Quinone Epoxides. Part VIII.[1] *C*-Acetyl Fission and *C* → *O*-Acetyl Migration in Reactions of Acetylquinone Epoxides and Related Compounds

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Loss of the acetyl group occurs when 2-acetyl-1,4-naphthoquinone epoxide (I; R = H) is treated with hydrogen bromide in acetic acid, whereas the acetyl group in the 3-methyl homologue (I; R = Me) is retained under these conditions. However it is the acetyl group in the latter epoxide only which is lost when the compounds are reduced by catalytic hydrogenation. *C* → *O*-Acetyl migration occurs when 2-acetyl-*r*-2,3-epoxy-3,4-dihydro-*c*-4-hydroxynaphthalen-1(2*H*)-one (II; R = H) is treated with anhydrous magnesium bromide, and loss or *C* → *O* migration of the acetyl group is observed when 2-acetyl-*t*-3-bromo-2,3-dihydro-*r*-2-hydroxy-3-methyl-1,4-naphthoquinone (III; R = Me) is catalytically reduced. 3-Acetyl-3,4-dihydro-*t*-3,*c*-4-dihydroxy-*r*-2-methylnaphthalen-1(2*H*)-one (IX; R = Me), which is also formed in the latter reaction, undergoes a major conformational change on transferring from dimethyl sulphoxide to chloroform solution. The stereospecific formation of this compound and its lower homologue and the behaviour of compounds (I; R = H), (I; R = Me), and (III; R = Me) under conditions of catalytic reduction are interpreted in terms of competing processes at substrate–catalyst complexes.

As part of our studies on the stereospecific elaboration of quinone epoxides, we have examined the opening of epoxide rings under various reducing conditions. In several reactions of the 2-acetyl-1,4-quinone epoxides (I; R = H) † and (I; R = Me) fission of the *C*-acetyl group accompanied other transformations, but the conditions under which fission was observed were markedly different for the two compounds. Fission, and in some cases *C* → *O* migration, of the *C*-acetyl group was also observed in reactions of the dihydroquinone epoxide (II; R = H) and the bromohydrin (III; R = Me). We discuss these reactions here and suggest reasons for the structural sensitivity observed. We also present evidence for the stereochemistry of products formed and, in the case of catalytic reduction, account for the stereospecificity and the acetyl fission in terms of a substrate–catalyst complex.

When the quinone epoxide (I; R = Me) was treated with hydrogen bromide in acetic acid a high yield of the bromohydrin (III; R = Me) was obtained. However under closely analogous conditions the lower homologue (I; R = H) was rapidly converted into the bromoquinone (IV; R = Br) in high yield. The bromohydrin (III; R = H) was isolated when anhydrous magnesium bromide in ether [2] was used to open the epoxide ring but this reaction was also accompanied by a competing reaction which gave the bromoquinone in 30% yield.

When the dihydroquinone epoxide (II; R = Me) was treated with hydrogen bromide in acetic acid the bromohydrin (V; R = Me) was formed,[1] together with some acetylquinol (VI; R = Me) and the quinol (VII; R^1 = H, R^2 = Me), but the lower homologue (II; R = H) gave a complex mixture of products with this reagent, and with hydrogen bromide in benzene. Treatment of the lower homologue with magnesium bromide–ether complex did not give the anticipated bromohydrin (V; R = H); instead the isomeric bromohydrin (VIII), which carries an *O*-acetyl group in the 4-position, was isolated.

In contrast to the reactions with hydrogen bromide, it was the acetyl group of the higher homologue which was lost under conditions of catalytic reduction. The triol (VII; R^1 = H, R^2 = Me) was formed in high yield when the epoxide (I; R = Me) was reduced with hydrogen in ethanol over palladised charcoal. The same product was also formed when either hydrogen over the less active palladised barium sulphate [3] or zinc and ammonium chloride in ethanol [4] was used as reducing agent. Some of the acetylquinol (VI; R = Me) was also formed when the former reagent was used. In each case the triol (VII; R^1 = H, R^2 = Me) was converted into the corresponding quinone (IV; R = Me) during work-up. The catalytic reduction of the bromohydrin (III; R = Me) over palladised calcium carbonate also gave the hydroquinone (VII; R^1 = H, R^2 = Me) as a major product, together with small and variable amounts of the tetralone (IX; R = Me). On one occasion the major product was a monoacetate of (VII; R^1 = H, R^2 = Me), formed by migration rather than

† Throughout this paper only one enantiomer of a racemic modification will be depicted.

