (789 mg), silver oxide (2 g), and anhydrous magnesium sulphate (2 g) in dry benzene (100 ml) was shaken in the dark at room temperature for 1 h, and then filtered through Celite. Removal of the solvent gave the orange-yellow quinone (778 mg, 98%), m.p. 73.5—75 °C, which after sublimation (80—85 °C/0.02 mmHg) had m.p. 75.5—76 °C (Found: C, 43.4; H, 1.9; Cl, 33.0. $C_8H_4Cl_2O_3$ requires C, 43.8; H, 1.8; Cl, 32.5%); δ(8%, C_6D_6) 2.05 (s, Me) and 6.46 (s, 3-H); $\nu_{max.}$ (Nujol) 1 725s and 1 705m cm^{-1}; *m/e* 220 (20%, $C_8H_6{}^{35}Cl_2O_3$), 205 (25), and 43 (100).

endo-4a-*Acetyl*-2,3-*dichloro*-4a,5,8,8a-*tetrahydro*-5,8-*methano*-1,4-*naphthoquinone* (6).—Freshly distilled cyclopentadiene (0.75 ml) was added to a solution of the above quinone (115 mg) in dry benzene (8 ml) at room temperature: the orange colour faded. After 1 h the solvent was removed, leaving a 23 : 2 mixture (124 mg, 96%) of the *endo* and *exo* [δ($CDCl_3$) 2.32 (s, Me)] adducts. Crystallisation from cyclohexane gave the endo-*adduct*, m.p. 104—105 °C (Found: C, 54.9; H, 3.7; Cl, 24.6. $C_{13}H_{10}Cl_2O_3$ requires C, 54.6; H, 3.5; Cl, 24.9%); δ (11%, $CDCl_3$, 60 MHz) 1.42 (dm, J_1 10 Hz, *anti* 9-H), 1.60 (dm, J_1 10 Hz, *syn* 9-H), 2.40 (s, Me), 3.56 (m, 8-H), 3.83 (m, 5-H), 3.96 (d, *J* 4 Hz, 8a-H), and 6.21 (m, 6-H + 7-H); *m/e* 284 (8%, $C_{13}H_{10}{}^{35}Cl_2O_3$), 242 (100), 207 (15), 179 (11), 66 (100), and 43 (80). Irradiation with visible light in degassed ethyl acetate gave the cage compound (12) quantitatively; δ[10%, $(CD_3)_2CO$] 2.28 (s, Me), and 1.5—3.5 (series of m, remaining H); *m/e* 284 ($C_{13}H_{10}{}^{35}Cl_2O_3$).

Thermolysis of endo-*Adduct* (6).—(*a*) A solution of the adduct (50 mg) in degassed [$^2H_6$]benzene (0.5 ml) in a sealed n.m.r. sample tube was heated at 80 °C for 6 h. A yellow precipitate separated, and the ^1H n.m.r. spectrum of the supernatant liquid was identical with that of authentic cyclopentadiene in [$^2H_6$]benzene. The precipitate was collected, washed with ether, and dried to give 4-*acetyl*-6,7,7′,8′-*tetrachloro*-3′*a*R*,9′*b*R*-*dihydro*-5,6′,9′-*trihydroxy*-*spiro*{3H-*benzofuran*-2S*,5′(1′-H)-*cyclopenta*[c][2]*benzopyran*} (13) (42 mg, 95%), m.p. 220 °C (decomp.) (Found: C, 50.1; H, 2.7; Cl, 28.2. $C_{21}H_{14}Cl_4O_6$ requires C, 50.0; H, 2.8; Cl, 28.2%. Found: M^+, 505.9467. $C_{21}H_{14}{}^{35}Cl_2{}^{37}Cl_2O_6$ requires *M*, 505.9485); δ[15%, $(CD_3)_2SO$] 2.61 (s, Me), 2.80—3.30 (m, 9′b-H + 2 × 1′-H), 3.41 (d, *J* 18 Hz, 1 × 3-H), 4.31 (d, *J* 18 Hz, 1 × 3-H), 4.94 (m, 3′a-H), 6.00 (m, 3′-H), 6.30 (m, 2′-H), 9.26 (s, OH), 9.28 (s, OH), and 11.62 (s, 5-OH) (assignments of C*H* confirmed by spin-decoupling); $\nu_{max.}$ (Nujol) 3 450br 1 640s, and 1 585s cm^{-1}; *m/e* 504 (<2%, $C_{21}H_{14}{}^{35}Cl_3{}^{37}ClO_6$), 486 (<2), 284 (100), and 43 (80). The *triacetate* (Ac_2O, NaOAc, N_2, reflux) formed colourless prisms (from Bu^nOH), m.p. 245—246.5 °C (Found: C, 51.1; H, 3.2; Cl, 23.0. $C_{27}H_{20}Cl_4O_9$ requires C, 51.5; H, 3.2; Cl, 22.6%. Found: M^+, 629.9769. $C_{27}H_{20}{}^{35}Cl_3{}^{37}ClO_9$ requires *M*, 629.9832); δ(12%, $CDCl_3$) 1.63 (s, Me), 2.36 (s, Me), 2.39 (s, Me), 2.46 (s, Me), 2.65 (m, 2 × 1′-H), 3.10 (m, 9′b-H), 3.48 (d, *J* 18 Hz, 1 × 3-H), 4.12 (br d, *J* 18 Hz, 1 × 3-H), 5.06 (m,

