Reactions of 2-Ethyl- and 2-Benzyl-1,4-naphthoquinone with *N*-Methylcyclohexylamine

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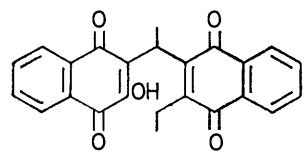
2-Ethyl- and 2-benzyl-1,4-naphthoquinone on treatment with *N*-methylcyclohexylamine in ethanol give 5b,11a-epoxy-5a-ethyl-5a-5b,11a,12a-tetrahydro-12-methyl-12*H*-dibenzo[*b,h*]fluorene-5,6,11,13-tetraone (IIIa) and its 5a-benzyl-12-phenyl analogue (IIIb), respectively. Reduction of the epoxides under a variety of conditions eliminates the epoxy-group, and gives various reduction products of the dibenzo[*b,h*]fluorene-5,13:6,11-quinone system.

THE dimerisation of naphthoquinones under a variety of conditions has recently received considerable attention, and a number of novel products have been identified.[1] The formation of a linear polycyclic diquinone from 2-methyl-1,4-naphthoquinones in the presence of *N*-methylcyclohexylamine has been described.[2] We have now found that extension of this reaction to other 2-alkyl-1,4-naphthoquinones does not lead to the analogous 6,13-dialkylpentacene-5,7:12,14-diquinones. When 2-ethyl-1,4-naphthoquinone[3] was treated with ethanolic *N*-methylcyclohexylamine at room temperature in the presence of air, a non-quinonoid product, compound A ($C_{24}H_{18}O_5$) was isolated in 23% yield.

(I)



When compound A was treated with aqueous ethanolic sodium hydroxide it was converted into an isomeric diquinone (I) which suggested that compound A contained units structurally related to the 1,4-naphthoquinone system. The identification of compound (I) was based partly on its n.m.r. spectrum, which showed the presence of ethyl and ethylidene groups but no quinonoid protons. The extinction coefficient of the long-wavelength absorption band (at 333 nm) was approximately twice that of the absorption band usually present in this region in the spectrum of a 1,4-naphthoquinone, suggesting that two 1,4-naphthoquinone units were present. That the quinone (I) contained a hydroxyquinone unit was deduced from the observation that it gave a red solution in the presence of a trace of alkali ($\lambda_{max.}$ 480 nm; *cf.* 2-hydroxy-1,4-naphthoquinone,[4] $\lambda_{max.}$ 455 nm).

The i.r. spectrum of compound A showed the absence of a hydroxy-group but suggested that several carbonyl groups were present. The absence of a hydroxy-group was supported by our failure to acetylate compound A under a variety of conditions. The u.v. spectrum of compound A showed the absence of naphthoquinone and hydroxynaphthoquinone systems but was consistent

[1] F. M. Dean and L. E. Houghton, *J. Chem. Soc.* (*C*), 1971, 1920, and references therein; K. Chandrasenan and R. H. Thomson, *Tetrahedron*, 1971, **25**, 2529; W. Storck and G. Manecke, *Chem. Ber.*, 1971, **104**, 1207.

[2] I. Baxter, D. W. Cameron, and R. B. Titman, *J. Chem. Soc.* (*C*), 1971, 1253.

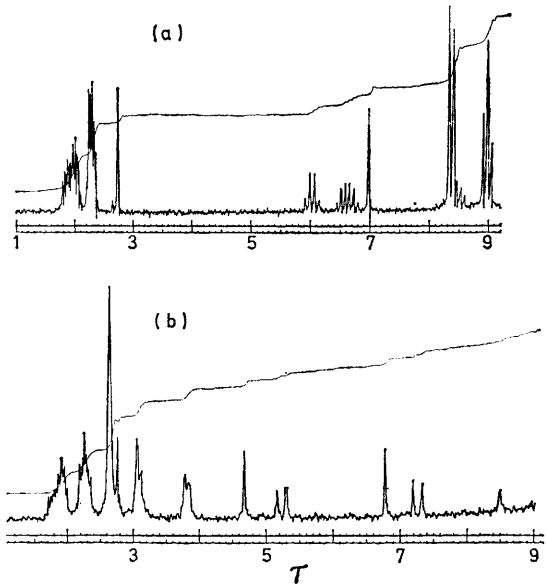
[3] L. F. Fieser, W. P. Cambell, E. M. Fry, and M. D. Gates, *J. Amer. Chem. Soc.*, 1939, **61**, 3216.