[1] Part VII, G. Read and M. V. Ruiz, *J.C.S. Perkin I*, 1973, 235.

[2] W. E. Bachmann, J. P. Horwitz, and R. J. Warzynski, *J. Amer. Chem. Soc.*, 1953, **75**, 3268.

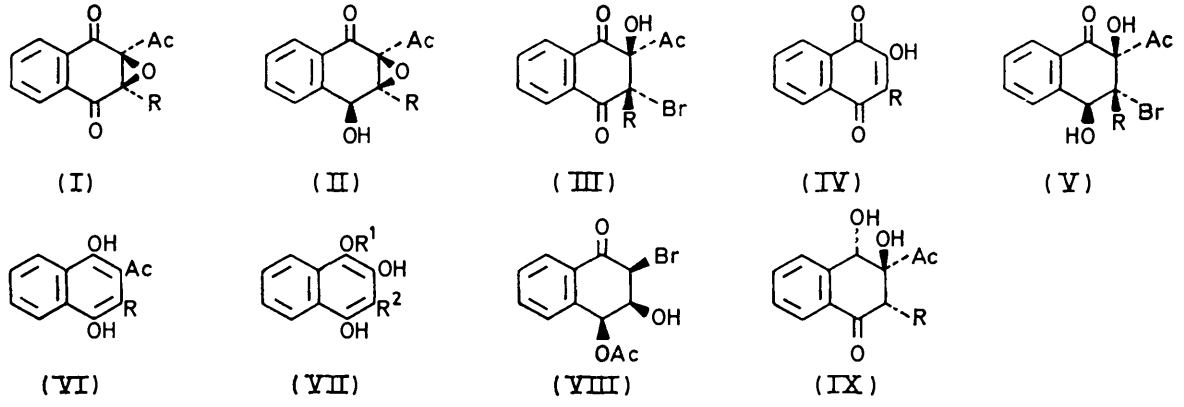
[3] R. Kuhn and H. J. Haas, *Angew. Chem.*, 1955, **67**, 785.

[4] R. E. Lutz and J. L. Wood, *J. Amer. Chem. Soc.*, 1938, **60**, 229.

elimination of the *C*-acetyl group (see later). Catalytic reduction of the quinone epoxide (I; R = H) proceeded smoothly over palladised charcoal to give a high yield of the acetyltetralone (IX; R = H) and a small amount of the acetylquinol (VI; R = H).

Most of the products from the foregoing reactions were identified by direct comparison with authentic samples, but the structure and stereochemistry attributed to the bromohydrin (VIII) are based on the following evidence. Elemental analysis and mass spectroscopy gave the molecular formula, and the u.v. spectrum clearly indicated a tetralone chromophore. The i.r. spectrum revealed the presence of a hydrogen bonded hydroxy-group (3475 cm^{-1}), a hydrogen-bonded ester system (1728 cm^{-1}), and an α-bromo-ketone conjugated to an aromatic ring (1703 cm^{-1}). The stretching frequency of the aryl ketone indicated that the predominant conformation of the molecule is that in which the bromine atom is equatorial.[5] In the n.m.r. spectrum a methine signal at τ 5·38 showed coupling to an exchangeable proton, indicating a secondary hydroxy-group. The same signal also showed coupling to two other methine groups [τ 4·38 (*J ca.* 2·1 Hz) and 3·74 (*J ca.* 3·0 Hz)], *i.e.* those carrying the bromine and the acetoxy-residue, respectively, which establishes the substitution pattern in the tetralone ring. The small vicinal coupling constants between these groups eliminates the possibility of any *trans* diaxial protons and, since the evidence points to an axial H-2, H-3 is assigned an equatorial position. The C-4 acetoxy-group is also assigned an equatorial position in order to accommodate the hydrogen bond with the secondary hydroxy-group. This relative stereochemistry at C-3 and C-4 is to be expected on the basis of the structure of the starting material and on conformational grounds. The bromohydrin reacted readily with aqueous sodium hydrogen carbonate to give a product which was quickly transformed into 2-bromo-1,4-naphthoquinone in air and is therefore assumed to be 2-bromonaphthalene-1,4-diol.

