# Stereoselective Formation and Rearrangements of Naphthalen-2(1H)-one Epoxides

By **John Carnduff** * and **David G. Leppard,** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland †

Epoxidation of 1-hydroxy-1-isopropylnaphthalen-2(1H)-one (1) with alkaline hydrogen peroxide occurs exclusively from the face *trans* to the hydroxy-group. The epoxide (2) is isomerised in mild base by a ketol rearrangement and epoxide ring opening to r-2.3-epoxy-3.4-dihydro-*t*-4-hydroxy-2-isopropylnaphthalen-1(2H)-one (3) ; stronger bases produce 2-isopropylnaphthoquinone and 1.4-dihydroxy-1-isopropylnaphthalen-2(1H)-one (5). Treatment of the epoxide (1) with acetic acid yields 2-hydroxy-2-isopropylnaphthalene-1.3(4H)-dione (10). The acetoxy-epoxide (15) obtained analogously and stereospecifically from 1-acetoxy-1-isopropylnaphthalen-2(1H)-one rearranges in acetic acid to 1-acetoxy-3-hydroxy-1-isopropylnaphthalen-2(1H)-one (16).

DURING an investigation of hydroperoxynaphthalenones [1,2] a product was isolated which appeared to be an epoxide of the hydroxynaphthalenone (1). We report here the deliberate epoxidation of this enone and of its acetate and some products of rearrangement of the epoxides in base and in acid.[3]

The hydroxynaphthalenone (1) [1] was epoxidised with hydrogen peroxide and sodium hydroxide or sodium carbonate in ethanol and gave a single epoxide in over 90% yield. Although the faces of the enone are not equivalent, no stereoisomeric by-product was detected by n.m.r. or t.l.c. The spectra of the epoxide show that no rearrangement has occurred during its preparation. It shows absorptions corresponding to a simple benzene-type chromophore, a saturated cyclohexanone carbonyl
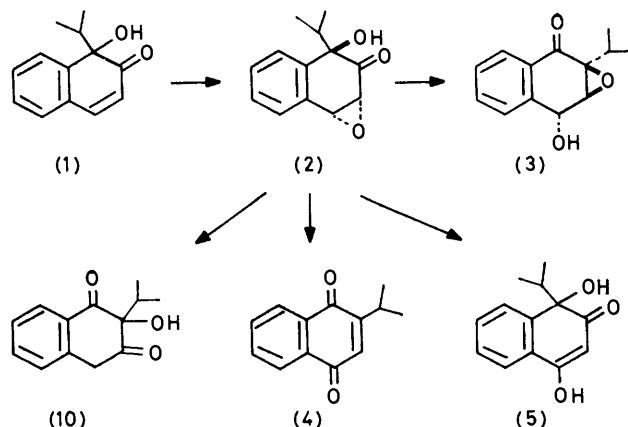

group, oxiran protons deshielded about equally by the aryl and acyl substituents, and an isopropyl group in which the methyl groups are magnetically non-equivalent.

To establish the stereochemistry of this epoxide, its reactions with bases were examined in the expectation

that these might induce S_N2 ring opening of the oxiran by the anion of the hydroxy-group provided that the hydroxy-group and oxiran oxygen were *trans*-disposed on the cyclohexane ring. In the event, heating with sodium carbonate in ethanol did isomerise the epoxide cleanly to a single product, shown by its spectra to be a hydroxy-oxo-epoxide but of skeletally rearranged struc-

SCHEME
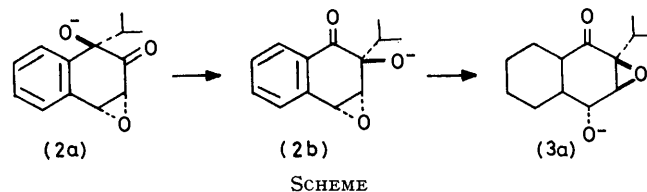
ture. This new epoxide shows an α-tetralone-type carbonyl i.r. band at 1 690 cm⁻¹ and an α-tetralone-type u.v. absorption. The hydroxy-group is secondary and benzylic since the epoxide can be oxidised with loss of two hydrogen atoms by either chromium trioxide in pyridine or manganese dioxide in acetone. The product from this oxidation was the epoxide of 2-isopropyl-naphthoquinone. The new epoxide is therefore most likely to be one of the stereoisomeric 2,3-epoxy-3,4-di-hydro-4-hydroxy-2-isopropylnaphthalen-1(2H)-ones, of which the *trans*-isomer (3) ‡ is more likely in view of the probable mechanism of the isomerisation (2) ⟶ (3).