[4] M. G. Ettlinger, *J. Amer. Chem. Soc.*, 1950, **72**, 3085.

with the presence of two 2,3-dihydro-1,4-naphthoquinone units; comparison with the spectra of 2,3-dihydro-2-methyl-1,4-naphthoquinone epoxide and related compounds [5] showed that the general profiles of the curves were similar. Moreover the extinction coefficient of the maximum at 227 nm in compound A was twice that of the monomeric epoxide.

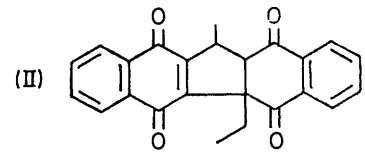
The n.m.r. spectrum of compound A is shown in Figure 1a. Spin-decoupling experiments were useful in assigning the signals. Irradiation at the frequency of the one-proton broadened quartet at τ 6·04 caused the high-field doublet to collapse to a singlet, and irradiation of the one-proton sextet centred at τ 6·63 converted the high-field triplet into a doublet. Thus it appeared that compound A contained both an ethylidene and an ethyl group, the latter located in a position which rendered the methylene protons non-equivalent to an unusually large extent (sextets at τ 6·63 and 8·43). The signal at τ 6·99, assigned to C*H*·CO, was a narrow doublet (*J ca.* 1 Hz) coupled to the broadened quartet at τ 6·04.

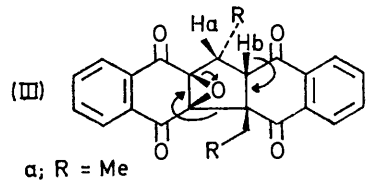
To assist the interpretation of this spectrum, we studied the behaviour of analogues of compound A.



N.m.r. spectra of (a) compound (IIIa) and (b) compound (IIIb)

2-Isopropyl-1,4-naphthoquinone yielded no recognisable products when treated with *N*-methylcyclohexylamine but 2-benzyl-1,4-naphthoquinone formed an analogue in 56% yield. The n.m.r. spectrum of the latter is shown in Figure 1b. The quartet in the spectrum of compound A was replaced by a broadened singlet and the two sextets, assigned to the methylene protons, were replaced by a pair of doublets at τ 5·24 and 7·26. Furthermore the geminal coupling constant between these methylene protons (14 Hz) is twice the vicinal coupling constant (7 Hz) between the methylene and methyl protons in compound A. The combination of these two coupling interactions would be expected to result in the appearance of the signal for the ethyl group in compound A as a triplet and two sextets, if the methylene protons are non-equivalent.





a; R = Me
b; R = Ph

Reduction of compound A, either catalytically or (less efficiently) with potassium iodide–acetic acid,[6] gave a naphthoquinone of gross structure (II). This assignment is based upon spectroscopic evidence; in particular the n.m.r. spectrum showed, in addition to signals assigned to an ethyl group and the methyl of an ethylidene group, a two-proton multiplet at τ 6·78. The latter signal was resolved by addition of Eu(dpm)$_3$ [7] and shown to consist of a one-proton doublet (*J* 10 Hz) and a one-proton multiplet, assigned to a CH_3·C*H*·C*H*·CO grouping.

Compound A was readily reformed from the quinone (II) by treatment with alkaline hydrogen peroxide, a reagent normally employed for the epoxidation of quinones.[8] On the basis of the foregoing chemical and spectroscopic evidence, we suggest that compound A is an epoxide of the quinone (II). Quinone (II) also gives compound A when treated with *N*-methylcyclohexylamine under the same conditions as the original 2-ethyl-1,4-naphthoquinone but quinone (I) does not.

Addition of Eu(dpm)$_3$ to a solution of compound A in [^{2}H]chloroform caused extensive downfield shifts of all resonances [see Table; the corresponding shifts for the quinone (II) are given for comparison and in both cases, the observed shift of the methyl of the ethylidene group

Relative Eu(dpm)$_3$-induced shifts

	Shift	
Protons	Compound A	Compound(II)
CH_3·CH	1·0	1·0
CH_3·C*H*	3·0	1·5
CH_3·CH_2	4·15 and 1·67	1·0
CH_2·CH_2	0·85	0·5
C*H*·CO	3·0	1·8

[5] L. F. Fieser, *J. Biol. Chem.*, 1940, **133**, 391; R. H. Thomson, *J. Chem. Soc.*, 1950, 1737.

