

THE PHOTOCHEMICAL REARRANGEMENT
OF PHENOXYACETIC ACIDS

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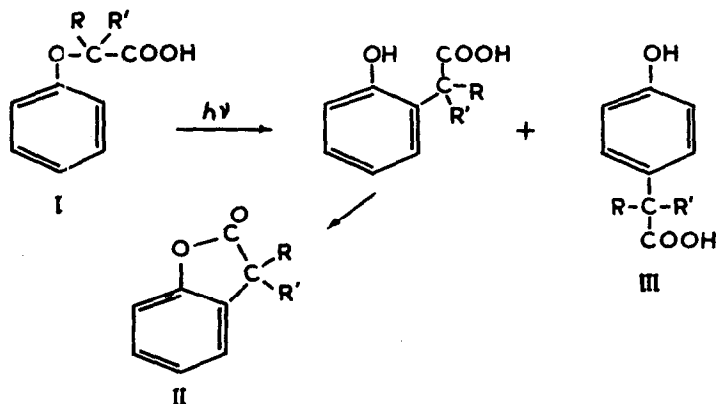
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The photolysis of a number of phenoxyacetic acids of biological importance has been reported¹ to yield mixtures in which phenolic material could be detected. More recently the aluminium chloride - induced rearrangement of 4-methylphenoxyacetic acid has been found² to yield 3-methylphenoxyacetic acid. We wish to report that the irradiation of phenoxyacetic acids can lead to a migration of the acetic acid residue from the ether oxygen to the aromatic nucleus.

Photolysis³ of phenoxyacetic acid (4 g.) in 95% ethanol (80 cc.) for 6 hr., using a 125 watt high pressure mercury vapour lamp in a quartz immersion tube, gave a mixture which could be separated into a volatile fraction and a non-volatile fraction by vacuum distillation. The volatile fraction was chromatographed on silica gel, giving 2-coumaranone (II, R, R' = H; 18%)⁴ and phenol (27%). From the non-volatile fraction p-hydroxyphenylacetic acid (10%) was obtained.



Lactonisation occurs during the distillation, since the I.R. band of the γ -lactone at $1790-1800\text{ cm}^{-1}$ is absent from the crude irradiation mixture.

Irradiation of α -phenoxypropionic acid in ethanol followed by the same work-up gave 3-methyl-2-coumaranone (II, $R = H$, $R' = CH_3$; 14%), phenol (18%) and *p*-hydroxyhydratropic acid (III, $R = H$, $R' = CH_3$; 9%). Similarly α -phenoxyisobutyric acid gave 3,3-dimethyl-2-coumaranone (II, $R, R' = CH_3$; 12%), phenol (13%) and *p*-hydroxy- α -methylhydratropic acid (III, $R, R' = CH_3$; 10%).

We have also examined two examples with substituents in the aromatic ring. 4-Methylphenoxyacetic acid yielded 5-methyl-2-coumaranone (22%) and *p*-cresol (7%) while 2,6-dimethylphenoxyacetic acid gave 3,5-dimethyl-4-hydroxyphenylacetic acid (4%) and 2,6-dimethylphenol (8%).

The coumaranones were identified by their typical absorption band in the I.R. at $1790-1800\text{ cm}^{-1}$. All showed single peaks on G.L.C. The I.R. spectrum of the 2-coumaranone was identical with that of authentic material. The 5-methyl-2-coumaranone had m.p. 71° (lit.⁵ m.p. 73°).

Phenol and the substituted phenols were isolated as the corresponding benzoates which were compared with authentic material. The *p*-hydroxyphenylacetic acid (m.p. 145°) and *p*-hydroxyhydratropic acid (m.p. 132°) were identical with authentic material. The *p*-hydroxy-*o*-methylhydratropic acid (m.p. 154°; lit.⁶ m.p. 153°) and 3,5-dimethyl-4-hydroxyphenylacetic acid (m.p. 138°, lit.⁷ m.p. 143°) were identified by their p.m.r. spectra.

A preliminary report⁸ of the photochemical rearrangement of phenylbenzyl ether, phenylallyl ether and diphenyl ether has been published. In each case phenol and the *para*-substituted phenol were obtained. Unlike our reaction, no *ortho*-substituted phenol was isolated.

Further studies of this rearrangement are in progress.

REFERENCES

1. G. R. Bell, *Botan. Gaz.* **118**, 133 (1956).
2. N. B. Mulchandani and M. S. Chada, *Indian J. Chem.* **1**, 273 (1963).
3. The photolyses were carried out under nitrogen with external water cooling.
4. The yields quoted are calculated from amounts isolated.
5. A. Siegel and H. Keckeis, *Monatsh.* **84**, 910 (1953).
6. A. Jonsson, *Acta Chem. Scand.* **8**, 1211 (1954).
7. P. D. Gardner, H. S. Rafsanjani and L. Rand, *J. Amer. Chem. Soc.* **81**, 3364 (1959).
8. M. S. Kharasch, G. Stampa and W. Nudenberg, *Science*, **116**, 309 (1952).