The monoacetate isolated on one occasion from the reduction of bromohydrin (III; R = Me) was smoothly converted into 3-methylnaphthalene-1,2,4-triyl triacetate with acetic anhydride and sulphuric acid and into 2-hydroxy-3-methyl-1,4-naphthoquinone (IV; R = Me) on treatment with sodium hydrogen carbonate solution. The monoacetate differed from 2-acetoxy-3-methylnaphthalene-1,4-diol; it was therefore the 1-acetoxy- or the 4-acetoxy-isomer. It is moderately stable in air, although breakdown to give compound (IV; R = Me) does occur over a period of days, which suggests that the acetoxy-group is in the 1-position and that the monoacetate has structure (VII; R^1 = Ac, R^2 = Me). This view is reinforced by the acetoxy carbonyl stretching frequency which, at 1742 cm^{-1}, is low for an aryl acetate.



This is however almost the same value as found for 2-acetoxy-3-methylnaphthalene-1,4-diol (1743 cm^{-1}). Intramolecular hydrogen bonding occurs in pyrocatechol monoacetate, which shows two carbonyl bands at 1778 and 1736 cm^{-1} associated, respectively, with a near-planar conformation in which the hydroxy-group is hydrogen-bonded to the ethereal oxygen atom of the ester, and with a non-planar conformation in which the hydroxy-group is hydrogen-bonded to the carbonyl oxygen atom of the ester.[6] Steric influences would prevent the adoption of conformations of the former type in the 1- and 2-isomers of 3-methylnaphthalene-1,2,4-triol acetate. The stretching frequency of the acetoxy-group in 4-acetoxy-3-methylnaphthalene-1,2-diol would be expected to be close to that found for the 4-acetate of (VI; R = Me),[1] which, at 1760 cm^{-1}, is in the normal aryl acetate stretching frequency range. Fieser [7] claims to have prepared 1-acetoxynaphthalene-2,4-diol in good yield by partial deacetylation of the triacetate with hydrogen fluoride, but attempts to prepare the 3-methyl homologue by this method gave only a complex mixture of fully and partially deacetylated products.

The structures of the tetralones (IX; R = Me) and (IX; R = H) follow directly from their analyses and spectroscopic properties. The assignment of their stereochemistries, which are of particular interest,[1] is based on the following arguments. The n.m.r. signals

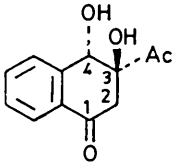
[5] L. J. Bellamy, 'Advances in Infra-red Group Frequencies,' Methuen, London, 1968, p. 142.

[6] R. Biggins, T. Cairns, G. Eglington, E. Haslam, and R. D. Haworth, *J. Chem. Soc.*, 1963, 1750.

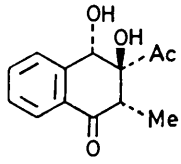
[7] L. F. Fieser, M. T. Leffler, and Co-workers, *J. Amer. Chem. Soc.*, 1948, **70**, 3186.

from the axial and equatorial protons at C-2 in (IX; R = H) are well separated at τ 6·88 and 7·48, respectively.[8] Since a 2-methyl group would cause a 2-proton signal to move downfield by about 0·3 p.p.m., the position of the latter signal in the spectrum of (IX; R = Me), at τ 7·25, is in accord with this proton being equatorial in dimethyl sulphoxide solution. The C-3 acetyl groups in both compounds are considered to occupy predominantly equatorial positions in this solvent, on the basis of analogies from earlier studies and our findings (see later). Also in dimethyl sulphoxide, the chemical shifts of the C-4 protons are very similar and the magnitudes of their couplings to the vicinal hydroxy-protons are the same (Table). These values

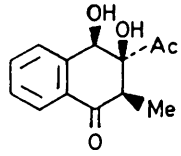
N.m.r. spectra * of the tetralone diols



(IX; R = H)



(IX; R = Me)



(X)

Proton	in $(CD_3)_2SO$	in $CDCl_3$	in $(CD_3)_2SO$	in $CDCl_3$	in $(CD_3)_2SO$	in $CDCl_3$
Aromatic	2·04—2·70	1·75—2·80	2·08—2·88	1·80—2·70	2·00—2·80	1·80—2·80
4-H	5·15 (d)	4·96 (d)	5·0 (d)	4·71 (d)	4·67 (d)	4·65 (d)
$J_{H,OH}$	6·0	4·0	6·0	3·0	9·5	12·0
3-OH	3·93	5·83	4·08	4·98	4·88	5·80
2-H	6·88 (d) 7·48 (d)	6·72 (d) 7·08 (d)	7·25 (q)	7·00 (q)	6·75 (q)	6·98 (q)
$J_{ax,eq}$ or $_{H,Me}$	17·0 17·0	18·0 18·0	7·2	6·6	6·6	6·6
4-OH	3·96 (d)	7·13 (d)	3·63 (d)	6·89 (d)	4·10 (d)	7·19 (d)
$J_{H,OH}$	6·0	4·0	6·0	3·0	9·5	12·0
3-Ac	7·80	7·82	7·78	8·32	7·67	7·60
2-Me			8·93 (d)	8·84 (d)	9·03 (d)	8·93 (d)
$J_{H,Me}$			7·2	7·2	6·6	7·2