[6] M. M. Shemyakin, D. A. Bochvar, and L. A. Shchukina, *Zhur. obshchei. Khim.*, 1952, **22**, 439; R. E. Lutz and J. L. Wood, *J. Amer. Chem. Soc.*, 1938, **60**, 229.

[7] (*a*) J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, in the press; (*b*) J. K. M. Sanders and D. H. Williams, *ibid.*, 1971, **93**, 641.

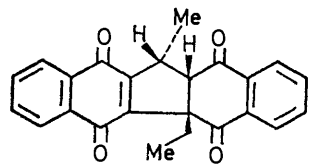
[8] See, for example, A. Rashid and G. Read, *J. Chem. Soc.* (*C*), 1967, 1323.

was arbitrarily assigned as unity]. The equilibrium constants for the binding of compound A and quinone (II) to $Eu(dpm)_3$ were shown to be 390 and 270 respectively, by the competition method developed in this laboratory.[7a] These results confirm that 30% of the co-ordination to compound A is at the epoxide oxygen atom. In compound A, the relative shifts of the CH_3·CH and CH_3·C*H* protons clearly indicate that it is the latter which is *cis* to the epoxide ring; similarly it can be seen that the ethyl group and the C*H*·CO proton are also *cis* to the three-membered ring.[7b] Models indicate that for co-ordination at the epoxide oxygen atom variations in the angular variables should be small compared with the r^{-3} term.

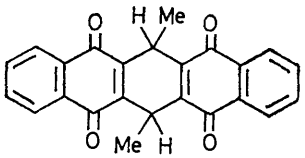
The much greater non-equivalence of the methyl protons of the ethyl group in compound A compared to quinone (II) adds further support to the *cis* relationship of the ethyl group and epoxide ring.

Thus formula (IIIa) is proposed for compound A and by analogy (IIIb) for the product from 2-benzyl-1,4-naphthoquinone. There is an apparent anomaly in the observed coupling constant for the *cis* methine protons H_a and H_b (1 Hz) in epoxide (IIIa)—a larger value might be anticipated for the *cis* vicinal coupling constant in a cyclopentane system. The vicinal coupling constant for the corresponding methine protons in the quinone (II) is 10 Hz, which is consistent with a *cis* arrangement for these protons. It seems unlikely that epimerisation at C-11a of the epoxide would occur under the conditions used for hydrogenation. We therefore tentatively assign the stereochemistry as shown in (IV) to quinone (II) and attribute the variation in coupling constant to conformational change associated with epoxidation. The use of $Eu(dpm)_3$ to assist in the assignment of stereochemistry of quinone (II) is unsatisfactory because of uncertainties concerning the actual binding sites.

(IV)



(V)

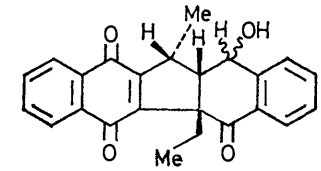


The formation of the diquinone (I) from (IIIa) on treatment with alkali can be readily rationalised as shown by the arrows in the formula.

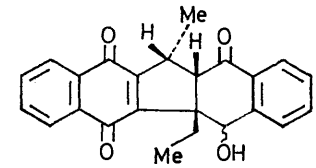
More prolonged catalytic hydrogenation of the epoxide (IIIa) gave a complex mixture of products from which three quinones were isolated. One of these was identified as the known compound (V).[9] The formation of this product is not understood but it might be an artefact arising from a primary reduction product during the course of the chromatographic work-up. The i.r. spectra of the other two compounds (hereafter called X and Y) were very similar and were consistent with each containing quinonoid carbonyl systems, an aromatic carbonyl group, and a hydroxy-group. Their u.v. spectra too were similar and contained maxima consistent with the presence of one naphthoquinone system (*ca.* 250 and 335 nm) and an aromatic carbonyl group (*ca.* 275 nm).

