

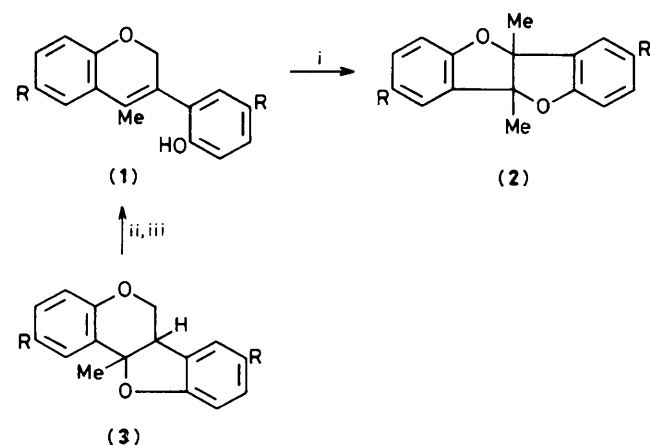
Novel Photochemical Transformation of 4-Methyl-2'-hydroxyisoflavenes to Benzofuro[3,2-*b*]benzofurans

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The photolysis of 4-methyl-3-(2-hydroxyphenyl)chrom-3-enes (1) in methanol at 300 nm affords 4b,9b-dihydro-4b,9b-dimethylbenzofuro[3,2-*b*]benzofurans (2), in good yield and the reaction rate is accelerated by sodium methoxide.

As a part of our studies on the photochemistry of 11a-methylpterocarpan, we studied the photolysis of 4-methyl-3-(2-hydroxyphenyl)chrom-3-enes (1). The compounds (1) on photolysis for 8 h in methanol using an RUL-3000 Å source



Scheme 1. i, $h\nu$, 300 nm, MeOH; ii, *p*-MeC₆H₄SO₃H, Ac₂O, heat; iii, KOH, MeOH, room temp.

in an RPR-208 reactor yielded (60–70%) the 4b,9b-dihydro-4b,9b-dimethylbenzofuro[3,2-*b*]benzofurans (2) which were identical in all respects with authentic samples^{1b} (Scheme 1, Table 1). The reaction is complete in 2 h in the presence of sodium methoxide (10 equiv.) in methanol. The title compounds (1),[†] hitherto unknown,² were prepared by the reaction of toluene-*p*-sulphonic acid-acetic anhydride with 11-methylpterocarpan, followed by base hydrolysis of the acetates (Scheme 2) in an overall yield of 60%.

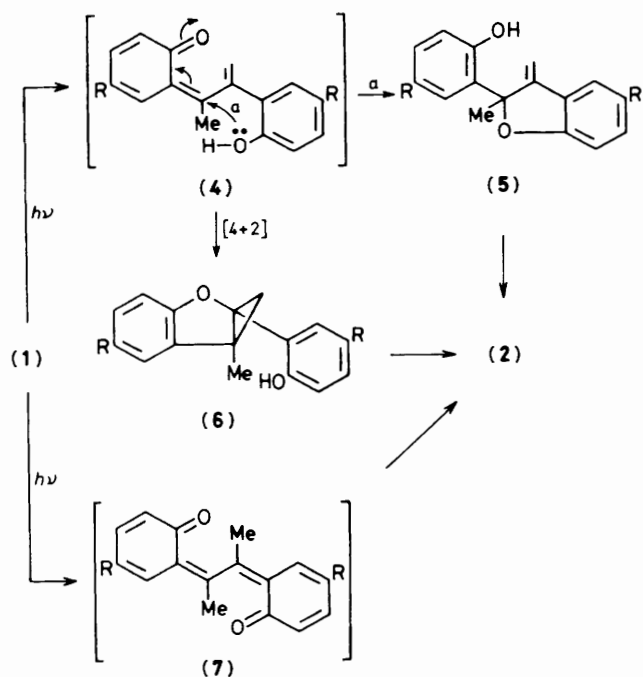
These results are unexpected in view of the reported photolysis

Table 1

Compound	R	% Yield ^a of (2)
a	H	70
b	Me	70
c	OMe	66
d	Cl	60

^a Isolated yield. The structures of (2) were confirmed by spectroscopic and mixed m.p. comparison with authentic samples.

[†] Satisfactory ¹H n.m.r. spectra of the phenols and their acetates were obtained. (1a) shows λ_{\max} (MeOH) 276 (ϵ 4800) and 317 nm (ϵ 4700).



Scheme 2

of chrom-3-enes³ to yield the solvent addition product, via a quinone allide intermediate, depending on the substitution pattern in the pyran ring, and is significant in the light of the reported pterocarpan-2'-hydroxyisoflavan photochemical interconversion.⁴

This transformation may involve any one of the following pathways and intermediates (Scheme 2). (a) The quinone allide intermediate (4) undergoes an intramolecular Michael addition with the phenol to give the dihydrobenzofuran derivatives (5), which in turn either photochemically or thermally can give the product (2). (b) The quinone allide (4) alternatively can undergo an intramolecular [4 + 2] cycloaddition to form the oxabicyclo[3.1.0] intermediate (6), which can afford the final product (2). This assumption is supported by a similar observation in the case of 2*H*-pyrans,⁵ dihydroquinolines,⁶ isochromenes^{3c} etc. (c) The bis *o*-quinone methide intermediate (7) on electron reorganisation can give the product. In this regard, it is of interest that products similar in structure to (2) have also been reported from the photochemical rearrangement of anthracene endoperoxides.⁷

We are currently investigating the photolysis of (1) at low temperature and also trying to synthesise the exomethylene-benzofuran (5)⁸ with a view to a study of its behaviour under the irradiation conditions. It is possible that one of the steps in the reaction is favoured by converting the phenolic OH group into the corresponding anion (*e.g.* step a in Scheme 2), as significant rate acceleration has been observed by Kitamura *et al.*⁹ in the photolysis of *o*-allyl phenols in the presence of sodium methoxide. However a similar comparative study of *o*-propenyl-phenols and *o*-hydroxy-stilbenes has not yet been carried out.

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