A New Route to 2-Alkyl-1,4-naphthaquinones involving Skeletal Rearrangement

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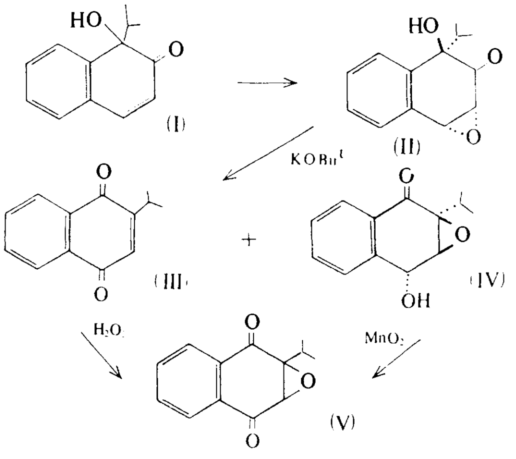
WE recently reported[1] the ready conversion of 1-isopropyl-2-naphthol into 1-hydroxy-1-isopropyl-2(1*H*)-naphthalenone (I). We have observed that (I) gives an epoxide (II) which undergoes an unexpected rearrangement in the presence of base to give the substances (III) and (IV).

Treatment of (I) with hydrogen peroxide and sodium hydroxide gives in 90% yield a single crystalline epoxide. The expected structure (II) for this material is confirmed by its analysis and its spectral characteristics, λ_{max} (EtOH) 265, 271 and 278 mμ (log ϵ 2·66, 2·77 and 2·70), ν_{max} (Nujol) 3400 (OH), 1710 (C=O) and several bands between 800 and 1050 cm.$^{-1}$, n.m.r. (CDCl$_3$) τ 2·3—2·8 (m, 4H, aromatics), τ 5·8 and 6·2 (two d, J 4, each 1H, $-\overset{O}{CH-CH}-$), τ 6·4 (s, 1H, OH), τ 7·45 (septet, J 7, 1H) and τ 9·15 [d, J 7 c./sec., 6H, $CH(CH_3)_2$]. The stereochemistry cannot be deduced from these spectral data but is established by the following isomerisation.

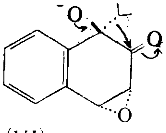
When the epoxide (II) is heated under nitrogen with potassium t-butoxide in benzene it is converted into a mixture of substances which have all been identified. One of these (18%) is a neutral non-polar yellow material, $C_{13}H_{12}O_2$, m.p. 45—47°, which was shown to be 2-isopropyl-1,4-naphthaquinone[2] (III) by its spectroscopic properties and comparison with a sample of this substance obtained by isopropylation of 1,4-naphthaquinone with isobutyric acid and red lead.[3] The quinone so obtained was identical to that obtained from the epoxide (II).

The main product (52%) from the reaction of the epoxide (II) with potassium t-butoxide is a neutral substance isomeric with (II), mass spectrum molecular ion at *m/e* 218. Its spectral properties show it to be a hydroxy-ketone, ν_{max} (Nujol) 3400, 1690, 1040 and several bands between 800 and 1000 cm.$^{-1}$ That the carbonyl group is conjugated to an aromatic ring is confirmed by its u.v. spectrum, λ_{max} (EtOH) 251, 286 mμ (log ϵ 3·87, 3·00). [α-Tetralone has λ_{max} 248 and 293 (log ϵ 4·1 and 3·3).[4]] The n.m.r. spectrum (CCl_4) of this hydroxy-ketone shows four aromatic hydrogens as a multiplet at τ2·3—3·0, two magnetically non-equivalent methyl groups at τ 9·07 and 9·13 (each a doublet, J 7 c./sec.) coupled to an otherwise unsplit methine hydrogen at τ 7·63 (septet, J 7 c./sec.), and a hydroxyl proton at τ 6·52. The two remaining hydrogens form an AB system isolated from other hydrogens. They appear as two doublets (J 3 c./sec.) at τ 5·22 and 6·53 which is compatible with the part structure $-O-\overset{|}{C}H-\overset{|}{C}H-O-$. The hydroxyl group is secondary and benzylic since the hydroxy-ketone is readily acetylated and is oxidised by chromium trioxide in pyridine or by manganese dioxide in cold acetone to a diketone, ν_{max} (film) 1695 cm.$^{-1}$, n.m.r. ($CDCl_3$) τ 2·0—2·5 (m, 4H, aromatics) τ 6·32 (s, 1H), τ 7·38 [septet, J 7 c./sec., 1H, $CH(CH_3)_2$], τ 8·98 and 9·10 [two doublets each J 7 c./sec., total 6H, $CH(CH_3)_2$].

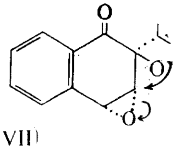
This diketone is the epoxide (V) of 2-isopropyl-1,4-naphthaquinone (III) and is identical to material obtained from (III) by epoxidation with hydrogen peroxide and sodium carbonate. The hydroxy-ketone must therefore have the structure (IV) which is entirely in accord with its spectral properties. The above evidence does not, however, establish its stereochemistry.



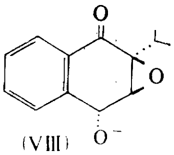
The isomerisation of (II) to (IV) can also be effected very smoothly by sodium carbonate in refluxing ethanol. Under these conditions no (III) is formed. The mechanism for this rearrangement presumably involves the ions (VI), (VII), and (VIII). The migration of the isopropyl group will be stereospecific. Attack by the negatively charged oxygen in (VII) on the epoxide function to form (VIII) should only occur if these groups are *trans*. We therefore conclude that the hydroxyl and epoxide functions are *trans* in the starting epoxide (II) and in the isomer (IV) as shown. The stereospecificity of the epoxidation of (I) and the generality of the rearrangements are being studied.



(VI)



(VII)



(VIII)

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