This reaction apparently involves a ketol (acyloin) rearrangement in which the isopropyl group migrates along one face of the molecule to give an isomeric alkoxide ion (2b) having the carbonyl group conjugated to the benzene ring (Scheme). S_N2 Attack by the new alkoxide on the epoxide ring would lead to (3a). For this rearrangement to occur, a *trans*-disposition of the oxiran and alkoxide oxygen atoms must be present in (2b),

---

‡ One enantiomer only is drawn for this and subsequent chiral substances. Our materials were racemic.

[1] J. Carnduff and D. G. Leppard, *J.C.S. Perkin I*, 1976, 2570.

[2] J. Carnduff and D. G. Leppard, *Chem. Comm.*, 1971, 975; following paper.

[3] Preliminary communication, J. Carnduff and D. G. Leppard, *Chem. Comm.*, 1968, 822.

(2a), and (3a). We therefore assign the *trans*-stereochemistry to the product (2) of epoxidation of (1), and the *trans*-stereochemistry to its rearrangement product (3). There are literature analogies for the rearrangement of the epoxides of allylic alcohols,[4,5] and for rearrangements under basic conditions of α-hydroxy-ketones[6] and of γ-hydroxy-cyclohexadienones.[7]

We have found the ketol rearrangement to occur with several 1-alkyl-1-hydroxynaphthalen-2(1H)-ones. The position of the equilibrium between the structural isomers depends on the substitution pattern. For the naphthalenones, both isomers have conjugated carbonyl groups and they are of similar stability. With 3,4-dihydronaphthalenones such as the epoxide (2) or 3,4-dihydro-1-hydroxy-1-isopropylnaphthalen-2(1H)-one (8), made by hydrogenation of (1), the conjugated naphthalen-1(2H)-ones are more stable. We have observed complete conversion of (8) into (9) with potassium t-butoxide in benzene.

(6)
(7)
(8)
(9)
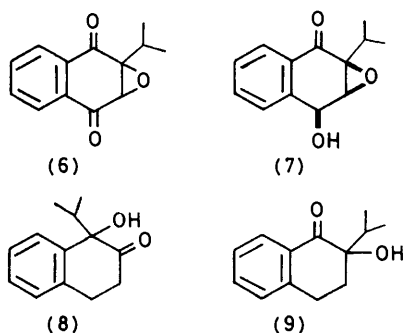
The product from the oxidation of the new epoxide (3) was an epoxy-dione. Its spectra suggested that it was the hitherto unknown epoxide of 2-isopropyl-1,4-naphthoquinone, and this was confirmed by synthesising this epoxide. 2-Isopropyl-1,4-naphthoquinone was prepared by radical alkylation of 1,4-naphthoquinone with isobutyric acid and trilead tetraoxide.[8] In this procedure the carboxylic acid is used as solvent and oxidant can be added until t.l.c. shows that little naphthoquinone remains. The cleaner procedure with peroxosulphate as oxidant, catalytic amounts of silver ion, and stoicheiometric amounts of the carboxylic acid[9] led in our hands to recovery of 60% of the starting quinone. Both procedures require chromatographic separation of the starting naphthoquinone from its mono- and any di-alkyl derivative. Treatment of the isopropylquinone with hydrogen peroxide and sodium carbonate[10] gave the expected epoxide (6), which had spectra identical with

those of the material made by oxidation of the epoxide (3).

Recently Read[11] has shown that reductions by sodium borohydride of the epoxide of several quinones lead predominantly or exclusively to epoxy-hydroxy-ketones in which the epoxide and hydroxylic oxygen atoms are *cis*-disposed. In the case of the 2-acetylnaphthoquinone epoxide reduction occurred preferentially at the less hindered carbonyl group in the ring. Read has also discussed the difficulties in using coupling constants to assign relative stereochemistry to these epoxy-alcohols, even when both isomers are in hand, because of uncertainty about the populations of different conformations of the cyclohexene system in these cases.

