Photo-oxidation of Aryldihydropyrans

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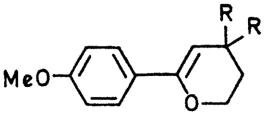
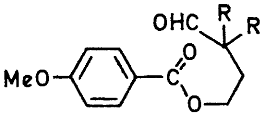
Summary Haematoporphyrin-sensitised photo-oxidation of the aryldihydropyran (I; R = H) gives the ester–aldehyde (II; R = H); the dimethyl analogue (I; R = Me) gives (II; R = Me) excluding the intermediacy of an allylic hydroperoxide.

THE best-known sensitised photo-oxidation pathway of olefins is that leading to allylic peroxides (the 'ene' reaction).[1] Carbonyl-containing fragments, often obtained as by-products in the above photo-oxidations were considered to have arisen by further decomposition of the initially formed, and often labile, hydroperoxides.[2] Recently, however it was shown that indene hydroperoxide did not lead, under photo-oxidation conditions, to homophthaldehyde, the major product from photo-oxidation of indene.[3]


(I)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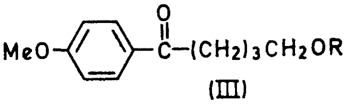
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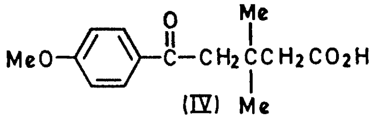
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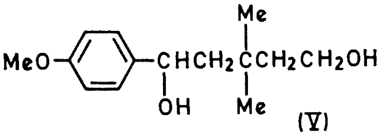
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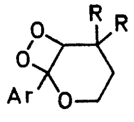
(VI)

Exposure of dihydropyran (I; R = H) b.p. 142—147°/2 mm,† ν_{max} (film) 1652 (m), 1610(s), 1517(s) to oxygen and daylight causes growth of a carbonyl band at 1705 cm^{-1} within a few hr. Photo-oxidation in dry pyridine (2% solution) using haematoporphyrin as sensitizer gave the ester–aldehyde (II; R = H), b.p. 165—170°/2 mm, (2,4-dinitrophenylhydrazone m.p. 141—142°) in 76% yield. N.m.r. (CCl_4); δ 1·75—2·68 ($-CH_2CH_2CHO$, m), 3·82 (–OMe, s), 4·24 ($-CH_2-O-$, t, *J* 6·5 Hz), 6·74, 6·89, 7·79, 7·95 (aromatic H, AA′BB′ system), 0·28 (C*H*O, t, *J* 1·2 Hz) p.p.m.

That this oxidation does not proceed *via* rearrangement of an allylic hydroperoxide is suggested by the fact that the dimethyl analogue (I; R = Me), b.p. 155—162°/2 mm undergoes a similar oxidation to give (II; R = Me), b.p. 175—180°/2 mm (2,4-dinitrophenylhydrazone m.p. 145—148°) in 70% yield.

Synthesis of (I; R = H) was carried out by brief treatment of the toluene-*p*-sulphonate (III; R = $SO_2C_6H_4Me$) m.p. 72·5—73° with potassium t-butoxide in t-butyl alcohol. The toluene-*p*-sulphonate was prepared from the corresponding alcohol (III; R = H) m.p. 49—53° itself prepared from ethyl γ-anisoylbutyrate m.p. 58—59° by acetalisation (ethylene glycol), $LiAlH_4$ reduction, and de-acetalisation. This method was unsuccessful for (I; R = Me) which was prepared from γ-anisoyl-$\beta\beta$-dimethylbutyric acid (IV) (oil; 2,4-dinitrophenylhydrazone m.p. 177·5—180°) by esterification, $LiAlH_4$ reduction to the diol (V), manganese dioxide oxidation of the benzylic hydroxyl,[4] and ring closure with toluene-*p*-sulphonic acid in benzene.

The simplest mechanistic explanation of the products is an intermediate dioxetan[5] (VI) analogous to that suggested in the photo-oxidation of indene.[3] Photo-oxidative cleavage of the olefinic double bond also occurs in the case of enamines[6] and appears to be characteristic of the more electron-rich olefins.‡

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† B.p.'s in bulb-tube distillations, bath temp. given.

‡ β-Methoxystyrene (ref. 6) is reported to be unreactive under photo-oxidative conditions which cleave enamines.

[1] "Oxidation of Organic Compounds," vol. III, Advances in Chemistry Series, No. 77, American Chemical Society, Washington, D.C., 1968.

[2] K. Gollnick in "Advances in Photochemistry," ed. W. A. Noyes, G. S. Hammond, and J. N. Pitts, Interscience, New York, 1968, vol. 6.

[3] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, **91**, 3396.

[4] E. Adler and H.-D. Becker, *Acta Chem. Scand.*, 1961, **15**, 849.

[5] F. McCapra, *Quart. Rev.*, 1966, **20**, 485; T. Goto and Y. Kishi, *Angew. Chem. Internat. Edn.*, 1968, **7**, 407.

[6] C. S. Foote and J. W. -P. Lin, *Tetrahedron Letters*, 1968, 3267; J. E. Huber, *ibid.*, 1968, 3271.