These data, together with the n.m.r. spectra, indicated that the quinones were alcohols closely related to the quinone (IV) and derived by reduction of one of the aromatic carbonyl groups. The n.m.r. spectrum of compound X contained signals, at τ 8·44, 6·80, 7·21, and 4·65, assigned by spin-decoupling to the grouping CH_3·CH_a·CH_b·CH_c·OH, with J_{ab} 7 and J_{bc} 5 Hz, and we have assigned structure (VI) to this material. Uncertainties

(VI)



(VII)



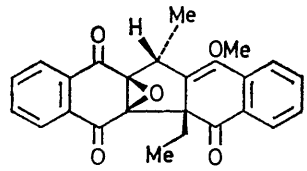
concerning the conformation of this compound preclude a definitive assignment of stereochemistry at C-11. In the n.m.r. spectrum of compound Y, a quintet and doublet (J 7 Hz) at τ 6·38 and 7·24 were present and could be assigned to a CH_3·C*H*·C*H* grouping. However, the signal arising from the *CH*·OH system at τ 4·94 appeared to be a singlet. Thus compound Y may be either the C-11 epimer of X or have structure (VII). This quinone was the only product isolated from the reduction of the epoxide (IIIa) with zinc and acetic acid. Reduction of the epoxide (IIIb) with this latter reagent led to the isolation of a naphthoquinone Z, which contains an aromatic carbonyl group and a hydroxy-group as evidenced by its i.r. spectrum. Its n.m.r. spectrum contained two doublets (J 7 Hz) at τ 5·33 and 6·55 assigned to the PhC*H*·C*H* unit, but the C*H*·OH signal appeared to be a singlet. Thus it seems probable that this product is an analogue of quinone Y.

Methylation of the epoxide (IIIa) with methyl iodide and sodium hydride in dimethylformamide gave an *O*-methyl derivative, which re-formed the epoxide (IIIa) on acidic hydrolysis and is presumably the enol ether (VIII). Support for this structure comes from its n.m.r. spectrum (Experimental section), which showed a three-proton singlet at τ 6·33 (OMe). In other respects, the spectrum corresponded to that of the epoxide (IIIa)

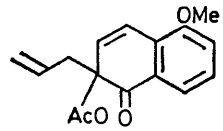
[9] R. H. Thomson, *J. Chem. Soc.*, 1953, 1196.

except that there was no signal corresponding to the one-proton doublet at τ 6·99. The u.v. spectrum showed, in addition to maxima assignable to a naphthoquinone epoxide system (272 and 310 nm), two significant absorption bands at 241 and 364 nm, similar to those observed in the spectrum of compound (IX) at 240 and 370 nm.[10]

(VIII)

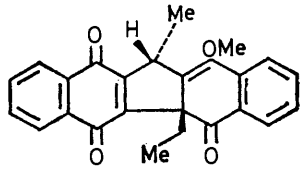


(IX)

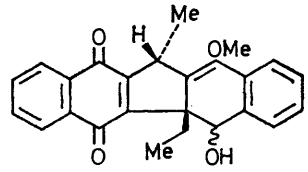


Catalytic hydrogenation of the ether (VIII) in methanol gave two products. One of these had maxima at 254 and 341 nm in the u.v. and a strong peak at 1670 cm^{-1} in the i.r. These data are consistent with this compound being a naphthoquinone, and we assign it structure (X) (for n.m.r. see Experimental section). The second product had similar spectral properties to (X) but in addition had a peak at 3420 cm^{-1} in its i.r. spectrum; we propose structure (XI) for this quinone.

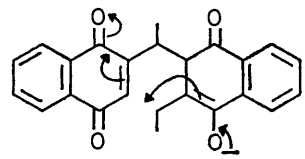
(X)



(XI)



(XII)



Formation of the epoxide (IIIa) may be visualised as proceeding *via* base-catalysed epoxidation of the quinone (IV), one of whose internuclear linkages (the ethylidene bridge) being formed as in the dimerisation of 2-methyl-1,4-naphthoquinone [2] to give compound (XII). Intramolecular cyclisation (arrows) followed by oxidation would yield the quinone (IV). Alternatively if the intermediate (XII) undergoes oxidation to the corresponding diquinone, formation of the second internuclear bond would be analogous to the trimerisation of naphthoquinone in the presence of *N*-methylcyclohexylamine,[11] a process possibly involving radical intermediates. Support for the intermediacy of the quinone (IV) in the formation of compound (IIIa) comes from the observation that when a mixture of 2-ethyl-1,4-naphthoquinone and *N*-methylcyclohexylamine is left under nitrogen, the quinone (IV) may be detected by t.l.c., the oxidation steps in this reaction presumably being effected at the expense of starting quinone. The formation of the epoxide (IIIa) was not detected under these conditions, and this presumably indicates that the epoxidation reaction involves air, *e.g.* hydrogen peroxide could be generated by aerial oxidation of quinol intermediates. Similar, remarkably mild epoxidation has been observed elsewhere, also involving base-catalysed aerial oxidation of quinols.[12]

