A Derivative of Tricyclo[6.3.1.0^{2,7}]dodecane from the Reaction between 2,6-Dimethyl-1,4-benzoquinone and a Quinonylmethyl Carbanion; Transformations involving Nucleophilic Attack at Carbonyl Oxygen, and a Rearrangement to a Spirobenzofuran Derivative related to Usnolic Acid

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2,6-Dimethyl-1,4-benzoquinone resembles other quinones in that, in weakly basic media, it reacts with the 3-methyl-1,4-naphthoquinon-2-ylmethyl carbanion (I) to give a derivative (III) of fluorene as one of two main products. But the other is the methylenediquinone (VI) and not the expected derivative (V) of xanthen.

In a more basic medium the chief reaction product is the bridge trione (Xa), which contains the tricyclo[6.3.1.0^{2,7}]-dodecane skeleton. The stereochemistry is partly defined by photoisomerisation of the acetate to the pentacyclo-[6.3.1.0^{2,7}.0^{4,10}.0^{5,9}]dodecane derivative (XII). In acidic media, a retroaldol reaction leads from the bridge to the hemiacetal (XIVa) with a quinol nucleus. Oxidation gives the quinone–quinone (XV) which is isomerised by acid to the benzofuran derivative (XVI), possibly through enolisation and nucleophilic attack by the enol upon carbonyl oxygen, with certain cycloadditions of the carbanion (I) providing examples of the base-catalysed counterpart.

In trifluoroacetic acid either the bridge trione (Xa) or the quinol hemiacetal (XIVa) gives, by dehydration and ring contraction, a red spiran (XVIIa) related to usnolic acid. The colour is believed to result from internal charge transfer of the quinhydrone type.

In continuing our exploration of the behaviour of the carbanion (I) towards quinones,[1-3] we have examined the reaction with 2,6-dimethyl-1,4-benzoquinone and discovered novelties both in the reaction itself and in the chemistry of one of the chief products, a bridge compound (X)† that undergoes a series of isomerisations and cyclisations some of which are of uncommon types.

We expected the carbanion (I) to react with dimethylbenzoquinone as it does with the homologous trimethylbenzoquinone.[2c] In parallel reactions, addition as in diagram (II) would give the fluorene derivative (III), addition as in diagram (IV) giving the xanthen derivative (V). In practice, the fluorene derivative could be obtained in up to 30% yield, whereas the xanthen derivative was not obtained at all, the methylenediquinone (VI) being isolated (43%) instead. Repetitive attack by the carbanion gave a trace of the triquinone (VII). These quinones are not the true primary products, which must be at the quinhydrone level of oxidation, but are generated by an additional oxidative step. Accordingly, an excess of the dimethylquinone was used and 2,6-dimethylquinol isolated.

The absent xanthen derivative (V) might have been formed in the usual way but rapidly destroyed by base since generation of the carbanion (VIII) would expose the system to the ring opening indicated and subsequent oxidation to the diquinone (VI). Nevertheless, experience in other series[2c,3] suggested that the carbanion should be trapped by a further condensation with an excess of dimethylbenzoquinone to give the bridge trione (IX). A bridge trione was indeed isolated in yields of up to 70% but it had structure (Xa), showing that the carbanion trapped was (XI) and not the expected one. Hence 2,6-dimethyl-1,4-benzoquinone differs from all other quinones studied so far in that it forms no xanthen derivatives with the carbanion (I).

† All structures in the paper refer to racemates.

[1] F. M. Dean, L. E. Houghton, and R. B. Morton, *J. Chem. Soc.* (*C*), 1967, 1980.

[2] F. M. Dean and L. E. Houghton, *J. Chem. Soc.* (*C*), (*a*) 1968, 2060; (*b*) 1970, 722; (*c*) 1971, 1902.

[3] F. M. Dean, K. B. Hindley, and L. E. Houghton, *J. Chem. Soc.* (*C*), 1971, 1171.

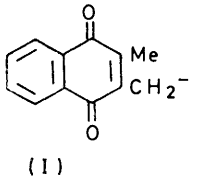
TABLE 1

^{1}H N.m.r. spectra (τ values) determined at 100 MHz for the bridge trione (Xa) and some transformation products

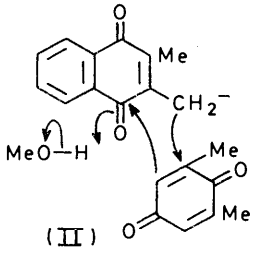
		Upper benzoquinone nucleus			Lower benzoquinone nucleus				ABC system			Naphthoquinone nucleus				
Compound	Solvent	H *a*	Me *b*	Me *c*	H *f*	Me *g*	H *d*	Me *h*	H *i*	H *j*	H *k*	Me *l*	H *n* (2 H)	H *m* (2 H)	OH	OAc[e]
Bridge trione (Xa)	$(CD_3)_2SO$	3.55	8.40	8.70	3.55	8.20	7.15	8.70				7.95	*ca.* 2.20	*ca.* 2.05	4.50	
Bridge trione (Xa)	$CDCl_3$–$Cl_3C{\cdot}CO{\cdot}NCO$	3.56	8.04	8.44	2.92	8.23	7.06	8.50		*ca.* 7.2 (3 H)		7.90	*ca.* 2.30	*ca.* 1.96		
Bridge trione acetate (Xb)	$CDCl_3$	3.63 (q, 2)	8.10 (d, 2)	8.59	3.00 (q, 2)	8.26 (d, 2)	7.16	8.51	6.9	*ca.* 7.4 (2 H)		7.92	*ca.* 2.32 (m)	*ca.* 1.93 (m)		8.14
Cyclobutane trione acetate (XII) *	$CDCl_3$	7.48 (dd, 2.5, 3.0)	8.63	8.59	6.69 (d, 2.5)	8.91	7.32 (d, 2.0)	8.41	7.26 (2 H)		7.68	7.81	*ca.* 2.26 (m)	*ca.* 1.90.(m)		8.29
Quinol hemiacetal (XIVa)	$CDCl_3$	3.58	7.87	7.80	4.25 (q, 2)	7.90 (d, 2)		8.46	6.62	*ca.* 7.0 (2 H)		8.00	*ca.* 2.38 (m)	*ca.* 1.98 (m)	6.60 †	
Quinol hemiacetal acetate (XIVb)	$CDCl_3$	3.44	7.88	7.74	4.21 (q, 0.5)	7.93		8.45	*ca.* 6.2	*ca.* 7.3 (2 H)		8.02	*ca.* 2.31 (m)	*ca.* 2.00 (m)		7.93
Quinone–quinone (XV)	$CDCl_3$	3.49 ‡ (q, 2)	8.10 § (d, 2)	7.75	3.54 ‡ (q, 2)	7.96 § (d, 2)		8.36	6.17	6.98	7.28	7.78	*ca.* 2.37 (m)	*ca.* 2.04 (m)		
Benzofuran (XVIa)	$CDCl_3$	3.47	7.90	7.63	3.32 (q, 1.5)	7.86 (d, 1.5)		8.41		7.33 (d, 13)	6.75 (d, 13)	8.06	*ca.* 2.3 (m)	*ca.* 2.0 (m)	*ca.* 5.7 †	
Benzofuran acetate (XVIb)	$CDCl_3$	3.37	7.73	7.63	3.27	7.86		8.38		7.32 (d, 13)	6.72 (d, 13)	7.16	*ca.* 2.33 (m)	*ca.* 1.98 (m)		7.96

* Values checked at 220 MHz. † Destroyed by deuterium oxide. ‡ Interchangeable values. § Interchangeable values.