Reduction of the epoxide of 2-isopropylnaphthoquinone with an excess of sodium borohydride gave a mixture of two compounds, which was separated by preparative t.l.c. The less polar, major component was a crystalline alcohol (7). Its n.m.r. spectrum shows a small coupling between the adjacent carbinol and oxiran protons, confirming that the less hindered carbonyl group has been reduced. In view of Read's work it can be assigned the *cis*-stereochemistry and its spectral similarity but nonidentity with the rearrangement product support the assignment of structure and stereochemistry to the latter (3). The diastereoisomers (3) and (7) have almost identical u.v. and n.m.r. spectra and similar i.r. spectra. The coupling constants between the *trans*-protons in the first case and the *cis*-protons in the second are almost identical. The minor and more polar product from the reduction has the spectral characteristics expected for an epoxy-diol resulting from further reduction of the ketone (7). No isomer (3) was detected among the products of reduction of the dione (6).

The behaviour of the hydroxynaphthalenone epoxide (2) with stronger bases was investigated. Potassium t-butoxide in benzene at reflux for 1 h converted the epoxide into a mixture of one acidic and two neutral components. Chromatography of the neutral components yielded the isomeric epoxide (3) (52%) and 2-isopropylnaphthoquinone (20%). The mechanism whereby rearrangement and dehydration to the quinone occur is not clear but the quinone may arise from the hydroxy-epoxide (3) by initial removal of a proton from the carbinol carbon atom as in the analogous dehydration of both isomeric 2,10-epoxy-10β-pinan-3-ols (11) to pinocarvone (12) with methanolic sodium hydroxide.[12]

The base-soluble material from the rearrangement of the epoxide (2) with potassium t-butoxide was a pale yellow solid (30% yield). Analysis showed it to be an isomer of (2). Hydroxy and carbonyl bands were

[4] V. N. Yandovskii, V. S. Karavan, and T. I. Temnikova, *Russ. Chem. Rev.*, 1970, **39**, 265, 269.

[5] For a recent example see H. Paulsen and V. Sinnwell, *Angew. Chem. Internat. Edn.*, 1976, **15**, 438.

[6] D. N. Kirk and M. P. Hartshorn, ' Steroid Reaction Mechanisms,' Elsevier, Amsterdam, 1968, pp. 297, 388; P. de Mayo in ' Elucidation of Structures by Physical and Chemical Methods,' ed. K. W. Bentley, Interscience, New York, 1963, p. 1125.

[7] A. Nishinaga, T. Itahara, T. Matsuura, S. Berger, G. Henes, and A. Rieker, *Chem. Ber.*, 1976, **109**, 1530.

[8] L. F. Fieser and F. C. Chang, *J. Amer. Chem. Soc.*, 1942, **64**, 2043.

[9] N. Jacobsen and K. Torssell, *Annalen*, 1972, **763**, 135; *Acta Chem. Scand.*, 1973, **27**, 3211.

[10] M. Tishler, L. F. Fieser, and N. L. Wendler, *J. Amer. Chem. Soc.*, 1940, **62**, 2869.

[11] A. Rashid and G. Read, *J. Chem. Soc.* (*C*), 1969, 2053: G. Read and V. M. Ruiz, *ibid.*, 1970, 1945; *J.C.S. Perkin I*, 1973, 235. We are indebted to Dr. Read for discussions of these reductions.

[12] J. M. Coxon, E. Dansted, R. P. Garland, M. P. Hartshorn, and W. B. Joss, *Tetrahedron*, 1971, 1287.

present in the i.r. spectrum, the latter (at 1 520 cm⁻¹) suggesting an enolised β-diketone system. The yellow material ($\lambda_{max.}$ 310 nm) gave a red anion ($\lambda_{max.}$ 338 nm) on addition of sodium hydroxide. No n.m.r. spectrum was obtained because of the compound's insolubility. Treatment with diazomethane gave a mixture of two methyl

(11)   (12)
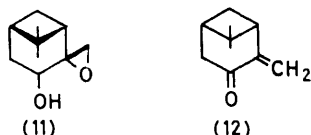
ethers, one of which was isolated in a pure state and was identified as 1-hydroxy-1-isopropyl-4-methoxynaphthalen-2(1H)-one on the basis of its i.r., n.m.r., and u.v. spectra which resemble those of the hydroxy-ketone (1). The β-diketone is therefore, 1,4-dihydroxy-1-isopropyl-naphthalen-2(1H)-one (5), in equilibrium in solution with its tautomers. In confirmation of this structure the reaction of isopropylmagnesium bromide with the anion (13) of 2-hydroxy-1,4-naphthoquinone gave, as the sole product soluble in aqueous sodium hydrogen carbonate, a modest yield of a yellow solid identical with that formed in the rearrangement of (2). The action of potassium t-butoxide in benzene on (2) therefore includes rearrangement of the epoxide unit by removal of the benzylic proton of the epoxide, as well as formation of the alkoxide ion and subsequent ketol rearrangement.