The formation of compounds (IIIa and b) contrasts with the dimerisation of 2-methyl-1,4-naphthoquinone. The latter leads primarily to pentacene-5,7:12,14-diquinone.[2] Formation of the pentacene skeleton, oxidation steps apart, involves two Michael-type additions, processes which would be expected to occur less readily in the ethyl and benzyl series. In the formation of compounds (IIIa and b) only one such process is required. Moreover compound (V), when treated with *N*-methylcyclohexylamine in air, did not undergo dehydrogenation to the fully aromatic system. Such a process in the methyl series must occur irreversibly.

EXPERIMENTAL

Unless otherwise stated i.r. spectra were measured for Nujol mulls and u.v. and visible spectra for solutions in chloroform. N.m.r. spectra were measured at 100 MHz for solutions in deuteriochloroform with tetramethylsilane as internal reference. All integrations gave results consistent with the structural assignments.

Reaction of 2-Ethyl-1,4-naphthoquinone with N-Methylcyclohexylamine.—The amine (3 ml) was added to a solution of the quinone [3] (2·10 g) in ethanol (150 ml) and the solution was kept in the dark for 2 days. A small amount of product was filtered off and the filtrate was concentrated to *ca.* 30 ml. The brown solid was collected, combined with that obtained above and recrystallised from benzene to give r-5b,11a-*epoxy*-c-5a-*ethyl*-5a,5b-c-11a,12a-*tetrahydro*-t-12-*methyl*-12H-*dibenzo*[b,h]*fluorene*-5,6,11,13-*tetraone* (IIIa) (0·50 g), m.p. 198—199° (Found: C, 74·5; H, 4·7%; M^+, 386. $C_{24}H_{18}O_5$ requires C, 74·6; H, 4·7%; *M*, 386), $\lambda_{max.}$ (EtOH) 227 and 306 nm (log ε 4·79 and 3·63); $\nu_{max.}$ 1710, 1695, 1680, and 1590 cm^{-1}. This material did not react with either acetic anhydride or *o*-phenylenediamine.

3-*Ethyl*-3′-*hydroxy*-2,2′-*ethylidenedi*-1,4-*naphthoquinone* (I).—A solution of the foregoing compound (200 mg) in a mixture of aqueous 10% sodium hydroxide (8 ml) and ethanol (12 ml) was kept at 70° for 5 min, acidified with

[10] W. Eisenhuth and H. Schmid, *Helv. Chim. Acta*, 1958, **41**, 2021.

[11] D. W. Cameron, R. G. F. Giles, and R. B. Titman, *J. Chem. Soc.* (*C*), 1969, 1245.

[12] F. R. Hewgill and S. L. Lee, *J. Chem. Soc.* (*C*), 1968, 1549; I. Baxter and W. R. Phillips, *J.C.S. Chem. Comm.*, 1972, 78; R. G. F. Giles, personal communication.

dilute hydrochloric acid, and extracted with dichloromethane. The dried extract was chromatographed on silicAR CC7; elution with dichloromethane gave the *quinone* (80 mg), m.p. 205° (from benzene) (Found: C, 74·4; H, 4·7. $C_{24}H_{18}O_5$ requires C, 74·6; H, 4·7%), *m/e* 386 (M^+), $\lambda_{max.}$ (acidified EtOH) 250 and 333 nm (log ε 4·60 and 3·81), $\lambda_{infl.}$ 268 nm (log ε 4·50), $\lambda_{max.}$ (basified EtOH) 250, 273 and 480 nm (log ε 4·58, 4·60, and 3·64), $\lambda_{infl.}$ 293 and 325 nm (log ε 4·42 and 3·94); $\nu_{max.}$ 3320, 1673, 1660, 1633, and 1590 cm^{-1}, τ 1·8—2·4 (m, ArH), 5·25 (q, C*H*Me), 7·16 (q, C*H*$_2$Me), 8·24 (d, CH·C*H*$_3$), and 8·86 (t, CH$_2$·C*H*$_3$).