Multiplicities and splittings (Hz) (in parentheses) are given when resolution permitted measurement. Line broadening was observed for some protons associated with vinylic or aromatic systems but is not indicated.



(I)



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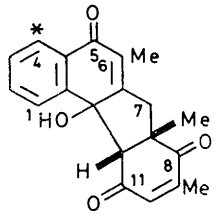

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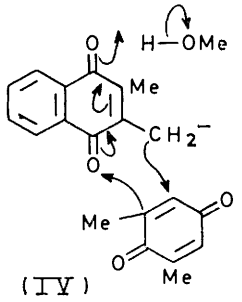

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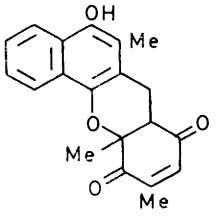
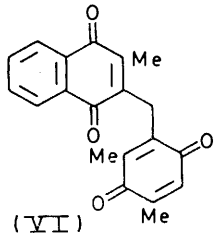
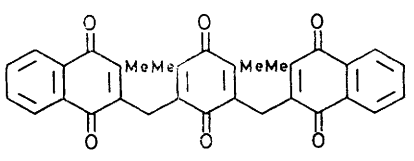


(V)



(VI)



(VII)

The bridge trione (Xa) is a tertiary alcohol esterified by acetic anhydride when sulphuric acid, but not pyridine, is the catalyst. Both the alcohol and the acetate (Xb) show several complex i.r. bands in the carbonyl region that are not amenable to the making of specific assignments since they all correspond to conjugated carbonyl groups in similar environments. The n.m.r. spectra (Table 1) show that two vinylic methyl systems are present; it is evident, however, that these and other features would be much the same in the bridge trione (IX) or in some similar bridge compound derived by the addition of a dimethylquinone nucleus across the fluorene alcohol (III). Thus the assignment of structure (Xa) required special care. From models of the fluorene alcohol (III) it appears that only the starred aromatic proton is within the deshielding cone of a carbonyl group, and accordingly the n.m.r. spectrum reveals that there is only one proton resonating at the appropriately low field (τ 2.02). In contrast, and in agreement with its naphthoquinone structure (Xa), the bridge trione has a two-proton resonance at this point (Table 1). The mass spectral fragmentation of the bridge trione also excludes a formulation based upon a fluorene nucleus. The bridge trione easily loses its bridge (as 136, 137, or 138 m.u.) as do the other bridge compounds [2c,3] presumably because a dimethylbenzoquinone nucleus is lost as such or in combination with one or more hydrogen atoms.[4] There is no loss of an enedione grouping (94, 95, or 96 m.u.) such as characterises the most important fragmentation in the fluorene alcohol (III) (Table 2). We have observed the loss of such fragments from fluorene derivatives before [2] and associated it with the production of a relatively stable ethylenic bond in the remainder. Thus it is not seen in the spectra of 2,6-dimethylbenzoquinone or of the related quinones (VI) and (VII), but it might be formulated for the fluorene alcohol (III) as in Scheme 1.

In the ^{1}H n.m.r. spectrum of the bridge trione acetate

[4] R. W. A. Oliver and R. M. Rashman, *J. Chem. Soc.* (*B*), 1971, 341.

(Xb) (Table 1) a complex set of peaks is seen between τ 6.6 and 7.3 which we have not attempted to analyse completely but which persists with little variation

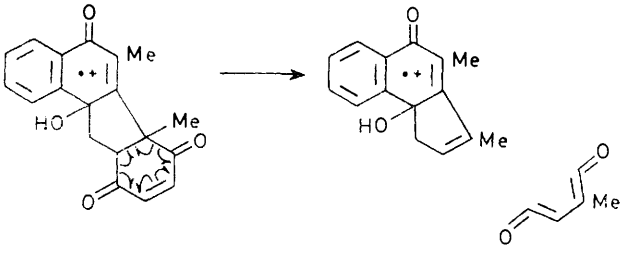
TABLE 2

Mass spectral fragmentations * (at 70 eV)

Methylenediquinone (VI)	320 (100), 305 (56), 291 (10), 277 (45), 249 (17), 186 (4) [a]
Fluorene alcohol (III)	322 (7), 304 (28),[b] 210 (43),[c] 209 (50),[c] 208 (19),[c] 186 (100) [a]
Bridge trione acetate (Xb)	500 (57), 457 (100), 440 (45), 412 (26), 364 (12),[d] 322 (75),[d] 305 (49),[d] 255 (24),[e] 227 (20),[e] 186 (79),[a] 138 (69),[f] 137 (64) [f]
Quinol hemiacetal (XIVa)	458 (100), 440 (26),[b] 423 (17),[b] 320 (10),[d] 305 (10),[d] 273 (66),[e] 272 (77),[e] 255 (53),[b,e] 254 (47),[b,e] 186 (30),[a] 185 (16),[a] 138 (23)[f]
Quinone–quinone (XV)	456 (43), 441 (17), 438 (14),[b] 423 (8),[b] 411 (13), 360 (16),[c] 297 (14),[b,c] 271 (100), 186 (31),[a] 175 (26) [c,e]
Benzofuran (XVI)	456 (38), 360 (18),[c] 345 (8),[c] 271 (100),[e] 189 (4), 186 (3),[a] 176 (6),[c,e] 175 (7),[c,e] 135 (6),[f] 97 (6),[g] 96 (3)[g], 95 (5) [g]
Red spiran (XVIIa)	440 (100), 425 (32), 407 (6),[b] 397 (8), 281 (10), 255 (69),[e] 186 (7) [a]
Spiran acetate (XVIIb)	482 (100), 467 (35), 440 (97), 412 (12), 407 (12), 397 (15), 323 (10), 255 (89),[e] 242 (31), 226 (32), 215 (26), 198 (22), 186 (22),[a] 135 (11) [f]

* Relative abundances in parentheses. Peaks arising merely from losses of CH_3, CO, CHO, keten, or acetate are not specifically identified. Peaks of diagnostic value are indicated by the following superscripts, which identify the fragment in itself or the fragment(s) lost to produce it: [a] $C_{12}H_9O_2$ or $C_{12}H_{10}O_2$; methylnaphthoquinonylmethyl residue; [b] by loss of H_2O, [c] by loss of CO·C(Me):CHCO, often plus H or 2H; [d] by loss of $C_8H_8O_2$, $C_8H_9O_2$, or $C_8H_{10}O_2$; dimethylbenzoquinone; [e] by loss of methylnaphthoquinonylmethyl residue; [f] dimethylbenzoquinone residue; [g] CO·C(Me):CH·CO, often with extra hydrogen.

through transformations to be discussed below and which can only be assigned to an ABC spin system that includes the methylene group of the original carbanion (I). This established the point at which the carbanion



SCHEME 1

is attached to the first benzoquinone nucleus and leaves no choice but to add the second (bridging) benzoquinone nucleus across the first as shown in diagram (Xa). Features of diagram (Xa) now requiring proof are (i) the stereochemistry of the bridge with respect to the naphthoquinonyl grouping, (ii) the *endo*-relation between the two benzoquinone nuclei, and (iii) the head-to-tail relation between the same two nuclei.