Attention was then turned to rearrangement of the epoxide (2) in acid. When the epoxide was refluxed in glacial acetic acid it was isomerised in high yield to a new isomer with two carbonyl i.r. bands (1 730 and 1 675 cm⁻¹) and a u.v. spectrum similar to those of (7)

(13)   (14)

(15)   (16)
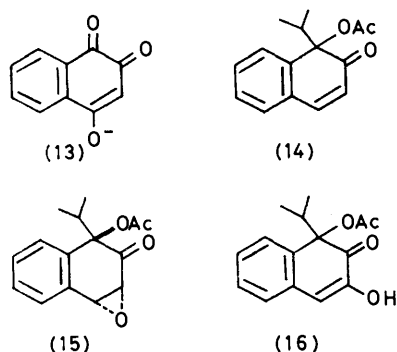
and (9). The compound is slightly soluble in aqueous sodium hydrogen carbonate and readily soluble in aqueous sodium hydroxide, giving a red anion. The isopropyl and hydroxy-groups are still detectable in the n.m.r. spectrum, as are signals for two non-equivalent protons at about τ 6. We assign to this material the structure (10) resulting perhaps from acid-catalysed isomerisation of the epoxide to an α-dione and acid-catalysed ketol rearrangement. Breakage of the benzylic C–O

* Not 61—62° as stated in ref. 3.

[13] S. P. Pappas, R. M. Gresham, and M. J. Miller, *J. Amer. Chem. Soc.*, 1970, **92**, 5797.

bond of the epoxide under acidic conditions is to be expected, and has been observed in other naphthalen-2(1H)-one epoxides.[13,14]

Epoxidation of 1-acetoxy-1-isopropylnaphthalen-2(1H)-one (14) with hydrogen peroxide and sodium carbonate proceeds, as with hydroxynaphthalenone, to give a single epoxy-acetate (15) in good yield. When this acetoxy-epoxide was refluxed in glacial acetic acid it rearranged to an isomer to which we assign the 3-hydroxynaphthalen-2(1H)-one structure (16). Ketol rearrangement is, of course, not possible, but the αβ-epoxy-ketone has rearranged to an α-dione as expected.[13,14] The structure follows from the presence of hydroxylic and conjugated carbonyl i.r. bands, a naphthalen-2(1H)-one-type u.v. spectrum, the bands of which shift markedly to longer wavelength on addition of sodium hydroxide, and the presence in the n.m.r. spectrum of a singlet due to one alkenyl proton, at τ 3.4. The H-4 signal of 3-hydroxy-1,1-dimethylnaphthalen-2(1H)-one appears at τ 3.2.[13]

The relative stereochemisty of the epoxide (15) is not clarified by this rearrangement but it was easily determined. Mild hydrolysis of the acetate group with warm dilute sodium carbonate yielded the epoxide (2). Thus epoxidation of the 1-hydroxy- and the 1-acetoxy-naphthalenones both proceed with high stereoselectivity to yield the *trans*-isomers (2) and (15). The limitations and explanation of this stereospecific epoxidation are being investigated

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. Unless otherwise stated u.v. spectra were measured for solutions in ethanol and i.r. spectra for Nujol mulls. N.m.r. spectra were run for solutions in deuteriochloroform with tetramethylsilane as internal standard. Light petroleum refers to the fraction b.p. 60—80 °C. T.l.c. was carried out on Kieselgel G with 20% ethyl acetate in light petroleum unless otherwise stated.