3'a-H), 5.97 (m, 3'-H), 6.27 (m, 2'H) (spin-decoupling gave $J_{1',9'b}$ 8; $J_{2',3'}$ 6; $J_{3'a,9'b}$ 5 Hz); δ(12%, C_6D_6) 1.40 (s, Me), 1.78 (s, 2 × Me), 2.08 (s, Me), 2.35 (br d, J 8 Hz, 2 × 1'-H), 2.65 (m, 9'b-H), 3.40 (d, J 18 Hz, 1 × 3-H), 3.95 (d, J 18 Hz, 1 × 3-H), 4.84 (m, 3'a-H), and 5.78 (br m, 2'-H + 3'-H); $\nu_{max.}$ (Nujol) 1 775s and 1 685s cm^{-1}; *m/e* 630 (25%, $C_{27}H_{20}O_9{}^{35}Cl_3{}^{37}Cl$), 588 (38), 546 (35), 528 (45), 486 (100), and 43 (100). The *trimethyl ether* (aqueous 5% NaOH, Me_2SO_4, N_2) was colourless; δ(9%, $CDCl_3$) 2.62 (s, Me), 2.9—4.3 (complex, 14H), 5.07 (m, 3'a-H), 6.05 (m, 2'-H or 3'-H), and 6.36 (m, 3'-H or 2'-H); *m/e* 546 (40%, $C_{24}H_{20}{}^{35}Cl_3{}^{37}ClO_6$), 513 (12), 297 (90), 246 (100), and 43 (100). The *2',3'-dihydro-compound* (H_2, Pd–C, THF) was yellow (Found: M^+, 505.9698. $C_{21}H_{16}{}^{35}Cl_3{}^{37}ClO_6$ requires M, 505.9671); δ[10%, $(CD_3)_2SO$] 2.60 (s, Me), 3.40 (d, J 18 Hz, 1 × 3-H), 4.23 (d, J 18 Hz, 1 × 3-H), 9.23 (br s, 2 × OH), and 11.55 (br s, 5-OH), remaining resonances complex m, no absorption δ 5—8 region; *m/e* 506 (10%), 488 (<5), 470 (<5), 273 (10), and 43 (100).

(*b*) A solution of the adduct (23 mg) and tetracyanoethylene (10 mg) in [$^2H_6$]benzene was treated as described under (*a*). After 1 h at 80 °C the solution had signals at δ 2.05 and 6.48 due to 2-acetyl-5,6-dichloro-1,4-benzoquinone, and at δ 2.48 and 5.52 due to 5,5,6,6-tetracyanonorbornene, identical with authentic material.[33] The latter resonances were still present after 18 h at 80 °C, but the quinone had been reduced to its hydroquinone, some of which crystallised out. The spiro-compound (13) was not detected.

(*c*) A suspension of the adduct (1.218 g) in dry (P_2O_5) acetic acid (70 ml) was degassed, and the containing vessel was then sealed and heated at 80 °C for 4 h. The adduct dissolved, and a yellow precipitate of the spiro-compound (13) (603 mg) separated. The solvent was removed from the mother-liquor, and the dark yellow residue (513 mg) was rinsed with cold ether (2 × 5 ml), and then sublimed at 140 °C/0.05 mmHg to give *8-acetyl-5,6-dichloro*-cis-3a,8b-*dihydro*-1H-*cyclopenta*[b]*benzofuran-7-ol* (14) (277 mg) as yellow needles, m.p. 176—177 °C, from 95% ethanol (Found: C, 55.0; H, 3.6; Cl, 25.4. $C_{13}H_{10}Cl_2O_3$ requires C, 54.8; H, 3.5; Cl, 24.8%. Found, M^+, 284.000 754. $C_{13}H_{10}{}^{35}Cl_2O_3$ requires M, 284.000 695); δ[11%, $(CD_3)_2CO$] 2.20—2.80 (m, dominated by dm, J_1 17 Hz, 1-H + 8b-H), 2.74 (s, Me), 3.19 (' dd ', J_1 17, J_2 9 Hz, 1-H), 4.67 (' td ', J_1 8, J_2 3 Hz, 3a-H), 5.95 (br d, J 6 Hz, 3-H), 6.0 (m, dominated by br d, J 5 Hz, 2-H), and 12.50 (s, OH); $\nu_{max.}$ (Nujol) 1 630s cm^{-1}; *m/e* 284 (100%), 269 (100), and 43 (95). The colourless *acetate* (Ac_2O, NaOAc, 70 °C), had m.p. 94—95 °C (from C_6H_{12}) (Found: M^+, 326.007 050; $C_{15}H_{12}{}^{35}Cl_2O_4$ requires M, 326.008 308); δ(10% $CDCl_3$, 60 MHz) 1.9—3.4 (m, 2 × 1-H + 8b-H), 2.36 (s, Me), 2.50 (s, Me), 4.46 (' td ', J_1 8.5 J_2 3.5 Hz, 3a-H), and 5.8—6.3 (m, 2-H + 3-H); $\nu_{max.}$ ($CHCl_3$) 1 780s and 1 700s cm^{-1}. The *2,3-dihydro-compound* (H_2, Pd–C, THF), yellow, had m.p. 87—88.5 °C (Found: M^+, 286.014 184. $C_{13}H_{12}{}^{35}Cl_2O_3$ requires M, 286.016 344).

Fragmentation of Adduct (11).—A solution of the adduct (5 mg) in dry (P_2O_5) trifluoroacetic acid (1.5 ml) was kept at room temperature for 1 h: it became yellow. Removal of the solvent and crystallisation of the residue from chloroform–hexane (1 : 1) gave yellow needles, m.p. 219—220 °C, identical with 2-acetyl-5,6-dichlorohydroquinone. The soluble fraction had *m/e* 290 (80%, anthranol trifluoroacetate), 194 (82%, anthranol), and 193 (100%); t.l.c. (silica gel) gave a major spot identical with that of authentic anthrone.

We thank the S.R.C. for the award of Research Studentships (to H. F., L. M. J. H., and I. D. H.).

[1/531 *Received*, 6th *April*, 1981]

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