Feature (i) is determined by the fact that the naphthoquinonyl grouping will screen its side of the molecule from the approach of the benzoquinone nucleus that is to form the bridge. Feature (ii), the *endo*-configuration, is demanded by the fact that irradiation of the acetate (Xb) unites the two vinylic systems to form the cyclobutane derivative (XII), the i.r. spectrum of which shows that the naphthoquinone residue persists, but that the other conjugated carbonyl groups have become saturated and strained ($\nu_{max.}$ *ca.* 1 730 cm^{-1}). The n.m.r. spectrum agrees, for it contains no vinylic resonances but has new bands between τ 7 and 8 as is usual in cyclobutane derivatives and at the same time two methyl resonances that have moved upfield from around τ 8.2 to a region near 8.8. While it is difficult to assign some of these new bands unambiguously, the doublet at 6.9 (J 2.3 Hz) can be assigned to H^f in (XII) because it is at a relatively low field we have come to associate with the proximity of an acetoxy-group. The field-independent splitting accords with its 1,3-*cis*-relation with H^a in the cyclobutane ring and the absence of other splitting accords with the configuration assigned to the naphthoquinonylmethyl group since a W interaction with H^i is not possible for this placing. For H^a a doublet of doublets is appropriate since coupling is possible with both H^f and H^d, and accounts for a band (two doublets merging to form a triplet) at 7.53 exhibiting field-independent splittings of appropriate sizes (J 2.4 and 3.4 Hz). Resonances for H^d could not be distinguished amongst overlapping signals.

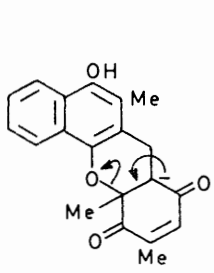
Because the transformations undergone by the bridge trione have been monitored mainly by n.m.r. spectroscopy we have found it best to label the protons as in diagram (X) and have retained these labels throughout to facilitate comparisons. As the alcohol was not very soluble we first assigned resonances to protons in the acetate (Xb) and obtained an unambiguous fit (Table 1) except for the angular methyl groups Me^c and Me^h the resonances of which could, perhaps, be interchanged. Of the two vinylic methyl groups, Me^g is assigned the resonance at higher field because it lies under an enedione ethylenic bond and should be shielded by it as happens in similar bridge compounds.[3] On the other hand, the adjacent vinylic proton H^f is assigned the resonance at τ 3.00, which is at exceptionally low field because, we believe, it is deshielded by the adjacent acetoxy-carbonyl group. Thus the alcohol (Xa) (in dimethyl sulphoxide) exhibits both vinylic resonances near τ 3.55 which is the usual position; and in agreement, the alcohol in deuteriochloroform also shows two resonances near τ 3.5, one of which shifts downfield to 3.0 upon addition of trichloroacetyl isocyanate,[5] only H^f being near enough to be so affected.

Attempts to use trifluoroacetic acid as a solvent for n.m.r. studies disclosed that it readily converts the bridge trione alcohol (Xa) into a red compound with a different kind of structure. The first stage could be induced selectively by warm chloroacetic acid and begins with a retroaldol condensation at one bridgehead of (Xa); accordingly, the acetate (Xb) is stable. In turn this change allows what was the bridge ring to aromatise, producing the quinol derivative (XIII) which is readily

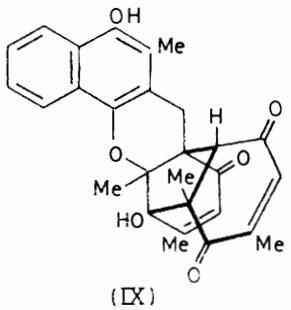
[5] I. R. Trehan and C. Monder, *Tetrahedron Letters*, 1968, 67.

isolated but appears to exist as the tautomeric hemiacetal (XIVa). The fact of aromatisation establishes point (iii) above, the head-to-tail relation between the two benzoquinone nuclei in (Xa).

(Table 2) supports a quinol nucleus because it shows an important fragment ion *m/e* 138 (dimethylquinol equivalent) but none at *m/e* 136 (dimethylquinone equivalent) such as characterises the parent bridge trione. The



(VIII)



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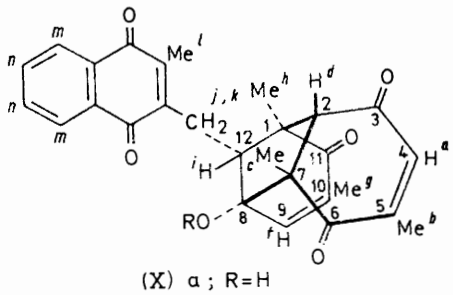
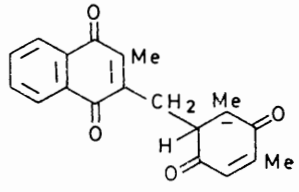
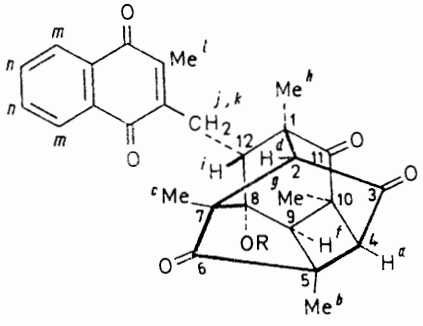


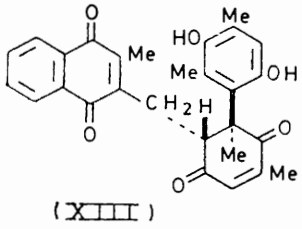
(X) a ; R=H
b ; R=COMe^{e}



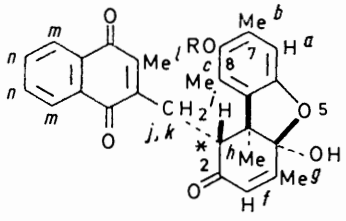
(XI)



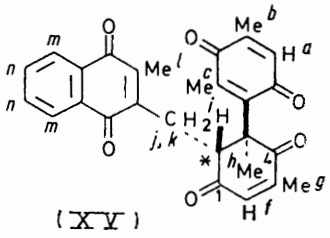
(XII) R=COMe^{e}



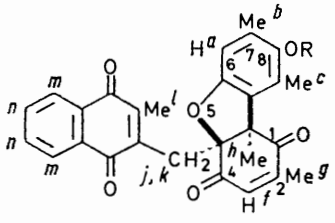
(XIII)



(XIV) a; R = H
b; R = COMe^{e}



(XV)



(XVI) a; R = H
b; R = COMe^{e}

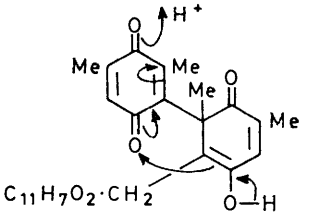
The existence in the hemiacetal (XIVa) of a quinol residue was difficult to establish directly. The n.m.r. technique does not clearly distinguish between quinone and quinol nuclei, but the coupling between H^{a} and Me^{b} is smaller in the aromatic nucleus. The mass spectrum electronic spectrum agrees. We have deduced from various compilations of u.v. data [6] and from isolated

[6] 'Organic Electronic Spectral Data,' ed. J. Kamlet, Interscience, New York, 1960, vols. 1—8; DMS UV Atlas of Organic Compounds, Butterworths, London, vols. 1—5.

observations (*e.g.* ref. 7) that, provided no further conjugation is present, quinol and its alkyl derivatives and ethers all absorb close to 295 nm even when further hydroxy- or alkoxy-groups are attached. Other hydroxylated benzene nuclei absorb near 285 nm much as phenol does. Esterification of either or both the quinol hydroxy-groups induces a blue shift and a reversion to the usual ' phenolic ' spectrum. The hemiacetal (XIVa) displays a band near 300 nm (Figure) not found in naphthoquinone, enone, or enedione spectra, and which can therefore be assigned to a quinol nucleus. Since acetylation gives a monoacetate showing the blue shift, (Figure) it follows that its structure is (XIVb); as pyridine was the catalyst the surviving hydroxy-group is confirmed as hindered (tertiary). Other indications of hemiacetal formation are the simplicity of the i.r. spectrum, which shows only bands appropriate to the naphthoquinone system, and the ready loss of H_2O in the mass spectrum (Table 2). The n.m.r. spectrum (Table 1) provides independent evidence of the hemiacetal structure because it shows that the resonance attributed to H^f occurs at fields about 0.7 p.p.m. higher in the quinol derivative (or its acetate) than in the parent bridge trione (Xa). Since no reasonable explanation offers itself in terms of shielding effects, the shifts must mean that deshielding has been removed, *i.e.* that the electron-withdrawing effect of a carbonyl group is no longer active. This view at once leads to a hemiacetal structure and identifies the carbonyl group responsible. Other details of the n.m.r. spectrum confirm that the naphthoquinone and three-proton spin system have not been modified, while a pronounced downfield shift in the resonance of Me^c is as expected for the change from an angular methyl group to an aromatic one.