Epoxidation of 1-Hydroxy-1-isopropylnaphthalen-2(1H)-one (1).—1-Hydroxy-1-isopropylnaphthalen-2(1H)-one (2.0 g) in ethanol (100 ml) containing acetone (4 ml) was treated dropwise with a solution of hydrogen peroxide (28%; 20 ml) and anhydrous sodium carbonate (1.0 g) in water (10 ml). The mixture was stirred at 40 °C for 1 h then poured into water and extracted with ether. After drying, the ether layer was evaporated leaving an oil which crystallised from light petroleum. Two more crystallisations gave the *epoxide* (2) (1.66 g) as needles, m.p. 71—72°,* $\lambda_{max.}$ 265, 271, 278, and 298 nm (ε 460, 540, 500, and 160), $\nu_{max.}$ (CCl₄) 3 500 and 1 715 cm⁻¹, τ 9.15 and 9.16 (total 6 H, two doublets, each J 7 Hz), 7.45 (1 H, sept), 6.4 (1 H, s), 6.2 (1 H, d, J 4 Hz), 5.8 (1 H, d, J 4 Hz), and 2.8—2.3 (4 H, m), τ (benzene) 9.15 (3 H, d), 9.12 (3 H, d), 7.35 (1 H, sept), 6.65 (1 H, d), 6.55 (1 H, d), and 6.23 (1 H, s) (Found: C, 71.4; H, 6.3. $C_{13}H_{14}O_3$ requires C, 71.55; H, 6.4%). The mother liquors from these crystallisations contained 0.40 g of material, mainly the epoxide (2). The n.m.r. spectrum shows that this contains about 6% of starting material and 6% of the isomer of the starting material arising by base-

[14] L. F. Fieser and L. W. Newton, *J. Amer. Chem. Soc.*, 1942, **64**, 917.

induced ketol rearrangement (see accompanying paper). The epoxidation therefore yields at least 92% of (2) with 1% of recovered enone (1) and 1% of the isomeric enone. There was no evidence of an epoxide stereoisomeric with (2).

Rearrangement of the Epoxide (2) *with Sodium Carbonate.*— The epoxide (2) (0.2 g) was dissolved in ethanol (10 ml) and sodium carbonate (0.1 g) in water (6 ml) added. The mixture was refluxed for 2 h and became red. T.l.c. showed the presence of only one component. The mixture was poured into water and extracted with ether. The extract was washed with water, dried, and evaporated to give r-2,3-*epoxy*-3,4-*dihydro*-t-4-*hydroxy*-2-*isopropylnaphthalen*-1(2H)-*one* (3) as an oil (0.17 g), $\lambda_{max.}$ 251 and 286 nm (ε 9 500 and 1 300), $\nu_{max.}$ (CCl$_4$) 3 500 and 1 690, $\nu_{max.}$ (film) 3 400, 1 695, 1 610, 1 300, 1 040, 940, 900, 870, 830, 755, 725, and 680 cm^{-1}, τ 9.05 (3 H, d, J 7 Hz), 8.95 (3 H, d, J 7 Hz), 7.43 (1 H, sept), 7.0 (1 H, s), 6.23 (1 H, d, J 3 Hz), 4.85 (1 H, d, J 3 Hz), 2.8—2.3 (3 H, m), and 2.15 (1 H, m) (Found: C, 71.4; H, 6.3. C$_{13}$H$_{14}$O$_3$ requires C, 71.55; H, 6.4%).

Oxidation of the Epoxy-oxo-alcohol (3).—The epoxide (3) (0.2 g) was oxidised with chromium trioxide (0.2 g) in pyridine (5 ml) at room temperature for 24 h. The slurry was poured into water and extracted with ether. The extract yielded 2-isopropylnaphthoquinone epoxide (6) (0.18 g), identical with material made by epoxidation of the quinone (see below).

2-*Isopropyl*-1,4-*naphthoquinone* (4).—1,4-Naphthoquinone (1.0 g) and malonic acid (1.0 g) were dissolved in isobutyric acid (26 ml) and heated to reflux. Trilead tetraoxide (*ca.* 6 g) was added in small amounts until t.l.c. showed there was no starting quinone left. The mixture was poured into water and extracted with ether; the extract yielded an oil which was chromatographed on silica. Elution with 5% ether–petroleum gave the isopropylquinone (0.8 g), which crystallised from ethanol as yellow spars, m.p. 45—47° (lit.,[15] 43—44°; lit.,[16] 45—46.5°).