2-*Benzyl*-1,4-*naphthoquinone*.— 2-Benzyl-1-naphthol [13] (1·5 g) was dissolved in ether (30 ml) and the solution added to a vigorously stirred solution of Fremy's salt (4 g) in water (200 ml) buffered at pH 7. After 6 h the ether layer was removed and the aqueous layer was extracted with more ether. The combined, dried extracts were evaporated to give a residue which when recrystallised (charcoal) from methanol gave the *quinone* (0·57 g), m.p. 94·5—95° (Found: C, 82·1; H, 4·8. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·9%), $\lambda_{max.}$ (EtOH) 247, 252, and 333 nm (log ε 4·28, 4·28, and 3·46); $\nu_{max.}$ 1670, 1660, 1625, and 1595 cm^{-1}, τ 1·8—2·4 (m, ArH), 2·72 (m, side-chain ArH), 3·40 (s, CH=C), and 6·12 (s, C*H*$_2$Ar).

Reaction of 2-*Benzyl*-1,4-*naphthoquinone with* N-*Methylcyclohexylamine*.—The quinone (0·47 g) in ethanol (50 ml) was treated with the amine (0·5 ml) overnight and the mixture was worked up as described for compound (IIIa) to give c-5a-*benzyl*-r-5b,11a-*epoxy*-5a,5b-c-11a,12a-*tetrahydro*-t-12-*phenyl*-12H-*dibenzo*[b,h]*fluorene*-5,6,11,13-*tetraone* (IIIb) (0·27 g), m.p. 250—260° (decomp.) (from benzene) (Found: C, 80·0; H, 4·45. $C_{34}H_{22}O_5$ requires C, 80·0; H, 4·35%), *m/e* 510 (M^+), $\nu_{max.}$ 1705, 1680, and 1590 cm^{-1}; for n.m.r. spectrum see text.

Reduction of the Epoxide (IIIa).—(*a*) A mixture of the epoxide (0·20 g), potassium iodide (0·20 g), and glacial acetic acid (8 ml) was heated on a boiling water bath for 2 h and then filtered and poured into aqueous sodium thiosulphate. The precipitate was collected and chromatographed on silicAR CC-7. Elution with benzene–chloroform (5 : 1) gave a gum which crystallised from methanol to give r-5b-*ethyl*-5b-c-11a-*dihydro*-t-12-*methyl*-6,11-*dioxo*-12H-*dibenzo*[b,h]*fluorene*-5,13-*quinone* (IV), (27 mg), m.p. 173—174° (Found: C, 77·7; H, 4·7. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%), $\lambda_{max.}$ 254, 295, and 337 nm (log ε 4·47, 3·67, and 3·52), $\lambda_{infl.}$ 267 and 308 nm (log ε 4·18 and 3·61), $\nu_{max.}$ 1690 and 1674 cm^{-1}, τ 1·8—2·4 (m, ArH), 6·78 (m, MeC*H*·CH; d, *J* 10 Hz, MeCH·C*H*), 7·56 (m, C*H*$_2$·CH$_3$), 8·37 (d, *J* 6 Hz, C*H*$_3$·CH), and 9·08 (t, *J* 7 Hz, CH$_2$·C*H*$_3$). The signals at τ 6·78 were separated by the addition of Eu(dpm)$_3$.

(*b*) A suspension of the epoxide (400 mg) in methanol (100 ml) was stirred with platinum oxide at room temperature under hydrogen for 2 h. The solution was filtered and evaporated to dryness. Recrystallisation of the residue from methanol gave the quinone (II) (160 mg), m.p. 173—174°. The i.r., u.v., and n.m.r. spectra of this material were identical with those of the compound described in (*a*).