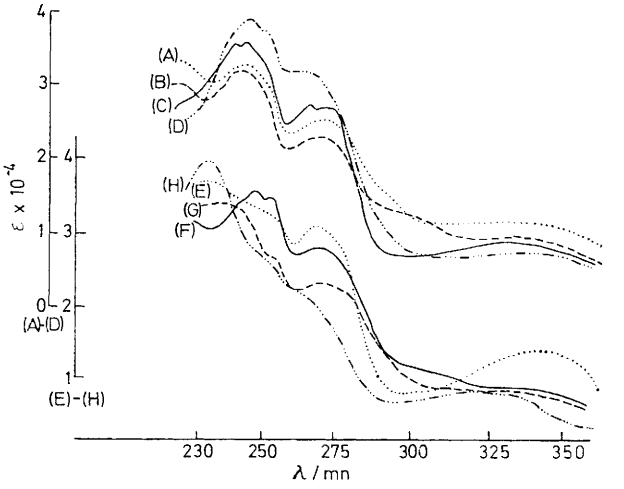
Since the quinol derivative (XIVa) is readily oxidised to the quinone–quinone (XV), many of the points used as evidence for the quinol nucleus were tested by reference to this. Thus the mass spectrum (Table 2) shows the loss of a fragment of 136 instead of 138 m.u. in accord with the presence of a dimethylquinone instead of a dimethylquinol nucleus; the quinol u.v. band near 300 nm has vanished (Figure); the carbonyl stretching region of the i.r. spectrum is now very complex; all hydroxylic characteristics are absent; and H^f resonates at the same field as in the bridge trione.

Being now satisfied with structure (XIVa) for the quinol hemiacetal, we treated this with trifluoroacetic acid and obtained the red compound as easily as from the original bridge trione and in about the same, rather poor, yield (about 20%). The rest of the product was unmanageable. Structure (XIVa) or the tautomer (XIII) offers opportunities for redox reactions which, amongst other possibilities, could produce the quinone–quinone (XV) together with some reduced body. Before proceeding, therefore, we examined the effect of trifluoroacetic acid upon the quinone–quinone and found that it produced in high yield a new compound which, however, was not closely related to the red one. The new compound has the benzofuranoid structure (XVIa) and appears to result from an isomerisation in which an enolic system engages a quinone nucleus, thus:



If the proton is attached first, the cyclisation becomes a modification of a coupling reaction between a phenolic (enolic) residue and a phenoxylium ion.[8] If cyclisation occurs first, the enolate must attack carbonyl oxygen instead of carbon, a mode strongly favoured by the concurrent development of aromaticity. There is now a parallel with the cyclisation in (IV), the reaction being essentially a Michael addition where the terminal atom in a dienone system happens to be oxygen instead of carbon.

As a quinol derivative, the benzofuran (XVIa) has a u.v. absorption band near 300 nm (Figure) shifted



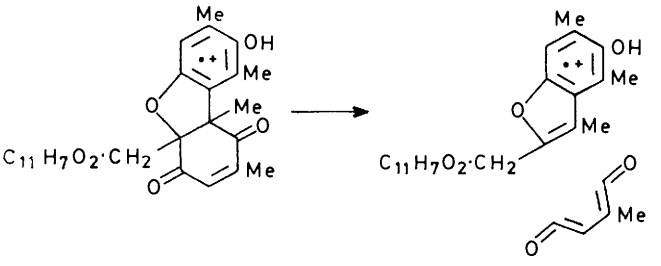
U.v. spectra (*ca.* 10^{-4}M-solutions in ethanol) of (A) the hemiacetal acetate (XVIb); (B) the hemiacetal (XVIa); (C) the bridge trione acetate (Xb); (D) the quinone–quinone (XV); (E) the red spiran (XVIIa); (F) the benzofuran (XVIa); (G) the benzofuran acetate (XVIb); and (H) the spiran acetate (XVIIb)

hypsochromically by acetylation to (XVIb); and, in the n.m.r. spectrum, it has diminished coupling between H^a and Me^b. A simple AB quartet (J 13 Hz) confirms the removal of the third proton, H^i. The mass spectrum (Table 2) shows that the naphthoquinone residue is intact, in that the methylnaphthoquinonylmethyl grouping is still readily lost as a unit—indeed, the loss is greatly enhanced by the ether oxygen atom now attached at the point of fission. In contrast, the dimethylbenzoquinone

[7] D. C. Laidman, R. A. Morton, J. Y. F. Patterson, and F. J. Pennock, *Biochem. J.*, 1960, **74**, 541; T. Nakamura and S. Kijima, *Chem. and Pharm. Bull.* (*Japan*), 1971, **19**, 2318; 1972, **20**, 794.

[8] M. S. Chauhan, F. M. Dean, K. B. Hindley, and M. L. Robinson, *Chem. Comm.*, 1971, 1141.

residue has been modified: fragmentation ejects mainly an enedione segment in its place; again this is an unusually important fragmentation, evidently because now the residue is not merely an alkene but also an aromatic (furanoid) system (Scheme 2).

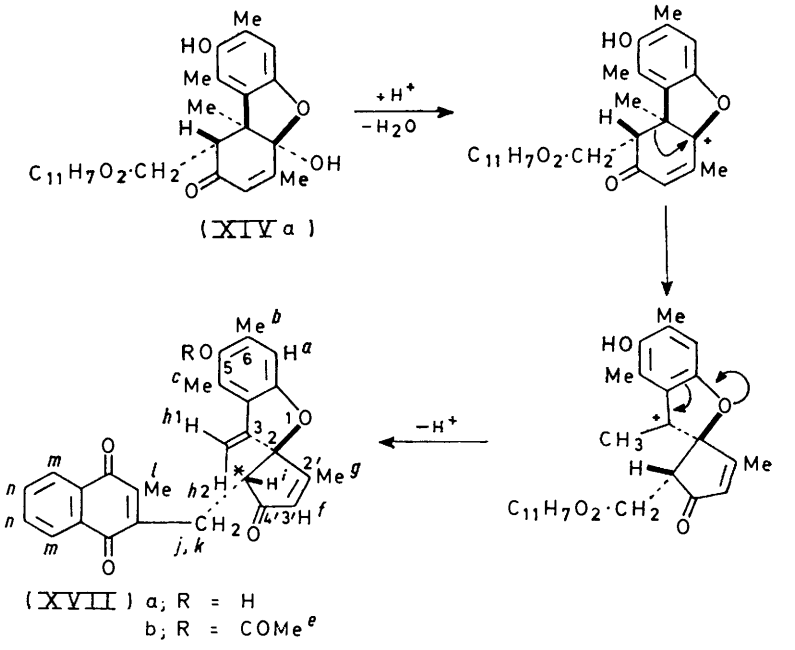


SCHEME 2

Returning to the process by which trifluoroacetic acid converts the bridge trione (Xa) *via* the hemiacetal (XIVa) into the red compound, one notes that, analytically, the reaction is a dehydration which destroys a methyl group without loss of carbon. The ^{1}H n.m.r. results (Table 3) suggest, but do not prove, that it is the angular methyl group in (XIVa) that is modified. The naphthoquinone nucleus is not changed, for its characteristics are clear in n.m.r., i.r., and mass spectral patterns. The three-proton ABC spin system is also in evidence, as is one phenolic or enolic hydroxy-group. No other features were discerned unambiguously except for a new i.r. band close to 1 700 cm^{-1} that was taken as an indication of the presence of a cyclopentenone carbonyl group, and therefore of the occurrence of a ring contraction.

