Rearrangement of a Hydroperoxy-enone in Alkali-promoted Intra- and Inter-molecular Epoxidations

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Summary The products of the reaction of the hydroperoxy-enone (I) with OH$^-$ have been identified and appear to arise by competing intra- and inter-molecular oxygen transfers followed by skeletal rearrangements.

ALTHOUGH hydroperoxy-cyclohexadienones are fairly well known, their reactions are relatively unexplored. We have studied the behaviour of 1-hydroperoxy-1-isopropyl-2(1*H*)-naphthalenone (I)[1] in various basic media. Deprotonation of (I) would give an anion which might attack the carbonyl carbon atom or might attack the β-carbon of the enone leading to formation of an epoxide.[2] In the event, reactions of both of these types occurred but so did various unexpected rearrangements.

On treatment with sodium hydroxide in aqueous ethanol at room temperature for 3 h, followed by acidification, the hydroperoxide (I) gives six products, (II) 25%,† (III) trace, (IV) 15%, (VI) 20%, (VII) 3%, and (VIII) 6%, which were separated by extraction of the acidic component (IV) with sodium hydrogen carbonate solution and chromatography of the neutral ones. The neutral components (II), (VII), and (VIII) are known substances. The epoxide (VII) can be made by the stereospecific epoxidation of (II)[1] with

hydrogen peroxide and is known to give (VIII) on treatment with base.[3] The alcohol (II) when treated with sodium methoxide in methanol for 1·5 h at room temperature followed by addition of water was incompletely converted into the isomer (III). On standing, pure (III) slowly and partially reverts to (II). The trace of (III) derived from the decomposition of the hydroperoxide is assumed to arise by isomerisation of (II).

The u.v. and i.r. spectra of the fifth neutral product, which is isomeric with (I) and (VII), suggest it is an α-tetralone carrying a hydroxy-group. The n.m.r. spectrum shows an intact isopropyl group and an AB quartet, *J* 4 Hz, at τ 5·93 and 6·13, not coupled to other protons, and attributed to an epoxide group with a proton attached to each of the *O*-carbons. The compound must therefore be one of the stereoisomers of 3,4-epoxy-2-hydroxy-2-isopropyl-α-tetralone (VI). This epoxide, unlike (VII), did not rearrange on further treatment with base. If the hydroxyl and epoxide oxygens were *trans*, a rearrangement like that of (VII) to (VIII) would be expected. The *cis*-arrangement of the hydroxyl and epoxide oxygens in the new epoxide was confirmed by its formation as the only product of the epoxidation of the alcohol (III) with *m*-chloroperoxybenzoic

† The percentages refer to isolated pure material.

acid. Epoxidation of allylic alcohols with peroxy-acids occurs from the face *cis* to the hydroxy-group.[4] The new epoxide therefore has the structure and stereochemistry (VI).
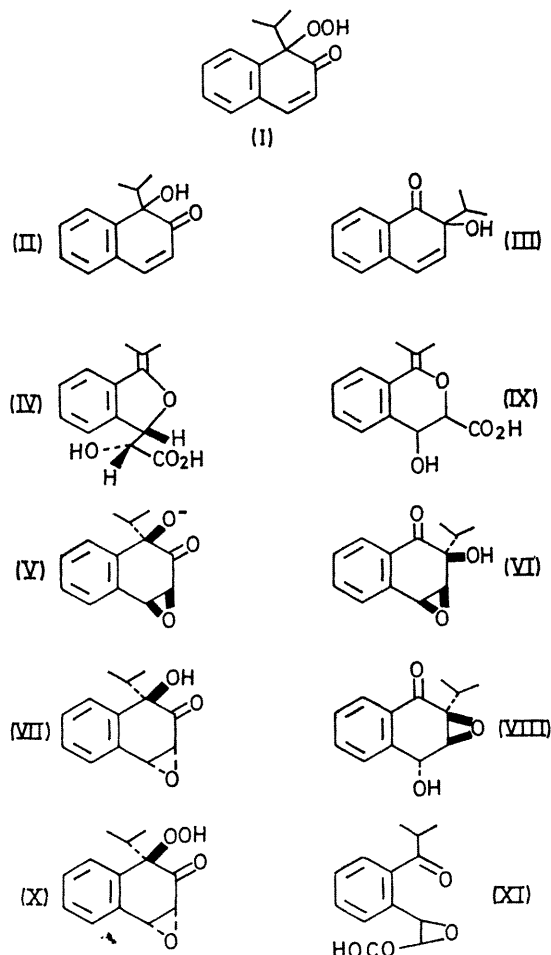
The bicarbonate-soluble fraction of the products of decomposition of (I) consists of a single carboxylic acid which was converted, using diazomethane, into its more tractable methyl ester, $C_{14}H_{16}O_4$. The acid is therefore a product of oxidation of (I). The i.r. spectrum of the ester showed a hydroxy-group, the proton of which appeared in the n.m.r. spectrum as a doublet at τ 7·22 coupled (J 8 Hz) to one proton at τ 5·52 which was further coupled (J 2 Hz) to a single proton at τ 4·35. The structure $\rangle$CH·CHOH· is therefore present. The methyl groups of the alkyl substituent appear as singlets at τ 8·03 and 8·17 so an iso-propylidene group is present. The structures (IV) and (IX) are compatible with all the spectral evidence, but the chemical shifts of the two methine protons are better accommodated by structure (IV). Oxidation of the methyl ester with ruthenium tetroxide in carbon tetra-chloride[5] or with ozone gave a trisnorlactone–ester in which the isopropylidene group has been cleaved to a carbonyl group but the rest of the molecule including the hydroxy-group is unchanged. The lactone carbonyl group absorp-tion at 1784 cm^{-1} in CCl$_4$ suggests that the lactone ring is five-membered.[6] Hydrolysis of the lactone in base, acidi-fication, and re-esterification with diazomethane re-formed the original lactone–ester, confirming that it is a γ-lactone. The acid is therefore assigned the structure (IV). Re-arrangement during the oxidation of the acid to the lactone is unlikely.

The decomposition of (I) appears to take two main courses. The formation of (VI) probably involves *intra*-molecular epoxidation[2] of the enone group by the anion of the hydroperoxide to give (V) followed by a ketol rearrange-ment which involves a shift of the isopropyl group along one face of the ring and which converts (V) entirely into the thermodynamically more stable anion of (VI). *Inter*-molecular epoxidation of the enone group of one molecule of (I) by another would lead to (II) and to (X). By analogy with the epoxidation[3] of (II) to (VII) this would give (X) with the relative stereochemistry shown. Epoxida-tion by (X) of another enone would lead to (VII) while rearrangement of (X) to (XI) and then to (IV) has analogy in the cleavage of simple α-hydroperoxy-ketones to acids.[7] Mechanistic studies to be described elsewhere suggest that epoxidation to (X) does precede ring cleavage and, there-fore, that the relative stereochemistry of (IV) is as shown.

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