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## Participation by the Nitro-group in the Ring-opening Reactions of Substituted o-Nitrophenylethylene Oxides

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Summary Ethereal hydrogen chloride converts substituted o-nitrophenylethylene oxides into products identified as tautomeric 3,4-dihydro-1,3-dihydroxy-4oxoquinoline derivatives: a course for these reactions involving participation by the nitro-group in the acidcatalysed opening of the epoxide ring is discussed.

THERE is now ample evidence for the ability of an aromatic nitro-group to function as the electrophile in intramolecular aldol-type condensations.<sup>1</sup> The dipolar nitro-group is also a potential nucleophile but reactions in which it functions as such are rare.<sup>2</sup> The most clear-cut examples are found in reactions of nitrobenzene derivatives which involve intramolecular oxygen transfer between the nitro-group and an ortho-side-chain.<sup>2,3</sup> Recent interest in this type of neighbouring-group interaction has centred on the ability of an aromatic nitro-group to participate in the solvolytic reactions of ortho-substituents.<sup>4</sup> We now report acidcatalysed reactions of substituted o-nitrophenylethylene oxides which are explicable by a course involving participation by the nitro-group in the opening of the epoxide ring.

Treatment of the *trans*-epoxides (1a) and (1c) with ethereal hydrogen chloride afforded high-melting acidic products  $C_{15}H_{10}CINO_3$  (43%) and  $C_{10}H_8CINO_3$  (20%) subsequently identified as the tautomeric 1-hydroxyquinolones (2c) and (2d). Formation of these heterocycles from the epoxides (1a) and (1c) finds analogy in the synthesis of chlorinated N-hydroxyquinolones by condensation of o-nitrobenzaldehyde with  $\beta$ -dicarbonyl compounds in ethereal hydrogen chloride.<sup>5</sup> As in these reactions,<sup>6</sup>



ethereal hydrogen chloride in the presence of hydroquinone converted the epoxides (1a) and (1c) into the chlorine free products (2a) and (2b), respectively. These reactions are



explicable by a course  $[(11) \rightarrow (16)]$  involving intramolecular nucleophilic attack by the nitro-group on the

protonated epoxide. Analogy for the intermediate formation of the nitroso-ketone (14) is provided by the acidcatalysed conversion of o-nitrophenylethylene oxide into o-nitrosobenzoylmethanol.7 Conversion of the nitrosointermediate (14) into the chlorophenylhydroxylamine (15) is in accord with the known<sup>8</sup> reaction of nitrosobenzene with hydrogen chloride to give p-chlorophenylhydroxylamine. The formation of chlorine-free products in the presence of a mild reducing agent (i.e. hydroquinone) lends further support to a stepwise mechanism involving the reduction of a nitroso-intermediate. Nucleophilic attack by the nitro-group at the benzylic position in the conjugate acid (12) rather than at the carbon atom bearing the carbonyl group is indicated by the failure of the nitro-group to participate in ring-opening of the epoxide (8)<sup>9</sup> by ethereal hydrogen chloride. The chlorohydrin formed is assigned the structure (9) on the basis of its conversion in warm aqueous alkali into a mixture of benzaldehyde and anthroxanic acid (10). The latter product is presumably derived by cyclisation<sup>10</sup> of the o-nitrophenacyl chloride formed by retro-aldol scission of the chlorohydrin (9).

Ethereal hydrogen chloride converted the *cis*-epoxide (1b) in high yield (>90%) into the compound (2c). High



yields of the N-hydroxyquinolone (2d) were similarly obtained from the dicarbonyl derivatives (1d-e) with concomitant loss of one of the acyl groups. The enhanced yield of cyclised products in these reactions compared with those of the *trans*-epoxides (1a) and (1c) can be attributed to the steric effect of the *cis*-carbonyl group in the compounds (1b) and (1d-e). Models indicate that this will force the nitrophenyl group into a position favourable for intramolecular attack by the nitro-group on the epoxide ring but at the same time blocking the approach of an external nucleophile (*i.e.* chloride ion).

Treatment of the epoxides (1a - e) with ethereal hydrogen chloride provides a valuable method for the synthesis of the otherwise inaccessible heterocyclic *N*-oxides (2a - d) and thence by dithionite reduction the parent bases (3a - d). In addition, oxidation of the quinolones (2) and (3) by manganese dioxide affords high yields of the quinoline-3,4-quinones (4) and (5) which readily condense with o-phenylenediamine to yield quinolino[3,4-b]quinoxaline derivatives (6) and (7).

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