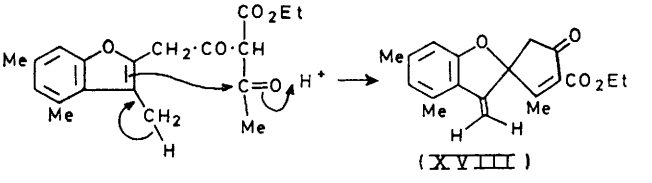
[9] F. M. Dean, P. Halewood, S. Mongkolsuk, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 1953, 1250; F. M. Dean, C. A. Evans, T. Francis, and A. Robertson, *ibid.*, 1957, 1577.

Initial attack by protons would remove the hemiacetal hydroxy-group from (XIVa) as in Scheme 3, which shows a rearrangement sequence terminating in structure (XVIIa) with a cyclopentenone ring system and destroying the angular methyl group as required. At each stage the carbocationic centres are stabilised by interaction with oxygen atoms in a manner impossible for the intermediates in any other acid-catalysed rearrangement we envisaged. Moreover, there is precedent for much of Scheme 3 in the acid-catalysed isomerisation [9] of the fungal metabolite usnic acid to usnolic acid and in related cyclisations illustrated in Scheme 4 by the formation of the spiran (XVIII). The ^{1}H n.m.r. features (Table 3) of the red compound or its acetate and of the spiran (XVIII) have the expected similarities and demonstrate clearly the presence of the exocyclic methylene groups, but they do not demonstrate directly the presence of a spiro-atom in either compound. They



SCHEME 3

do not even securely identify the quinol nucleus in the red compound. These points were best established by the ^{13}C n.m.r. spectrum of the acetate (XVIIb) in conjunction



SCHEME 4

with the spectra of selected reference compounds including the spiran (XVIII). The assignments are contained in Table 4, and the correlations are the closest possible; while in one or two instances assignments are ambiguous the discrepancies are too small to be of consequence for

this discussion. Only outstanding points need be discussed. There are signals (singlets) in spectra of the spirans at a shift of *ca.* 98 p.p.m. which are well clear of other signals and at a point difficult to explain except by sp^3 carbon atoms attached to (ether) oxygen and to other electronegative groupings as well, and it seems inevitable that they must be assigned to spiro carbon atoms. A signal at as low a field as 202 p.p.m. is not common in carbonyl compounds other than five-membered ring ketones, and confirms the cyclopentenone grouping. The exocyclic methylene carbon atom is defined by a signal (quartet) at 106.2 p.p.m. The quinol system is defined by the close correspondence between the figures shown and those ' calculated ' from shift tables [10] combined with those shown for the models; the same is true for the naphthoquinone residue.

Although these findings establish beyond reasonable doubt the natures of the various groupings present in the red compound (XVII), they do not completely establish the manner in which they should be assembled. In off-resonance decoupled ^{13}C spectra, the signal numbered 17 in Table 4 is a doublet, but if H^f is selectively saturated by irradiation then the signal collapses to a singlet. At the same time the signal from the spiro atom sharpens noticeably; before, it had been a ' singlet ' though rather a broad one. Hence the spiro carbon atom lies on a long-range coupling path to H^f as it does in diagram (XVII), and as H^f is connected by long-range coupling with Me^g

TABLE 3

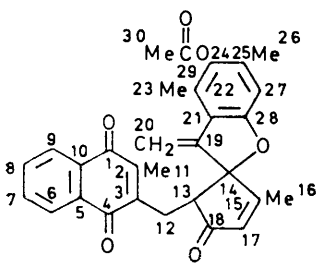
^1H N.m.r. spectra (τ values; splittings in Hz) for red spiran (XVIIa) and its relatives in $CDCl_3$ at 100 MHz

Compound	Quinol nucleus			Cyclopentenone nucleus		Ring or *exo*-methylene		ABC		Naphthoquinone nucleus			OH or OMe
	H^a	Me^b	Me^c	H^f	Me^g	H^{h1}	H^{h2}	$H^{i,j,k}$		Me^l	$H^{n,m}$	$OA^{c,e}$	
Red spiran (XVIIa)	4.17 (d?, 1)	8.00 (d, 1)	8.24	3.90 * (q, 1.5)	8.18 * (d, 1.5)	5.39 † (d, 1)	4.52 † (d, 1)	6.34 (mm, 6, 11?)	*ca.* 7.1	7.80	2.11—2.35 (mm)		7.0 ‡
Spiran acetate (XVIIb)	4.02br	7.96 (d, 1)	8.28br	3.91 (q, 2)	8.10 (d, 2)	5.34 (d, 1)	4.52 (d, 1)	6.37 (mm, 6, 11?)	*ca.* 7.1	7.89	2.10—2.40 (mm)	7.74	
Model spiran (XVIII)	3.42br (2 H)	7.67br	7.58br		7.86	5.22 (d, 1)	4.59 (d, 1)	6.97 (d, 18)	7.22 (d, 18)				6.15
Cyclobutane acetate (XIX)	3.41br	7.94br	8.48	3.89 (q, 2)	8.12 (d, 2)	7.82 (d, 15)	6.74 (d, 15)	6.30 (t, 7)	7.40 (d, 7?)	8.73	2.0—2.4 (mm)	7.84	

*, † Spin systems confirmed by decoupling. ‡ Removed by deuterium oxide.

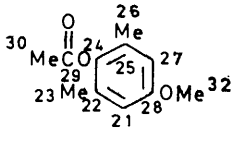
TABLE 4

^{13}C N.m.r. spectra (δ_C values; solvent deuteriochloroform)*

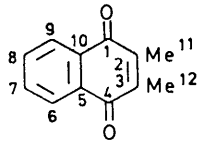


(A)

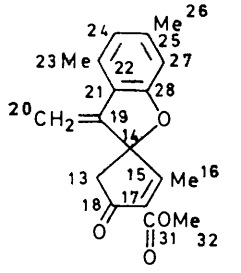
[≡ (XVIIb)]



(B)



(C)



(D)

[≡ (XVIII)]

Carbon no.† Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
(A)	183.7	144.5	144.4	183.7	132.0	132.0	125.7	125.6	132.0	131.6	12.8	22.8	57.1	97.9	172.5	13.1
(B)																
(C)	184.2	143.1	143.1	184.2	131.9	133.0	125.9	125.9	133.0	131.9	12.7	12.7				
(D)													50.7	92.4	178.7	12.95

Carbon no.† Compound	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
(A)	127.6	202.3	142.0	106.2	121.6	133.0	16.9	158.9	123.1	13.3	109.7	143.9	168.6	20.3		
(B)					113.6	130.9	16.5	156.9	130.9	16.5	113.6	141.9	168.7	20.2		55.2
(C)																
(D)	148.3	198.6	141.6	103.6	119.9	135.3	21.6	124.7	132.4	19.9	108.5	163.0			162.8	51.9

* Throughout, the multiplicities determined by off-resonance decoupling were those required by the assignments. † This numbering is used solely for the purposes of this Table.

