

## Photolysis of Aryloxyacetones

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IRRADIATION of aryloxyacetones (Ia—Ic) gives phenols (II) and 2-methylbenzofurans (IV). The benzofurans (IVa) and (IVb) were obtained directly, and the benzofuran (IVc) was obtained after acid treatment of the photo-product. All irradiations were carried out in methanol at room temperature using a high-pressure mercury-vapour

(III, R = OMe)] which was converted into (IVc) on drying<sup>1</sup> or on treatment with methanolic hydrogen chloride. When phenoxyacetone (Ia) was irradiated, *p*-hydroxybenzyl methyl ketone (V, R = H)<sup>2</sup> was formed [0.7% yield, isolated and identified as its benzoate: (V, R = COPh)] as well as (IIa) and (IVa).

TABLE

Aryloxyacetone	Reaction time (hr.)	Recovered starting material	Yield (%) <sup>a</sup>	
			Phenol (II)	Benzofuran (IV)
(Ia)	55	72	5 (17)	5 (17)
(Ib)	18	50	14 (28)	11 (23)
(Ic)	10	55	22 (48)	6 (13) <sup>b</sup>

<sup>a</sup> Figures in parentheses denote yield based on unrecovered starting material.

<sup>b</sup> After acid treatment.

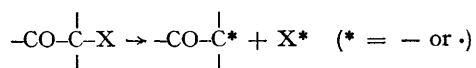
lamp as the light source. Product yields and reaction times are given in the Table.

The following findings indicate that hydroxyketones (III) are intermediates in the reaction leading to (IV). Photolysis of *p*-methoxyphenoxyacetone (Ic) gave phenol (IIc) and a solid [m.p. 85–86°;  $\nu_{\max}$  = 1702 and 3360 cm.<sup>-1</sup>; presumably

*p*-Nitrophenoxyacetone (Id) was found to be stable under the conditions used for photolysis of (Ia–c).

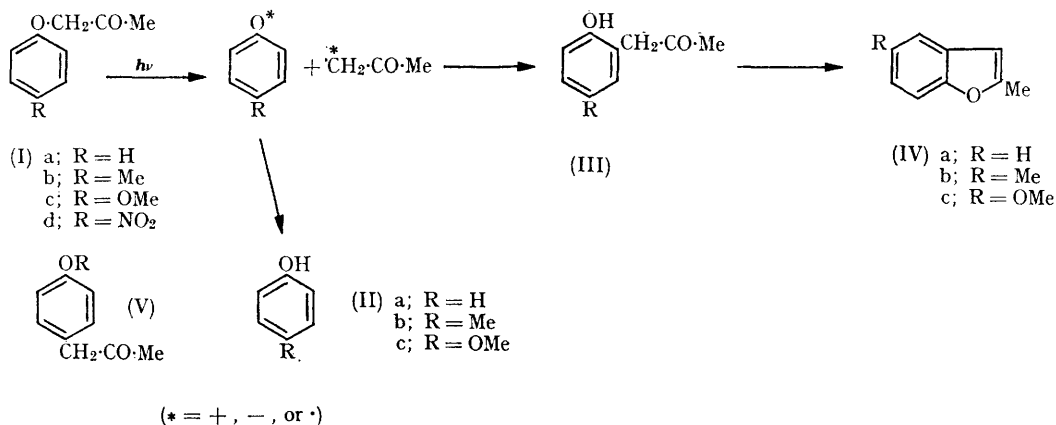
Phenol (IIa) was identified as its tribromoderivative and *p*-cresol (IIb) as its benzoate. All products were identified by comparison with authentic samples.<sup>3</sup>

Several examples<sup>4</sup> of the photo-reaction are



known, where X is an electronegative species (e.g., halogen). However, with aryloxyacetones, an increase in the electronegative nature of X

(*p*-methoxyphenoxy < phenoxy < *p*-nitrophenoxy) resulted in a decrease in the ease of photolysis. Related photo-rearrangements of alkyl aryl ethers (aryl allyl and aryl benzyl ethers,<sup>5</sup> and aryloxyacetic acids<sup>6</sup>) have been reported. Studies on the scope and mechanism of this photo-reaction are in progress.



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<sup>1</sup> For an earlier example of such a cyclisation see: S. W. Tinsley, *J. Org. Chem.*, 1959, **24**, 1197.

<sup>2</sup> J. M. Pepper and M. Saha, *Canad. J. Chem.*, 1964, **42**, 113.

<sup>3</sup> For the preparation of 2-methylbenzofurans see: G. Pappalardo and F. Duro, *Boll. sci. Fac. Chim. ind. Bologna*, 1952, **10**, 168.

<sup>4</sup> See: O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, 1964, **9**, 555 (references 7—10).

<sup>5</sup> M. S. Kharasch, G. Stampa, and W. Nudenberg, *Science*, 1952, **116**, 309.

<sup>6</sup> D. P. Kelly and J. T. Pinhey, *Tetrahedron Letters*, 1964, 3427.