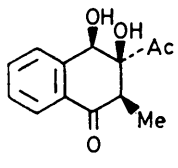
* τ Values; J in Hz.

are markedly different from those found for the H-4 signal from the tetralone (X)[1] (Table) and it seems probable that (IX; R = Me) and (IX; R = H) have *trans* disposed hydroxy-groups at C-3 and C-4. This view is strongly supported by a remarkable change in the n.m.r. spectrum of (IX; R = Me) on transferring from dimethyl sulphoxide to chloroform solution, which is most readily interpreted in terms of a change in the conformation of the alicyclic ring. The strong shielding of the C-3 acetyl methyl group in chloroform solution is consistent with this group occupying an axial position, for hydrogen bonding between the acetyl carbonyl and the 3-hydroxy-group will place the methyl within the shielding cone of the aromatic ring. This ' acetyl axial ' conformation also requires H-2 and H-4, in structure (IX; R = Me), to occupy quasi-axial and axial positions, respectively, which are the positions occupied by these protons in the normal ' acetyl equatorial ' conformation of the isomer (X). The Table shows that the chemical shifts of H-2 and H-4 in (IX; R = Me) and (X) correspond closely when chloroform is the solvent but that there is a marked difference in the coupling constants of

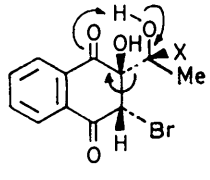
[8] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 238.

benzylic groups. This is also expected since, for optimum hydrogen bonding, the conformational requirements of the 4-hydroxy-groups in these compounds are markedly different.

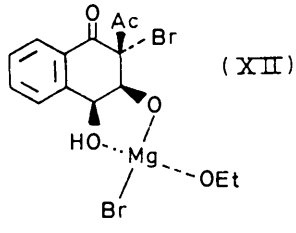
Two features of structure (IX; R = Me) appear to be responsible for the conformational changes observed. In the ' acetyl axial ' conformation both hydroxy-groups can contribute simultaneously to intramolecular hydrogen bonding, which will have a much greater bearing on the stability of the conformation in chloroform solution than in dimethyl sulphoxide. The high value of $J_{H,OH}$ for the tetralone (X), when in chloroform solution, is indicative of a similar grouping, but in this case the conformation is ' acetyl equatorial.' However, hydrogen bonding alone does not adequately account for the change in (IX; R = Me), for the lower homologue does not appear to adopt the ' acetyl axial ' conformation in chloroform. The second factor must be the



(X)



(XI)



(XII)

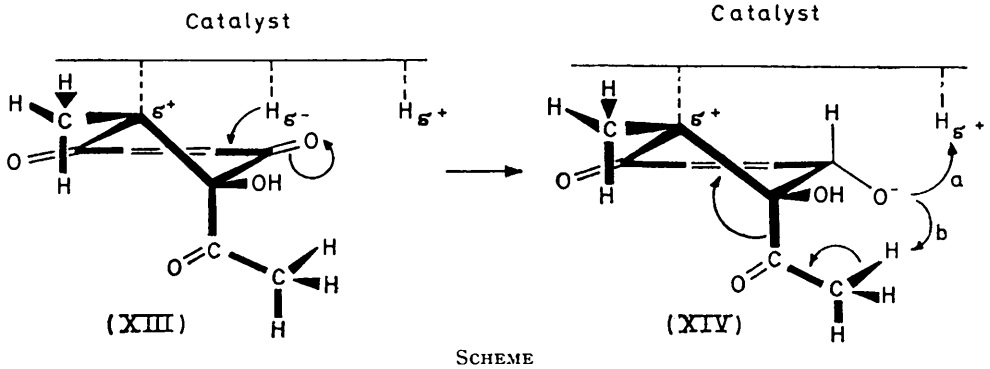
C-2 methyl group in (IX; R = Me) which can destabilise the ' acetyl equatorial ' conformation in both solvents by interacting with the quasi-axial hydroxy-

group at C-4 and restricting the free rotation of the C-3 acetyl group.