Epoxidation of the Isopropyl-quinone (4).—2-Isopropyl-1,4-naphthoquinone (0.1 g) in ethanol (5 ml) at 30 °C was treated with a mixture of hydrogen peroxide (28%; 0.5 ml), sodium carbonate (0.05 g), and water (1 ml). After 5 min the mixture was poured into water and extracted with ether. The extract was washed, dried, and evaporated to give the *epoxide* (6) as an oil (0.1 g), which could be distilled unchanged at 70° and 0.05 mmHg; $\lambda_{max.}$ 266 and 304 nm (ε 5 100 and 1 700), $\nu_{max.}$ 1 695 cm^{-1}, τ 8.95 (3 H, d, J 7 Hz), 8.85 (3 H, d, J 7 Hz), 7.2 (1 H, sept), 6.05 (1 H, s), and 3.2—2.6 (4 H, m) (Found: C, 71.9; H, 5.9. C$_{13}$H$_{12}$O$_3$ requires C, 72.2; H, 5.6%). A sample which had been refrigerated for over a year deposited crystals of the epoxide, m.p. 30—31°.

Reduction of the Quinone Epoxide (6) *by Borohydride.*— The quinone epoxide (557 mg) in ethanol (50 ml) was treated with sodium borohydride (50 mg) in water (8 ml) containing ethanol (2 ml). After 10 min, water and a few drops of hydrochloric acid were added to bring the pH to *ca.* 5. The solution was saturated with sodium chloride and extracted with 1 : 1 ether–petroleum to give a mixture (415 mg) of two components. Preparative t.l.c. yielded r-2,3-*epoxy*-3,4-*dihydro*-c-4-*hydroxy*-2-*isopropylnaphthalen*-1(2H)-*one* (180 mg) as fine needles, m.p. 104—105°, $\lambda_{max.}$ 252 and 288 nm (ε 11 400 and 1 300), $\nu_{max.}$ 3 400br, 1 705, 1 610, 1 310, 1 050, 990, 930, 905, 845, 780, 760, and 730 cm^{-1}, τ 9.05 (3 H, d, J 7 Hz), 8.98 (3 H, d, J 7 Hz), 7.40 (1 H, sept, J

7 Hz), 6.65br (1 H, s), 6.2 (1 H, d, J 2 Hz), 5.0br (1 H, s), 2.7—2.3 (3 H, m), and 2.2 (1 H, m) (on addition of D$_2$O the broad band at 6.65 disappears and the band at 5.0 sharpens to a doublet, J 2 Hz) (Found: C, 71.8; H, 6.5. C$_{13}$H$_{14}$O$_3$ requires C, 71.55; H, 6.4%). The second product was isolated from preparative t.l.c. as flakes (34 mg), m.p. 115—120°, $\nu_{max.}$ 3 300, 1 030, 990, and 740 cm^{-1}, τ 9.13 (3 H, d, J 7 Hz), 8.90 (3 H, d, J 7 Hz), 7.53 (1 H, sept, J 7 Hz), 7.4br (1 H), 6.55 (1 H, d, J 2 Hz), 5.2br (1 H, s), 5.15br (1 H, s), and 2.8—2.3 (4 H, m) (on addition of D$_2$O the broad band at τ 7.4 disappears, the band at 5.2 sharpens to a doublet, and that at 5.15 sharpens to a singlet).

Rearrangement of the Epoxide (2) *with Potassium t-Butoxide.* —The epoxide (2) (1 g) was dissolved in dry benzene (40 ml) and potassium t-butoxide (0.5 g) in dry benzene (150 ml) was added. The mixture was refluxed for 1 h under nitrogen. After cooling, water was added and the mixture shaken and separated into a neutral benzene layer and an aqueous layer. The neutral layer was washed, dried, and evaporated to give an orange oil (0.7 g), which was chromatographed on silica with petroleum–diethyl ether to yield 2-isopropyl-1,4-naphthoquinone (0.18 g), m.p. 45—47° (lit.,[15] 43—44°; lit.,[16] 45—46°), $\lambda_{max.}$ 249 and 333 nm (ε 19 000 and 3 600), $\nu_{max.}$ 1 675 cm^{-1}, τ 8.82 (6 H, d, J 7 Hz), 6.9 (1 H, sept), 3.5 (1 H, s), and 2.6—2.0 (4 H, m), followed by r-2,3-epoxy-3,4-dihydro-*t*-4-hydroxy-2-isopropylnaphthalen-1(2*H*)-one (3) (0.52 g) as an oil.