(*c*) Repetition of the reaction described in (*b*) except that a reaction time of 8 h was used led to the isolation of yellow solid. Recrystallisation of this material from methanol gave *compound Y* (see text) (20 mg), m.p. 205—208° (Found: C, 77·6; H, 5·5. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%), *m/e* 372 (M^+), $\lambda_{max.}$ 246 and 332 nm (log ε 4·47 and 3·53), $\lambda_{infl.}$ 251 and 275 nm (log ε 4·42 and 4·08), $\nu_{max.}$ 3550, 1690, 1675, and 1670 cm^{-1}, τ 1·8—2·7 (m, ArH), 4·94 (s, C*H*·OH), 5·42br (s, OH, removed by D_2O), 6·38 (quintet, MeC*H*·CH), 7·24 (d, *J* 7 Hz, CH·C*H*), 7·72 and 8·42 (2 sextets, C*H*$_2$Me), 8·34 (d, *J* 7 Hz, CH·C*H*$_3$), and 9·26 (t, *J* 7 Hz, CH$_2$·C*H*$_3$).

Chromatography of the mother liquors from the foregoing recrystallisation on silicAR CC-7 [elution with benzene–chloroform (3 : 2)] gave 6,13-dimethyl-6,13-dihydropentacene-5,7:12,14-diquinone (15 mg) (V), m.p. 305° (decomp.) (from ethyl acetate), identical with an authentic sample prepared by the method of Thomson,[9] τ (CF_3·CO_2H) 1·7—2·2 (m, ArH), 5·30 (q, *J* 7 Hz, C*H*Me), and 8·43 (d, *J* 7 Hz, CH·C*H*$_3$).

Further elution, with benzene–chloroform (1 : 2), gave a solid which crystallised from methanol to give *compound X* (see text) (35 mg), m.p. 215—218° (Found: C, 77·5; H, 5·3. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%), *m/e* 372 (M^+), $\lambda_{max.}$ 253 and 336 nm (log ε 4·43 and 3·55), $\lambda_{infl.}$ 275 nm (log ε 4·07), $\nu_{max.}$ 3520, 1690, 1675, and 1670 cm^{-1}, τ 1·8—2·7 (m, ArH), 4·65 (d, *J* 5 Hz, CH·C*H*·OH), 6·80 (quintet, MeC*H*·CH), 7·21 (dd, *J* 5 and 7 Hz, MeCH·C*H*·CH·OH), 7·40 and 7·71 (2 sextets, C*H*$_2$Me), 8·44 (d, *J* 7 Hz, CH·C*H*$_3$), and 9·01 (t, *J* 7 Hz, CH$_2$·C*H*$_3$).

(*d*) A mixture of the epoxide (240 mg), zinc dust (200 mg), and acetic acid (15 ml) was stirred at room temperature for 90 min, filtered, poured into water, and extracted with ether. Evaporation of the dried extract gave a solid which on recrystallisation from methanol gave the quinone Y (80 mg) m.p. 205—208°, identical with the material obtained earlier.

Reduction of the Epoxide (IIIb) *with Zinc in Acetic Acid*.—The epoxide (80 mg) was reduced as described in (*d*) and gave *compound Z* (see text) (8 mg), m.p. 126—128° (from ethanol) (Found: C, 82·1; H, 5·2. $C_{34}H_{24}O_4$ requires C, 82·3; H, 4·9%), *m/e* 496 (M^+), $\nu_{max.}$ 3430, 1690, 1675, and 1655 cm^{-1}, τ 1·8—3·6 (ArH), 4·78 (s, C*H*·OH), 5·33 and 6·55 (2d, *J* 7 Hz, Ph·C*H*·C*H*), and 6·0 and 7·46 (2d, *J* 14 Hz, PhC*H*$_2$).

Oxidation of the Quinone (IV) *with Alkaline Hydrogen Peroxide*.—To a stirred suspension of the quinone (70 mg) in methanol (10 ml) was added alkaline hydrogen peroxide solution [0·2 ml; prepared from 100 vol. hydrogen peroxide (4 ml), water (5 ml) and sodium carbonate (1 g)].[8] After 15 min the solution was acidified to pH 4 and extracted with chloroform. Evaporation of the dried extract ($MgSO_4$) gave a solid which gave the epoxide (IIIa) (50 mg), m.p. and mixed m.p. 198—199° (from benzene). The i.r. and n.m.r. spectra were identical with those of the authentic material.