The difference in reactivity between the two quinone epoxides must relate to the inductive or the steric influence of the C-3 methyl group in (I; R = Me), or both. Although the literature contains numerous examples of Lewis-acid catalysed epoxide openings which are accompanied by C–C fission and which lead to rearranged products,[9] there appears to be little analogy between these reactions and the loss, in the presence of hydrogen bromide, of the C-2 acetyl group in (I; R = H). We think it more probable that this fission is the result of the breakdown, by the mechanism indicated, of species such as (XI; X = Br or AcO), which may be expected to be in equilibrium with the corresponding bromohydrin. The 3-methyl group would inhibit the formation of such compounds and would also prevent the adoption of the conformation necessary for the breakdown.

In the rearrangement which accompanies the opening by magnesium bromide of the epoxide ring in the dihydroquinone epoxide (II; R = H), an early intermediate is lilely to be the complex (XII). It is possible that the metal ion participates in the acylation step, for an *axial* C-2 acetyl group in (XII) will be situated within the co-ordination sphere of the magnesium and close to the axial C-4 hydroxy-group.

bromohydrin (III; R = Me) and developing it to require a catalyst–substrate complex in which steric interaction between the catalyst and the substrate is minimised, leads to the complex (XIII) depicted in the Scheme. In such a complex an attack by ' nucleophilic hydrogen ' species at C-1 can compete with the reorganisation step, to give the complex (XIV) which can be converted further into the tetralone (IX; R = Me) by an ' electrophilic hydrogen ' attack on the oxygen anion (a) followed by further ' nucleophilic hydrogen ' attack at C-3 on the reorganised complex. This mechanism not only accounts for the stereospecificity but also for the very rapid reduction at C-1 relative to related benzylic ketones.[1] The tetralone (IX; R = Me) is however only the minor product of this reduction. The steric influence of the equatorial C-3 methyl group in the complex (XIV) would ideally align the axial C-2 acetyl group for the breakdown, initiated by the nucleophilic abstraction (b) of a proton from the acetyl methyl group, which leads to a ketonic tautomer of the major product (VII; R^1 = H, R^2 = Me) and keten. We suggest that the acetyl group is normally lost in this manner and that, on the one occasion noted, the surface conditions favoured attack by the keten at the newly generated hydroxy-group at C-1 giving, on desorption, 4-acetoxy-2-methylnaphthalene-1,3-diol (VII; R^1 = Ac, R^2 = Me). Again from the standpoint of an initial attack by an ' electrophilic



SCHEME

The features of the catalytic transformations are of particular interest. In Part VII we presented circumstantial evidence for the hydrogenolysis of a C–Br bond proceeding by attack from an ' electrophilic hydrogen ' species. In that case the carbonium ion intermediate (catalyst-stabilised) was considered to lose a proton before reorganisation of the catalyst–substrate complex permitted reduction at this centre by a ' nucleophilic hydrogen ' species. The concept of a catalyst–substrate complex which is subject to competing processes under hydrogenation conditions is in full accord with current views on catalytic reduction. However there appears to be little direct evidence for the participation of proton and hydride species in reactions at palladium surfaces.[10] Extending this argument to the hydrogenation of the hydrogen,' it is apparent that a mechanism for the ring opening of the epoxide (I; R = Me) can also be put forward which leads to the formation of complexes (XIII) and (XIV) and the elimination of the C-2 acetyl group as keten.

The formation of the tetralone (IX; R = H) from the lower homologue is also rapid and this, combined with the stereospecificity, reinforces our belief that reduction at the C-1 carbonyl group must be intimately associated with the ring opening reaction. The absence of any deacetylated products in this case may be due to the absence of any restriction on the conformation of the C-2 acetyl group, but it is unlikely that this alone would completely prevent elimination. On the basis of the foregoing mechanisms, a major factor could be the

[9] J.-L. Pierre, *Ann. Chim.* (*France*), 1966, 159; H. Grisebach, and W. Barz, *Chem. Ber.*, 1964, **97**, 1688; W. D. Ollis, K. L. Ormand, and J. O. Sutherland, *Chem. Comm.*, 1968, 1237.