The aqueous layer was acidified and extracted with ether and the extract washed, dried, and evaporated to give 1,4-*dihydroxy*-1-*isopropylnaphthalen*-2(1H)-*one* (5) (0.3 g) which crystallised from ethanol as pale yellow crystals, m.p. 150—153°, $\lambda_{max.}$ 230 and 310 nm (ε 11 100 and 5 800) (moving to 338 nm on addition of aq. NaOH), $\nu_{max.}$ 3 400 and 1 520 cm^{-1} (Found: C, 71.65; H, 6.4. C$_{13}$H$_{14}$O$_3$ requires C, 71.55; H, 6.4%).

Methyl Ethers of the β-Diketone (5).—The diketone (5) (0.10 g) was dissolved in ether and treated with an excess of diazomethane. After 30 min at 0 °C the solution was evaporated to give a mixture of the two isomeric ethers. Fractional crystallisation yielded 1-*hydroxy*-1-*isopropyl*-4-*methoxynaphthalen*-2(1H)-*one* as yellow rhombs, m.p. 106—107°, $\nu_{max.}$ 3 400 and 1 660 cm^{-1}, $\lambda_{max.}$ 228 and 300 nm (ε 10 900 and 5 700), τ 9.22 (6 H, d, J 7 Hz), 8.3 (1 H, m), 6.4 (1 H, s), 6.21 (3 H, s), 4.7 (1 H, s), and 3.1—2.3 (4 H, m) (Found: C, 72.3; H, 7.1. C$_{14}$H$_{16}$O$_3$ requires, C, 72.4; H, 6.9%). A small amount of the other isomer was isolated as an impure solid, $\lambda_{max.}$ 229, 250, and 281 nm, $\nu_{max.}$ 3 300 and 1 650 cm^{-1}, τ (CCl$_4$) 6.28 (3 H, s), 9.20 (3 H, d, J 7 Hz), and 9.25 (3 H, d, J 7 Hz).

1,4-*Dihydroxy*-1-*isopropylnaphthalen*-2(1H)-*one*   (5).— Sublimed 2-hydroxy-1,4-naphthoquinone (1.74 g) was dissolved in tetrahydrofuran (20 ml) and sodium hydride in oil (0.64 g of 50% dispersion) was added. A solution of the Grignard reagent from isopropyl bromide (8.1 g) and magnesium (0.96 g) was prepared in 40 ml of 1 : 1 ether–tetrahydrofuran and this solution was added dropwise to the sodium enolate. The crimson mixture was refluxed (60 °C) for 30 min, cooled, poured into water, acidified, and extracted with ether. The extract was extracted in turn with saturated sodium hydrogen carbonate solution; the latter extract was acidified and re-extracted with ether. This ether layer was dried, concentrated, and allowed to evaporate slowly; it deposited the β-diketone (5) (0.4 g,

[15] K. Täufel and R. Maune, *Fette, Seifen, Anstrichm.*, 1964, **66**, 260.

[16] I. Baxter, D. W. Cameron, J. K. M. Saunders, and R. B. Titman, *J.C.S. Perkin I*, 1972, 2046.

18%), m.p. 150—154°. The mother liquors from this crystallisation contained a considerable amount of unchanged hydroxynaphthoquinone.

Rearrangement of the Epoxide (2) *in Acetic Acid.*—The hydroxynaphthalenone epoxide (2) (0.6 g) was refluxed in glacial acetic acid for 2 h. The yellow solution was cooled, mixed with water, and extracted with ether. After washing, drying, and evaporation the ether layer yielded 2-*hydroxy*-2-*isopropylnaphthalene*-1,3(4H)-*dione* (10) (0.6 g), which afforded pale yellow crystals, m.p. 122.5—124.5° (from carbon tetrachloride), $\nu_{max.}$ 3 400, 1 730, and 1 675 cm^{-1}, $\lambda_{max.}$ 253 and 293 nm (ε 11 750 and 1 700) (changing on addition of aq. NaOH to 262, 317, and 489 nm), τ 9.15 (3 H, d, J 6 Hz), 9.05 (3 H, d, J 6 Hz), 7.68 (1 H, sept), 6.20 (1 H, s), 6.03 and 5.97 (total 2 H, both apparent s), and 2.7—1.9 (4 H, m) (Found: C, 71.3; H, 6.6. $C_{13}H_{14}O_3$ requires C, 71.55; H, 6.4%).