Methylation of the Epoxide (IIIa).—To a solution of the epoxide (140 mg) in dry dimethylformamide (13 ml) was added an excess of methyl iodide and sodium hydride. The mixture was kept overnight at 60°, poured into water and extracted with ether. Evaporation of the dried extract and crystallisation from methanol gave r-5a,12a-*epoxy*-c-5b-*ethyl*-5a,12a-*dihydro*-11-*methoxy*-t-12-*methyl*-12H-*dibenzo*-[b,h]*fluorene*-5,6(5bH),13-*trione* (VIII) (90 mg), m.p. 156—160° (Found: C, 74·7; H, 5·3. $C_{25}H_{20}O_5$ requires C, 75·0; H, 5·0%), *m/e* 400 (M^+), $\lambda_{max.}$ (EtOH) 241, 272, 310, and 364 nm (log ε 4·67, 3·87, 3·51, and 3·01), $\lambda_{infl.}$ 238 and 245 nm (log ε 4·65 and 4·64), $\nu_{max.}$ 1710, 1695, and 1600 cm^{-1}, τ 1·8—2·7 (m, ArH), 6·21 (q, *J* 7 Hz, C*H*Me), 6·33 (s, O·C*H*$_3$), 7·23 and 8·11 (2 sextets, C*H*$_2$·CH$_3$), 8·45 (d, CH·C*H*$_3$), and 9·22 (t, *J* 7 Hz, CH$_2$·C*H*$_3$).

[13] L. Claisen, F. Kremers, F. Roth, and E. Tietze, *Annalen*, 1925, **442**, 210.

A mixture of the product (VIII) (30 mg), acetone (4 ml), and concentrated hydrochloric acid (1 ml) was kept for 4 days at room temperature. The dark red solution was filtered and the solid recrystallised from benzene–light petroleum to give the epoxide (IIIa) (10 mg).

Reduction of the Ether (VIII).—A suspension of the ether (50 mg) in methanol (30 ml) was stirred under hydrogen in the presence of platinum oxide for 2 h. The solution was filtered and evaporated to dryness, and the residue was recrystallised from methanol to give r-5b-*ethyl*-5b,6-*dihydro*-11-*methoxy*-t-12-*methyl*-6-*oxo*-12H-*dibenzo*[b,h]*fluorene*-5,13-*quinone* (X) (10 mg), m.p. 175—176° (Found: C, 78·0; H, 5·0. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·3%), *m/e* 384 (M^+), $\lambda_{max.}$ 254, 270, and 341 nm (log ε 4·59, 4·19, and 3·60), $\nu_{max.}$ 1710, 1670 cm^{-1}, τ 1·8—2·8 (m, ArH), 5·84 (q, *J* 7 Hz, MeC*H*), 6·38 (s, O·CH_3), 7·74br (q, CH_2·CH_3), 8·40 (d, *J* 7 Hz, CH_3·CH), and 9·12 (t, CH_2·CH_3).

Chromatography of the mother liquors from the recrystallisation on silicAR CC-7 [elution with benzene–chloroform (25 : 3)] gave r-5b-*ethyl*-5b,6-*dihydro*-6-*hydroxy*-11-*methoxy*-t-12-*methyl*-12H-*dibenzo*[b,h]*fluorene*-5,13-*quinone* (XI) (8 mg), m.p. 154—155° (from methanol) (Found: C, 77·9; H, 5·8. $C_{25}H_{22}O_4$ requires C, 77·6; H, 5·8%), *m/e* 386 (M^+), $\nu_{max.}$ 3420 and 1670 cm^{-1}, τ 1·8—2·8 (m, ArH), 4·25 (s, OH, removed by D_2O), 4·88 (s, C*H*·OH), 5·77 (q, *J* 7 Hz, C*H*·CH_3), 6·38 (s, O·CH_3), 8·17 (m, CH_2·CH_3), 8·45 (d, *J* 7 Hz, CH·CH_3), and 9·34 (t, *J* 7 Hz, CH_2·CH_3).

2-*Isopropyl*-1,4-*naphthoquinone*.— 2-Isopropylnaphthalene [14] was oxidised with chromium trioxide in acetic acid.[15] After pouring into water, ether extraction gave a brown oil, which was fractionally distilled to give a yellow oil (b.p. 110—122° at 0·3 mmHg), which solidified. Recrystallisation from methanol gave the quinone, m.p. 45—46·5° (lit.,[16] 45—47°) $\nu_{max.}$ 1665, 1615, and 1598 cm^{-1}, τ 1·8—2·4 (m, ArH), 3·23 (s, C*H*=C), 6·75 (m, C*H*Me_2), and 8·80 (d, CHMe_2).

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