A New Synthesis of 3,4-Dihydro-7-hydroxynaphthalen-2(1*H*)-one. Photolysis of *p*-[2-(2-Halogenomethyl-1,3-dioxolan-2-yl)ethyl]phenol and 1,4-Dioxadispiro-[4,1,5,2]tetradeca-8,11-dien-10-one

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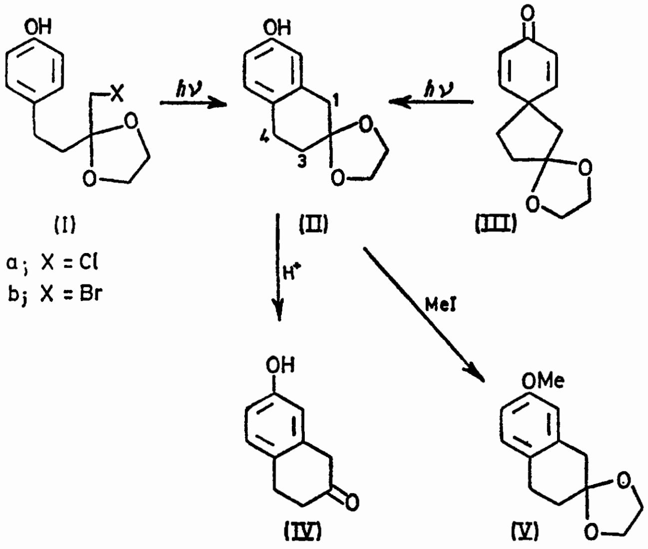
Summary Photolysis of *p*-[2-(2-chloromethyl-1,3-dioxolan-2-yl)ethyl]phenol and 1,4-dioxadispiro[4,1,5,2]tetradeca-8,11-dien-10-one gives in good yield 3′,4′-dihydro-7′-hydroxyspiro[1,3-dioxolan-2,2′(1′*H*)-naphthalene] which is hydrolysed to 3,4-dihydro-7-hydroxynaphthalen-2(1*H*)-one.

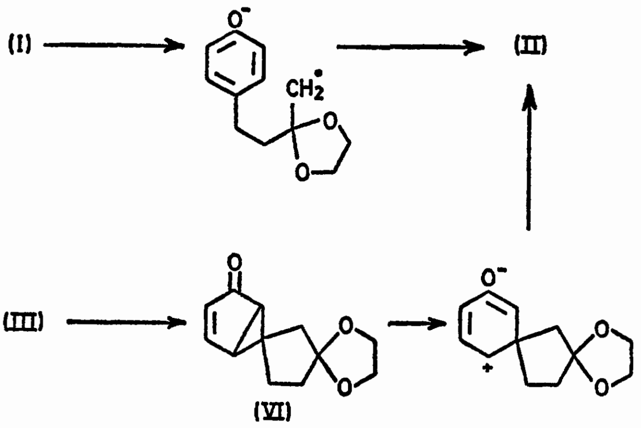
Derivatives of 3,4-dihydro-7-hydroxynaphthalen-2(1*H*)-one, starting materials for natural product syntheses, are usually prepared by the Birch reduction[1] of naphthol derivatives. We now report a new synthesis *via* a photochemical reaction.

A water-cooled solution of the chloro-compound (Ia)[2] (500 mg) and NaOH (190 mg) in H_2O (250 ml) was irradiated with a 100 W high-pressure mercury lamp for 3·5 h. Chromatography of the crude product gave the tetralone ethylene acetal (II) (16%), m.p. 152—154°. Hydrolysis of (II) with 10% HCl gave the hydroxytetralone (IV) (85%). Methylation of (II) with MeI and anhydrous K_2CO_3 in acetone gave the methyl ether (V) (60%), identical with an authentic sample prepared from 3,4-dihydroxy-7-methoxynaphthalen-2(1*H*)-one.[3] Photolysis of the bromo-compound (Ib) under similar conditions to those described above gave (II) (14%).



In order to prevent oxidation with dissolved oxygen and chlorine, sodium sulphite was added to the reaction mixture.

Photolysis of (Ia) in the presence of sodium sulphite (3·2 g) gave (II) (50%). This photochemical cyclization is a new synthetic route to 3,4-dihydro-7-hydroxynaphthalen-2(1*H*)-ones.



Photolysis of the spiro-dienone (III)[2] (94 mg) in a mixture of methanol (10 ml) and 0·1% aqueous sodium hydroxide (90 ml) for 3 h gave (II) (53%). The formation of (II) as major product in this photochemical rearrangement differs from the normal dienone–phenol rearrangement of (III)[2] in which 3,4-dihydro-6-hydroxynaphthalen-2(1*H*)-one is the major product. This photochemical rearrangement may proceed through the lumiketone intermediate (VI).[4]

(*Received, 22nd November* 1971; *Com.* 1998.)

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