1-*Acetoxy*-3,4-*epoxy*-1-*isopropylnaphthalen*-2(1H)-*one* (15). —1-Acetoxy-1-isopropylnaphthalen-2(1H)-one [1] (0.3 g) in ethanol (25 ml) containing acetone (4 ml) was mixed with hydrogen peroxide (28%; 5 ml) and sodium carbonate (0.04 g) in water (4 ml) and left at 60 °C for 6 h. The mixture was poured into water and extracted with ether, and the extract washed, dried, and evaporated leaving the crude epoxide (0.28 g) as an oil which solidified. Crystallisation from ethanol gave the *acetoxy-epoxide* (15) as white needles, m.p. 121—122°, $\nu_{max.}$ 1 740 and 1 725 cm^{-1}, $\lambda_{max.}$ 264, 270, 276, and 304 nm (ε 320, 320, 240, and 140), τ 9.12 (3 H, d, J 7 Hz), 9.04 (3 H, d, J 7 Hz), 8.0 (3 H, s), 7.62 (1 H, sept), 6.41 (1 H, d, J 4 Hz), 5.90 (1 H, d, J 4 Hz), and 3.0—2.4 (4 H, m) (Found: C, 69.05; H, 6.2. $C_{15}H_{16}O_4$ requires C, 69.25; H, 6.15%).

Rearrangement of the Acetoxy-epoxide (15) *in Acetic Acid.*— A solution of the *trans*-acetoxy-epoxide (0.2 g) in glacial acetic acid (10 ml) was refluxed for 1 h, cooled, poured into water, and extracted with ether. The extract was washed, dried, and evaporated to give 1-*acetoxy*-3-*hydroxy*-1-*isopropylnaphthalen*-2(1H)-*one* (16) (0.16 g), which crystallised from ethanol; m.p. 127—130°, $\lambda_{max.}$ 245, 251, and 338 nm (ε 13 000, 13 000, and 6 300) (changing to 240, 258, 313, and 400 nm on addition of aq. NaOH), τ (CCl$_4$) 9.20 (3 H, d, J 7 Hz), 9.15 (3 H, d, J 7 Hz), 8.0 (3 H, s), 7.9 (1 H, sept), 3.87 (1 H, s, exchangeable with D$_2$O), 3.4 (1 H, s), and 2.85 (4 H, s) (Found: C, 68.85; H, 5.75. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.15%).

Ketol Rearrangement of 3,4-*Dihydro*-1-*hydroxy*-1-*isopropylnaphthalen*-2(1H)-*one* (8).—Hydrogenation of 1-hydroxy-1-isopropylnaphthalen-2(1H)-one over platinum oxide in ethanol until uptake ceased gave a mixture of the dihydro- and tetrahydro-derivatives from which, by chromatography, the dihydro-derivative (8) was isolated as an oil, $\nu_{max.}$ (film) 3 400 and 1 720 cm^{-1}, τ 9.25 (3 H, d, J 7 Hz), 9.15 (3 H, d, J 7 Hz), 7.9 (1 H, sept), 7.6—6.5 (4 H, m), 6.38 (1 H, s, exchangeable with D$_2$O), and 3.2—2.5 (4 H, m). A solution of this saturated ketol (0.32 g) and potassium t-butoxide (0.15 g) in benzene (45 ml) was refluxed under nitrogen for 1 h. After cooling, water was added and the aqueous layer extracted with ether. The ether and benzene layers were combined, washed, dried, and evaporated to give 3,4-*dihydro*-2-*hydroxy*-2-*isopropylnaphthalen*-1(2H)-*one* (9) (0.3 g), which afforded crystals, m.p. 66—68° (from petroleum), $\lambda_{max.}$ 248 and 292 nm (ε 9 550 and 1 700), $\nu_{max.}$ 3 400 and 1 695 cm^{-1}, τ 9.32 (3 H, d, J 7 Hz), 8.97 (3 H, d, J 7 Hz), 8.4—6.8 (5 H, m), 6.60 (1 H, s), and 3.1—2.1 (4 H, m) (Found: C, 76.3; H, 7.8. $C_{13}H_{16}O_2$ requires C, 76.45; H, 7.85%).