[10] (*a*) G. C. Bond, (*b*) R. L. Burwell and K. Schrage, (*c*) B. J. Joice, J. J. Rooney, P. B. Wells, and G. R. Wilson, *Discuss. Faraday Soc.*, 1966, **41**, (*a*) 200, (*b*) 215, and (*c*) 223.

reactivity of the C-3 centre in the complex corresponding to (XIII). The delocalised carbonium ion would be less stable in this case and a relatively rapid reorganisation of the complex to allow hydrogenation at C-3 by a second ' nucleophilic hydrogen ' could compete successfully with the elimination reaction.

Whilst these suggested mechanisms form no more than a working hypothesis, it is of interest that where the same stereospecificity was observed in catalytic reductions reported in Part VII, more than one centre in the substrate was modified.

EXPERIMENTAL

U.v. spectra were measured with a Hilger Ultrascan recording spectrophotometer H999 Mark II, and i.r. spectra were determined for potassium bromide discs, unless otherwise stated, with a Hilger Infrascan recording spectrophotometer H900. N.m.r. spectra were recorded with a Perkin-Elmer R10 instrument at 60 MHz and mass measurements were made with a Hitachi–Perkin-Elmer RMU-6 instrument.

For column chromatography Mallinckrodt silicic acid and Merck silica gel were used. Merck DC-Fertigplatten Kieselgel F_{254} was used for t.l.c.

2-Acetyl-t-3-bromo-2,3-dihydro-r-2-hydroxy-3-methyl-1,4-napthoquinone (III; R = Me).—2-Acetyl-2,3-epoxy-2,3-dihydro-3-methyl-1,4-naphthoquinone [1] (2·0 g), dissolved in acetic acid (20 ml), was treated with 20% hydrogen bromide in acetic acid (10 ml). After 20 min at room temperature, the solvent and excess of reagent were removed under reduced pressure and the residue was dissolved in light petroleum (b.p. 80—100°) and treated with charcoal. After filtration, the cooled solution gave needles of the *2-acetyl bromohydrin* (III; R = Me) (2·48 g, 92%), m.p. 136—137° (decomp.) (Found: C, 50·1; H, 3·6. $C_{13}H_{11}BrO_4$ requires C, 50·2; H, 3·6%); $\nu_{max.}$ 3420 (OH str.), 1717 (acetyl C=O str.), and 1693 cm^{-1} (aryl ketone C=O str.); $\lambda_{max.}$ 235, 256, and 305 nm (log ε 4·28, 3·91, and 3·32); τ [$(CD_3)_2SO$–D_2O] 8·23 (3H, s, 3-Me), 7·71 (3H, s, Ac), and 2·80 (4H, m, aryl H).

Reaction of 2-Acetyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone with Hydrogen Bromide in Acetic Acid.—The epoxide [1] (1 g) in acetic acid (10 ml) was treated with 8% hydrogen bromide in glacial acetic acid (7 ml). After 15 min the red solution was diluted with water (*ca.* 100 ml) and extracted with chloroform (5 × 20 ml). The dried ($MgSO_4$) extract was evaporated under reduced pressure to give 2-bromo-3-hydroxy-1,4-naphthoquinone (0·8 g, 68%). A sublimed sample had m.p. 195·5—196° (decomp.) (Found: C, 47·6; H, 2·0. Calc. for $C_{10}H_5BrO_3$: C, 47·5; H, 2·0%); $\nu_{max.}$ 3240 (OH str.), 1675, 1651, and 1631 cm^{-1} (quinone C=O str.) (lit.,[11] m.p. 196—197°).

2-Acetyl-t-3-bromo-2,3-dihydro-r-2-hydroxy-1,4-naphthoquinone (III; R = H).—2-Acetyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (0·15 g) dissolved in anhydrous ether (10 ml) was treated with a solution of anhydrous magnesium bromide (20 ml).[2] After 5 min at 0°, 0·01M-hydrochloric acid (20 ml) was added to dissolve the complex formed and the product was extracted into ether (3 × 15 ml). The dried ($MgSO_4$) extract was evaporated and the residue crystallised from light petroleum ether to give the *bromohydrin* (76 mg, 37%), m.p. 89—90° (decomp.) (Found: C, 48·6; H, 3·2. $C_{12}H_9BrO_4$ requires C, 48·5; H, 3·1%); $\nu_{max.}$ 3440 (OH str.), 1726 (acetyl C=O str.), 1713 (chelated acetyl C=O str.), and 1690 cm^{-1} (aryl C=O str.); $\lambda_{max.}$ 232, 256, and 303 nm (log ε 4·44, 3·91, and 3·37); τ ($CDCl_3$–D_2O) 7·72 (3H, s, Ac), 4·96 (1H, s, 3-H), and 1·93 (4H, m, aryl H).

