

Reaction of Oxygen with Aryldihydropyrans

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Summary Reaction of the aryldihydropyran (I) with oxygen in the presence of pyridine and acetic anhydride gives the enol-acetate (V) and its acetolysis product (VI) in a combined yield of 70%.

THE reaction of the aryldihydropyrans (I) and (II) with singlet oxygen was recently reported,¹ giving rise to the formyl esters (III) and (IV) in good yield. The reactivity of (I) towards (ground state) oxygen is described here.

A solution of (I) in pyridine-acetic anhydride (3:1), protected from light and moisture, darkens over a period of one week. Examination of the oily residue by t.l.c. after removal of acetic anhydride and pyridine *in vacuo*, revealed the presence of two major products, both giving the same characteristic purple-red colour on development with sulphuric acid and heat. Alumina chromatography allowed separation of these two products identified as the enol-acetate (V) and the keto-diacetate (VI), in a combined yield of 70%.

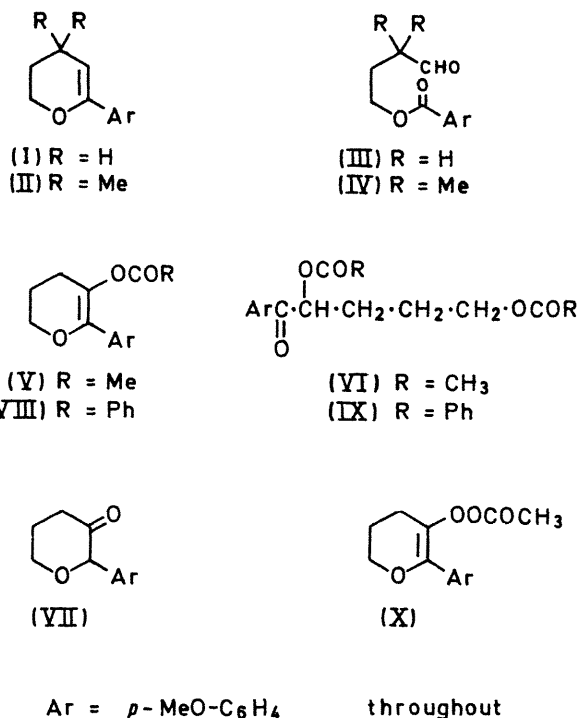
The structures of these two compounds follow unambiguously from their spectral data; (V) ν_{\max} 1755 cm^{-1} , M^+ 248, τ (CCl_4) 8.2–7.5 [$2 \times \text{H}(4)$, $2 \times \text{H}(5)$, m], 8.05 (OAc, s), 6.29 (OMe, s), 5.98 (OCH_2 , t, J 5 Hz), 2.58, 2.73, 3.20, and 3.35 ($4 \times \text{ArH}$, AA'BB'): (VI) i.r. ν_{\max} 1735, 1687, and 1603 cm^{-1} , M^+ 308, τ (CDCl_3) 8.4–7.8 [$2 \times \text{H}(2)$, $2 \times \text{H}(3)$, m], 7.98 and 7.84 ($2 \times \text{OAc}$, $2 \times$ s), 6.12 (OMe, s), 5.91 (OCH_2 , t, J 5.5 Hz), 4.13 (1-H, t, J 5.5 Hz), 1.98, 2.13, 2.98, and 3.13 ($4 \times \text{ArH}$, AA'BB').

Chemical evidence also supports the assigned structures: enol-acetate (V) is converted into the diacetate (VI) by treatment with acetic acid-acetic anhydride (3:1). Such a conversion may also take place in the oxidation reaction under study. In addition, hydrolysis of the enol-acetate (V) with sodium hydroxide-ethanol for a few minutes gave the ketone (VII) in good yield, characterised as its 2,4-dinitrophenylhydrazone, m.p. 149–151°.

The following observations are pertinent to the mechanism of this oxygenation. (a) Dihydropyran (I) was recovered unchanged if oxygen or acetic anhydride was separately excluded; (b) photo-oxidation of the dihydropyran (I) in pyridine-acetic anhydride (3:1) gave only the formyl ester (III); hence neither the putative dioxetan intermediate¹ nor singlet oxygen is involved in the present case; (c) *N*-acetoxy-pyridine is not responsible for the acetoxylation because the dihydropyran (I) was recovered unchanged after treatment with pyridine *N*-oxide, acetic anhydride, and pyridine under nitrogen. (d) Reaction of the dihydropyran (I) with benzoyl peroxide in pyridine gave two major products identified as the enol-benzoate (VIII) and the keto-dibenzoate (IX). This suggests that a peroxide such as (X), if formed, could acetoxylate another molecule

of dihydropyran (I) and be converted itself subsequently into (V) or (VI).

Stable enols and enolates react readily with oxygen to form α -hydroperoxides² though enol ethers are less reactive.³ However, direct attack of oxygen on double bonds is well known in various oxygen-olefin polymers⁴ and in electron-rich aromatic rings.⁵ The fact that oxygen is incorporated only in the presence of both pyridine and acetic anhydride remains to be explained. One possibility is that the dihydropyran in pyridine solution is in equilibrium with a small amount of an oxygen-complexed form, an equilibrium which is displaced by acetylation. No evidence for the presence of this adduct was available from the n.m.r. spectrum.



The highly electron-rich character of the double bond in dihydropyran (I) must play an important role in its abnormal reactivity towards (electrophilic) singlet and triplet oxygen. In both cases, the reactivity of the allylic 4-methylene group, the usual site of oxygen attack,⁴ is suppressed.

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