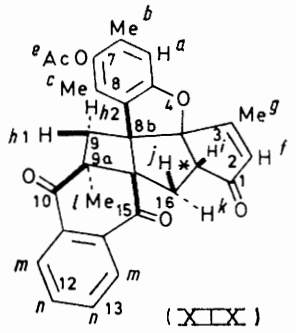
[10] G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley, New York, 1972, p. 81.

the vinylic methyl system must be part of a cyclopentenone ring also containing the spiro atom. This leaves structure (XVIIa) as the only valid one.

Nevertheless such a structure for the red product was difficult to accept because it contains several insulated chromophores none by itself capable of imparting so deep a colour. Eventually models showed that in this structure the quinone ring can be arranged to lie over the quinol ring and roughly parallel to it with the oxygen atoms aligned in much the same fashion as has been established crystallographically for some quinhydrones.[11] Hence the red colour can be attributed to an intramolecular charge transfer band and, accordingly, the spectrum was found to be independent of concentration (in the range 3.13×10^{-3} to 3.13×10^{-4}M) but to be strongly dependent upon changes in the quinol nucleus. Thus ionisation by hydroxide ion diminishes the band at 338 nm and produces a new one at 378 nm, acidification restoring the original spectrum. On the other hand, acetylation decreases the auxochromic effect of the phenolic residue and the acetate is merely deep yellow.

The quinhydrone-like arrangement envisaged for the red compound also permitted a simple explanation for the unusually high field signal necessarily assigned to the aromatic proton H^a in the quinol ring (Table 3), for this proton must lie in the shielding cone of the naphthoquinone benzene ring and consequently its signal must be shifted upfield by at least 0.5 p.p.m. Other groups in the vicinity lie near the edge of the cone and need not be expected to show any marked influence. In other respects the n.m.r. spectra are normal and bear the appropriate similarities to that of the model spiran [9] (XVIII).

Unlike the red compound, the acetate is unstable in daylight and is bleached during some hours. A similar difference between a phenol and its acetate has been noted in another study in this series and attributed to quenching of the excited system in one molecule by the phenolic residue in a second.[12] In the present case the product is clearly no longer a quinone; apart from the absence of colour, the characteristic pattern of quinone carbonyl absorption has given way to a new, intense band near 1 690 cm^{-1} as found in acetophenone derivatives. The resonance due to the methyl group Me^l has moved upfield to τ 8.7, and it follows that the ethylenic bond of the naphthoquinone unit has been saturated. The exocyclic methylene group has been similarly saturated; its proton resonances move upfield and J increases to 15 Hz (Table 3), and as there is no other major change the new compound must be the cyclobutane derivative (XIX). Other orientations can be rejected on the grounds that they would needlessly result in much greater ring strain. Indeed, the new position of the naphthalene system in (XIX) is attainable from the position in the quinhydrone-like precursor merely by a rotation through *ca.* 70° without a change of plane. In its new position, the benzene ring of the naphthalene system no longer shields the quinol proton but instead it lies over one of the quinol methyl groups (Me^c); accordingly, it is this that now registers a marked shift upfield (Table 3). The only feature not immediately explicable in terms of structure (XIX) is



(XIX)

the behaviour of the three-proton spin system, which appears for the first time as a triplet for one proton (H^i) and a doublet for two others (H^j and H^k). These protons are now rigidly held in position, and may be giving a ' deceptively simple ' spectrum.

In conclusion, we must justify some stereochemical assumptions made in passing. It is convenient to begin with the cyclobutane derivative (XIX) because this structure defines the configuration at the starred position unambiguously. If the system in the spiran (XVIIa) is to attain the quinhydrone-like orientation suggested for it, then again only one configuration is possible at the same centre; these configurations are congruent. The corresponding centre (position 4a) in the benzofuran nucleus of (XVIa) can be taken as having the equivalent configuration shown because the alternative ring fusion would be much more strained; we also note that in this configuration, despite the presence of both quinone and quinol nuclei in this molecule, these two units cannot be brought into a quinhydrone-like alignment and so this compound exhibits no unusual colour. The arguments cannot reach back to the parent quinone–quinone (XV), however, because the original configuration at the starred position could have been lost by enolisation during the cyclisation process; so here a configuration has been assumed for simplicity. Had the spiran (XVIIa) been formed as in Scheme 3 by essentially concerted reactions, then its structure demands for hemiacetal (XIVa) the configuration shown, but as it is produced in relatively low yield and the acid used could induce a preliminary inversion at the starred centre the stereochemical conclusion is only tentative. However, it is strongly supported by models, which demonstrate that this configuration will not allow the quinone and quinol nuclei to attain the quinhydrone-like relation required for the appearance of a charge-transfer band, whereas the alternative configuration would allow that. As there is no special colour in the hemiacetal the stereochemistry in

[11] R. Foster and M. I. Foreman, in ' The Chemistry of the Quinonoid Compounds,' ed. S. Patai, Interscience, London, 1974, ch. 6.

[12] F. M. Dean, G. H. Mitchell, B. Parvizi, and C. Thebtaranonth, *J.C.S. Perkin I*, 1976, 595.

(XIVa) seems justified. This brings us back to the first member of the series, the bridge trione (Xa), the stereochemistry of which was suggested by general considerations stated at the outset; it is satisfying to note that this stereochemistry is identical with that deduced for the derived hemiacetal and its transformation products.

EXPERIMENTAL

U.v. spectra were measured on solutions (*ca.* 10^{-3}M) in ethanol. I.r. spectra were usually determined on mulls in paraffin; only diagnostic bands are reported. Molecular weights were determined mass spectroscopically.

Interaction of the Carbanion (I) *and* 2,6-*Dimethyl*-1,4-*benzoquinone; Sodium Acetate as Base.*—3a,4,9,9a-Tetrahydro-9a-methyl-3*H*-benz[*f*]indazole-4,9-dione [1] (500 mg) in chloroform (5 ml) was mixed with 2,6-dimethylbenzoquinone (600 mg) in methanol (20 ml) at 22 °C and treated with sodium acetate trihydrate (650 mg) in methanol (8 ml). The solution reddened and nitrogen was evolved slowly but steadily. After 45 min, a slight precipitate was removed and purified from dioxan giving 2,6-*dimethyl*-3,5-*bis*-(3-*methyl*-1,4-*naphthoquinon*-2-*ylmethyl*)-1,4-*benzoquinone* (VII) as tiny yellow crystals (7 mg), m.p. 257—259°, $\nu_{max.}$ 1 660, 1 645, 1 605, 1 300, and 715 cm^{-1} (Found: *M*, 504. $C_{32}H_{24}O_6$ requires *M*, 504). Aside from identifying the molecular ion, the mass spectrum showed that the main fragmentations involved only the loss of methyl groups or a major fission into a diquinone segment (*m/e* 320) and a methylnaphthoquinonylmethyl segment (*m/e* 184).

The filtrate was slightly acidified with dilute hydrochloric acid and diluted with water. Organic materials were collected into ether, dried (Na_2SO_4), and recovered by evaporation under reduced pressure; they formed a gum that partly crystallised after its solution in methanol had been concentrated and left. The solid crystallised from methanol giving 3-*methyl*-2-(3,5-*dimethyl*-1,4-*benzoquinon*-2-*ylmethyl*)-1,4-*naphthoquinone* (VI) as yellow needles (295 mg), m.p. 143—144°, $\lambda_{max.}$ 252 and 326 nm (log ε 4.52 and 3.51), $\nu_{max.}$ 1 660, 1 645, 1 605, 1 595, 1 290, and 710 cm^{-1} (Found: C, 75.1; H, 4.85%; *M*, 320. $C_{20}H_{16}O_4$ requires C, 74.9; H, 5.0%; *M*, 320).