Acidification of the aqueous phase from the ether extract to pH 1·0 with hydrochloric acid and extraction with ethyl acetate gave 2-bromo-3-hydroxy-1,4-naphthoquinone (53·3 mg, 30%), identified by comparisons with the material obtained from the preceding experiment.

Reaction of 2-Acetyl-r-2,3-epoxy-3,4-dihydro-c-4-hydroxynaphthalen-1(2H)-one with Magnesium Bromide–Ether Complex.—The tetralone [1] (II; R = H) (324 mg) in anhydrous ether (35 ml) was treated with a solution of anhydrous magnesium bromide–ether [2] (50 ml). After 5 min at 0°, 0·01M-hydrochloric acid (80 ml) was added to decompose the bright green complex. The ether layer was separated and the aqueous layer was extracted with ether (5 × 50 ml). The combined ether extracts were dried and evaporated. The product, *c-4-acetoxy-r-2-bromo-3,4-dihydro-c-3-hydroxynaphthalen-1(2H)-one* (VIII) crystallised from benzene as fine needles, m.p. 177° (decomp.) (Found: C, 47·7; H, 3·6. $C_{12}H_{11}BrO_4$ requires C, 48·2; H, 3·7%); $\nu_{max.}$ 3475 (OH str.), 1728 (acetoxy C=O str.), and 1703 cm^{-1} (aryl C=O str.); $\lambda_{max.}$ 248 and 290 nm (log ε 4·06 and 3·22); τ [$(CD_3)_2SO$–D_2O] 7·79 (3H, s, Ac), 5·38 (1H, t, $J_{2,3} = J_{3,4}$ 2·3 Hz, 3-H), 4·38 (1H, d, $J_{2,3}$ 2·1 Hz, 2-H), 3·74 (1H, d, $J_{3,4}$ 3·0 Hz, 4-H), and 2·35 (4H, m, aryl H); *m/e* 300 (M^+ for ^{81}Br). The product decomposed during several weeks in the dark.

After a small sample of the tetralone in ethyl acetate had been shaken with sodium hydrogen carbonate solution for 5 min, 2-bromo-1,4-naphthoquinone, m.p. 131—132°, was isolated and was identical with an authentic sample.[12]

Hydrogenation of 2-Acetyl-2,3-epoxy-2,3-dihydro-3-methyl-1,4-naphthoquinone.—(a) *Over 5% palladium–charcoal.* The epoxide [1] (100 mg) in ethanol (25 ml) was hydrogenated in the presence of 5% palladium–charcoal (35 mg). After 10 min hydrogen uptake (1·6 equiv.) stopped and the catalyst was removed. The colourless solution, which turned red in contact with air, was diluted with water (250 ml) and acidified with dilute hydrochloric acid to pH 2—3. A solid precipitated which crystallised from ethanol–water to give yellow needles, m.p. 173—174° (75 mg, 91%), indistinguishable from authentic 2-hydroxy-3-methyl-1,4-naphthoquinone (Found: C, 70·3; H, 4·5. Calc. for $C_{11}H_8O_3$: C, 70·2; H, 4·3%); $\nu_{max.}$ 3340 (OH str.), 1658, and 1642sh cm^{-1} (quinone C=O str.) (lit.,[13] m.p. 173—174°).

(b) *Over 5% palladium oxide–barium sulphate.* The epoxide (100 mg) was reduced in ethanol over 5% palladium oxide–barium sulphate.[3] The ethanolic solution was diluted with water and the 2-acetyl-3-methylnaphthalene-1,4-diol was separated from the quinone by extraction into ethyl acetate (3 × 50 ml). Auto-oxidation of this product occurred in solution and the quinone formed was purified by crystallisation from benzene–light petroleum. The material obtained (50 mg, 55% yield) had m.p. 87—88° and was identical with authentic 2-acetyl-3-methyl-1,4-naphthoquinone.[1]

The aqueous phase from the ethyl acetate extract was acidified to pH 2—3 to precipitate 2-hydroxy-3-methyl-1,4-naphthoquinone (35 mg, 43%).