Removal of the rest of the methanol under reduced pressure at 5 °C left a dark red oil which, taken up in benzene and chilled, provided 2,6-dimethylquinol as platelets (65 mg), identified by comparison with an authentic sample.

Concentration of the benzene solution led to the slow deposition of a yellowish solid which, after several recrystallisations from benzene, supplied (7a*R**,11a*R**,11b*R**)-7,7a,11a,11b-*tetrahydro*-11b-*hydroxy*-6,7a,9-*trimethylbenzo*[c]*fluorene*-5,8,11-*trione* (III) as yellow prisms (43 mg), m.p. 186—189°, $\lambda_{max.}$ 248 and 280 nm (log ε 4.45 and 3.95), $\nu_{max.}$ 3 400 (OH), 1 685 (enedione C:O), 1 660 (acrylophenone (C:O), 1 635 (aromatic C:C), and 770 and 720 cm^{-1} (aromatic CH) (Found: *M*, 322.120 48. $C_{20}H_{18}O_4$ requires *M*, 322.120 50). The benzene mother liquors contained the bridge trione (Xa) but this was better obtained as in the following experiment.

Interaction of the Carbanion (I) *and* 2,6-*Dimethyl*-1,4-*benzoquinone*: *Sodium Hydroxide as Base.*—(i) *Synthesis of the bridge trione* (Xa). The above tetrahydroindazole derivative (168 mg) in tetrahydrofuran (1 ml) at 23 °C was added to 2,6-dimethylbenzoquinone (200 mg) in methanol (1 ml). The mixture was cooled in ice and aqueous 0.01M-sodium hydroxide was added in small droplets with gentle stirring until evolution of nitrogen was brisk and continuous. The volume of alkali required was about 0.4 ml but varied from experiment to experiment for reasons not understood; however, too little alkali produced a sluggish response and a complex mixture of products whereas too much produced a fast reaction but also destroyed the desired product. In successful preparations a yellow crystalline precipitate appeared within 30 s although the mixture was normally left in ice until gas evolution had ceased (about 2 h) and then acidified with dilute hydrochloric acid. The solid was collected, washed with a little methanol, and recrystallised from benzene or chloroform to give the bridge trione (Xa), (1R*,2R*,7R*,8S*,12S*)-8-*hydroxy*-1,5,7,10-*tetramethyl*-12-(3-*methyl*-1,4-*naphthoquinon*-2-*ylmethyl*)*tricyclo*[6.3.1.$0^{2,7}$]-*dodeca*-4,9-*diene*-3,6,11-*trione*, as yellow prisms (235 mg), m.p. 230—232°, that tended to retain solvent of crystallisation (Found: *M*, 458.1728. $C_{28}H_{26}O_6$ requires *M*, 458.1729). This compound had $\lambda_{max.}$ 246, 267, 273, and 334 nm (log ε 4.34, 4.20, 4.19, and 3.51), $\nu_{max.}$ 3 500 (OH), 1 660 (quinone and enedione C:O), 1 620 and 1 595 (naphthoquinone), and 720 cm^{-1} (naphthoquinone CH). Prepared and stored in the dark, the *acetate* (Xb) was obtained by use of acetic anhydride–sulphuric acid and separated from methanol as yellow needles, m.p. 186—188°, $\lambda_{max.}$ 246, 267, 273, and 334 nm (log ε 4.50, 4.37, 4.36, and 3.57), $\nu_{max.}$ 1730 (acetate), 1 665 (enedione C:O), 1 655 and 1 640 (naphthoquinone C:O), 1 630 and 1 595 (aromatic), and 730 cm^{-1} (naphthoquinone CH) (Found: C, 71.9; H, 5.7%; *M*, 500. $C_{30}H_{28}O_7$ requires C, 72.0; H, 5.6%; *M*, 500).

(ii) *Maximum yield of the fluorene alcohol* (III). The best yields of this compound appeared to result by the use of relatively high concentrations of sodium hydroxide for the shortest practicable time (not more than 5 min.). To the tetrahydroindazole derivative (420 mg) and 2,6-dimethyl-1,4-benzoquinone (500 mg) in methanol (25 ml) was added 0.1M-sodium hydroxide (0.1 ml) and the mixture was well shaken. After 4 min no further change was noted and the precipitate was collected and identified as the bridge trione (Xa) (95 mg). The filtrate was neutralised with 2M-hydrochloric acid and concentrated *in vacuo* until a second precipitate appeared. This was identified as the methylenediquinone (VI) (171 mg). Further concentration of the filtrate yielded the fluorene alcohol (III) as a yellow microcrystalline mass (190 mg).

Photocyclisation of the Bridge Trione (Xb).—The inside of a large Pyrex beaker was coated with a thin film of the bridge trione acetate (Xb) (100 mg) by deposition from chloroform and exposed to diffuse (window) daylight for 8 days, after which i.r. spectroscopy indicated little further change. The film was collected into chloroform and the product recovered and purified from benzene giving (1R*,2R*,-4S*,5R*,7R*,8R*,9R*,10S*,12S*)-8-*acetoxy*-1,5,7,10-*tetramethyl*-12-(3-*methyl*-1,4-*naphthoquinon*-2-*ylmethyl*)-*pentacyclo*[6.3.1.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]*dodecane*-3,6,11-*trione* (XII) as yellow granules (65 mg), m.p. 255—265° (decomp.), $\nu_{max.}$ 1 750 (acetate), 1 730 (cyclohexanone C:O under strain), 1 655, 1 620, 1 595, and 730 cm^{-1} (naphthoquinone pattern) (Found: *M*, 500.181 8. $C_{30}H_{28}O_7$ requires *M*, 500.1834). The chief mass spectral fragmentations were associated with elimination of keten and with the formation of a fragment ion *m/e* 458.

Isomerisation of the Bridge Trione (Xa) *to the Hemiacetal* (XIVa).—A mixture of the bridge trione (Xa) (200 mg)

and chloroacetic acid (4 g) formed a solution when kept at 70 °C under nitrogen for 14 min. After a further 5 min, the solution was poured into water and the fine beige precipitate was extracted into ether, freed from acid by washing with water and then aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and recovered by removing the solvent under reduced pressure. The residue was oily but a concentrated solution in benzene deposited a solid that, when again purified from benzene, gave the hemiacetal (1R*,4aS*,9bS*)-4a,9b-*dihydro*-4a,8-*dihydroxy*-4,7,9,9b-*tetramethyl*-1-(3-*methyl*-1,4-*naphthoquinon*-2-*ylmethyl*)-*dibenzofuran*-2(1H)-*one*, as tiny yellow crystals (120 mg), m.p. 189—190°, $\lambda_{max.}$ 240, 250sh, 270, 295sh, and 330 nm (log ε 4.40, 4.38, 4.22, 3.82, and 3.59), $\nu_{max.}$ 3 500 and 3 230 (OH), 1 650 (naphthoquinone and enone C:O), 1 620, 1 590, and 720 cm^{-1} (naphthoquinone pattern) (Found: C, 73.2; H, 5.8%; *M*, 458. $C_{28}H_{26}O_6$ requires C, 73.35; H, 5.7%; *M*, 458). The same compound resulted when the bridge trione was briefly treated with trifluoroacetic acid at 20 °C instead of chloroacetic acid but it was more difficult to free it from impurities and especially from the red spiran which was always formed to some extent with the stronger acid.