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Reduction of 2-Acetyl-2,3-epoxy-2,3-dihydro-3-methyl-1,4-naphthoquinone with Zinc and Ammonium Chloride in Ethanol.—The epoxide (150 mg) and ammonium chloride (150 mg), in 75% ethanol–water (20 ml) were stirred with zinc dust (1 g). After 1 h the solid were removed and the filtrate was evaporated to half volume. The solution, which became red on exposure to the air, was diluted with water (30 ml) and acidified to pH 2—3 with dilute hydrochloric acid. A yellow precipitate was filtered off and crystallised from ethanol–water to give material, m.p. 172·5—173·5°, indistinguishable from the 2-hydroxy-3-methyl-1,4-naphthoquinone isolated in the preceding experiment.

Hydrogenation of 2-Acetyl-t-3-bromo-2,3-dihydro-r-2-hydroxy-3-methyl-1,4-naphthoquinone.—The bromohydrin [1] (966 mg) in ethanol (40 ml) was catalytically reduced in the presence of calcium carbonate (300 mg) and 10% palladium–calcium carbonate (150 mg) at 1 atm and room temperature. When hydrogen uptake stopped (73 ml, 3 equiv.) after 15 min the catalyst was filtered off and the solution was concentrated to *ca.* 5 ml and diluted with ethyl acetate (30 ml). The ethyl acetate solution was washed, dried ($MgSO_4$), and evaporated to dryness. Crystallisation of the residue from benzene gave a white product which readily became oxidised in contact with air to form 2-hydroxy-3-methyl-1,4-naphthoquinone, m.p. 173—174°, indistinguishable from that obtained in the foregoing hydrogenation.

The benzene mother liquors were washed with dilute sodium hydrogen carbonate solution and concentrated under reduced pressure to give needles of *3-acetyl-3,4-dihydro-t-3,c-4-dihydroxy-r-2-methylnaphthalen-1(2H)-one* (IX; R = Me) (210 mg, 22%), m.p. 170—171° (from benzene) (Found: C, 66·4; H, 6·3. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%); $\nu_{max.}$ ($CHCl_3$) 3592 (OH str.), 3430 (chelated OH str.), 1707 (acetyl C=O str.), and 1689 cm^{-1} (aryl C=O str.); $\lambda_{max.}$ 251 and 290 nm (log ε 3·94 and 3·10); *m/e* 234 $(M)^+$, 216 $(M - 18)^+$, and 191 $(M - 43)^+$ (see Table for n.m.r. data).

On one occasion a similar hydrogenation gave 1-acetoxy-3-methylnaphthalene-2,4-diol (VII; R^1 = Ac, R^2 = Me). This was isolated from the benzene solution as crystals (475 mg, 49%), which after recrystallisation had m.p. 136—138° (decomp.); $\nu_{max.}$ 3300 (OH str.) and 1742 cm^{-1} (chelated aryl ester C=O str.); $\lambda_{max.}$ 244 and 294 nm (log ε 4·00 and 3·73); τ [$(CD_3)_2SO$–D_2O] 8·14 (3H, s, 3-Me), 7·90 (3H, s, Ac), and 2·25 (4H, m, aryl H); *m/e* 232 $(M)^+$ ($C_{13}H_{12}O_4$ requires *M*, 232).

The diol was acetylated with acetic anhydride and 1 drop of concentrated sulphuric acid. Crystallisation of the product from ethanol–water gave 1,2,4-triacetoxy-3-methylnaphthalene, m.p. 156—157°, indistinguishable from an authentic sample prepared by reductive acetylation of 2-acetoxy-3-methyl-1,4-naphthoquinone (lit.,[14] m.p. 158—159°).

Hydrogenation of 2-Acetyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone over 5% Palladium–Charcoal.—The epoxide (65 mg) in ethanol (20 ml) was hydrogenated over 5% palladium–charcoal (10 mg). After 15 min absorption of hydrogen ceased (total uptake 14·2 ml, 2 equiv.). The crude product (55 mg) was isolated and crystallised from benzene. Sublimation and recrystallisation from chloroform removed some contaminating 2-acetylnaphthalene-1,4-diol to give *3-acetyl-3,4-dihydro-r-3,t-4-dihydroxynaphthalen-1(2H)-one* (IX; R = H), m.p. 191—193° (Found: C, 65·6; H, 5·45. $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·5%); $\nu_{max.}$ 3460 (OH str.), 3305 (chelated OH str.), 1713 (acetyl C=O str.), and 1675 cm^{-1} (aryl C=O str.); $\lambda_{max.}$ 245 and 284·5 nm (log ε 4·12 and 3·20); *m/e* 220 $(M)^+$, 202 $(M - 18)^+$, 177 $(M - 43)^+$, and 43 (see Table for n.m.r. data).

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