Warmed gently until a clear solution resulted and then set aside, a mixture of the hemiacetal (50 mg) and acetic anhydride (5 ml) containing 2 drops of pyridine supplied a solid which, when purified from ethanol, gave the 8-*acetate* (XIVb) as yellow needles (39 mg), m.p. 264—266°, $\lambda_{max.}$ 244, 247, 252sh, 273, 290sh, and 330 nm (log ε 4.40, 4.40, 3.39, 4.26, 3.89, and 3.57), $\nu_{max.}$ 3 420 (OH), 1 740 (acetate), 1 660 (quinone and enone C:O), 1 622, 1 600, and 720 cm^{-1} (naphthoquinone pattern) (Found: C, 71.7; H, 5.8%; *M*, 500. $C_{30}H_{28}O_7$ requires C, 72.0; H, 5.6%; *M*, 500).

Oxidation of the Hemiacetal (XIVa).—The reaction between iron(III) chloride (50 mg) in ethanol (3 ml) and the hemiacetal (XIVa) (20 mg) in ethanol (5 ml) was complete after about 30 min (t.l.c.). The cream solid obtained by concentrating the solution under reduced pressure and diluting it with water was washed with water and crystallised from methanol to give the quinone–quinone (XV), (5R*,6S*)-5-(3,5-*dimethyl*-1,4-*benzoquinon*-2-*yl*)-3,5-*dimethyl*-6-(3-*methyl*-1,4-*naphthoquinon*-2-*ylmethyl*)*cyclohex*-2-*ene*-1,4-*dione*, as bright yellow prisms (15.5 mg), m.p. 186—187°, $\lambda_{max.}$ 247, 253sh, 264, and 335 nm (log ε 4.54, 4.52, 4.45, and 3.63), $\nu_{max.}$ 1 685sh, 1 675, 1 655sh, 1 650, 1 645sh, 1 635, 1 615, 1 598, and 710 cm^{-1} (Found: C, 73.35; H, 5.4%; *M*, 456. $C_{28}H_{24}O_6$ requires C, 73.7; H, 5.3%; *M*, 456).

Cyclisation of the Quinone–Quinone (XV).—A solution of the foregoing compound (150 mg) in trifluoroacetic acid (10 ml) was kept at 23 °C for 100 min and then diluted with water. The product was isolated by extraction with chloroform, dried (Na_2SO_4), and recovered by evaporation of the solvent under reduced pressure. Crystallised from benzene, the product supplied the benzofuran derivative (XVIa), (4aR*,9bS*)-4a,9b-*dihydro*-8-*hydroxy*-2,7,9,9b-*tetramethyl*-4a-(3-*methyl*-1,4-*naphthoquinon*-2-*ylmethyl*)*dibenzofuran*-1,4-*dione*, as yellow prisms (90 mg), m.p. 269°, $\nu_{max.}$ 3 470 (OH), 1 675 (enedione), 1 660, 1 625, 1 600, and 715 cm^{-1} (naphthoquinone pattern) (Found: C, 73.4; H, 5.4%; *M*, 456, $C_{28}H_{24}O_6$ requires C, 73.7; H, 5.3%; *M*, 456). The *acetate* (XVIb) (acetic anhydride–pyridine) separated from ethanol as yellow platelets, m.p. 231—233°, $\lambda_{max.}$ 238, 252, 270, and 325 nm (log ε 4.48, 4.35, 4.43, and 3.51), $\nu_{max.}$ 1 745 (OAc) and 1 660 cm^{-1} (quinone and enedione) (Found: C, 72.3; H, 5.3%; *M*, 498. $C_{30}H_{26}O_6$ requires C, 72.3; H, 5.3%; *M*, 498).

The Spiran (XVIIa).—The bridge trione (Xa) (500 mg) was left in trifluoroacetic acid (20 ml) at 23 °C for 2 h. The product was precipitated by water and partially purified by dissolving it in methanol and re-precipitating it by rapid concentration. Crystallisation from benzene then gave the spiran, (2R*,5'R*)-5-*hydroxy*-2',4,6-*trimethyl*-3-*methylene*-5'-(3-*methyl*-1,4-*naphthoquinon*-2-*ylmethyl*)-*benzofuran*-2(3*H*)-*spiro*-1'-*cyclopent*-2'-*en*-4'-*one*, as bright red needles (110 mg), m.p. 231—233°, $\nu_{max.}$ 3 450 (OH), 1 700 (cyclopentenone C:O), 1 650 and 717 cm^{-1} (naphthoquinone) (Found: C, 76.05; H, 5.65; *M*, 440. $C_{28}H_{24}O_5$ requires C, 76.35; H, 5.5%; *M*, 440). The compound was unchanged by refluxing in ethanol for several hours whether exposed to daylight or not. In ethanol, the compound had $\lambda_{max.}$ 234, 268, and 340 nm (log ε 4.46, 4.38, and 3.93). Addition of sodium hydroxide diminished the band at 340 nm and produced a new one at 356 nm (isosbestic points at 307 and 361 nm); on acidification, the spectrum reverted to that in neutral ethanol.

When the preparation time was reduced to below 20 min, the hemiacetal (XIVa) was also produced. In separate experiments the hemiacetal was found to serve as well as the bridge trione for the preparation of the spiran.

The spiran (50 mg), acetic anhydride (5 ml), and pyridine (2 drops) were rapidly warmed together on a steam-bath to form a solution which was kept at room temperature in the dark until t.l.c. showed acetylation to be complete (*ca.* 30 min.). The solution was poured into iced water and stirred until a yellow solid formed; this was collected, washed with water, and rapidly crystallised in the dark from ethanol giving the *acetate* (XVIIb) as yellow needles (22 mg), m.p. 204—208°, $\lambda_{max.}$ 233, 247sh, 262sh, 320, and 330 nm (log ε 4.57, 4.41, 4.30, 3.80, and 3.76), $\nu_{max.}$ 1 740 (OAc), 1 705 (cyclopentenone), 1 655 and 715 cm^{-1} (naphthoquinone) (Found: C, 74.2; H, 5.4%; *M*, 482. $C_{30}H_{26}O_6$ requires C, 74.7; H, 5.4%; *M*, 482).

Photocyclisation of the Spiran Acetate (XVIIb).—The foregoing acetate (0.1 g) dissolved in ethanol (10 ml) was exposed to diffuse daylight for 4 days, *i.e.* until the i.r. spectrum and t.l.c. showed the absence of starting material. During this time a solid separated which, crystallised from ethanol, gave the cyclobutane derivative (XIX), (3aR*,-8bS*,15aR*,16aR*)-7-*acetoxy*-9,9a,16,16a-*tetrahydro*-3,6,8,-9a-*tetramethyl*-4-*oxa*-1H-*indeno*[1''',2''':1'',6''a]*pentaleno*-[2'',1'':2',3']*cyclobuta*[1',2'-b]*naphthalene*-1,10,15-*trione*, as needles (60 mg), m.p. 224—225°, $\lambda_{max.}$ 230 and 295 nm (log ε 3.20 and 4.52), $\nu_{max.}$ 1 750 (OAc), 1 700 (cyclopentenone), 1 695, 1 685, 1 675, and 740 cm^{-1} (1,2-phthaloyl pattern) (Found: C, 73.4; H, 5.4%; *M*, 482. $C_{30}H_{26}O_6$ requires C, 74.7; H, 5.4%; *M*, 482).

4-*Methoxy*-2,6-*dimethylphenyl Acetate*.—Prepared from 4-methoxy-2,6-dimethylphenol, acetic anhydride, and pyridine, this *acetate* crystallised from light petroleum (b.p. 40—60°) as thin prisms, m.p. 44—46° (Found: C, 68.1; H, 7.1. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.2%).

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