The Photoreactions of an Aryloxyaryl Ester

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In an extension of previous studies of the photoreactions of aryl ethers,[1] the photoreactions of an aryloxyaryl ester are now reported.

4-(2,6-Dimethylphenoxy)-2,6-dimethylphenyl acetate (I), m.p. 123—124°, was irradiated in a number of solvents. Following the course of the reaction by thin-layer chromatography, a product with a higher R_F value than the starting material was detected. This product, compound (IV), m.p. 96·5—97·5°, was readily isolated by column chromatography (silica; light petroleum–ethyl acetate 99 : 1). Analysis by spectroscopic methods (i.r. and n.m.r.) indicated that this product must have resulted from the starting material by the loss of carbon dioxide according to

$$\mathrm{ArOCO{\cdot}R} \xrightarrow{h\nu} \mathrm{ArR} + \mathrm{CO_2}$$

This unusual type of photodecarboxylation has first been observed by Finnegan *et al.*[2] They reported the photodecarboxylation to be a minor reaction accompanying the photo-Fries rearrangement of aryl esters. In our case, however, the photo-Fries rearrangement being inhibited by *ortho-* and *para*-substitution, the decarboxylation appears to be a major reaction. The amount of decarboxylated product proved to be markedly dependent on the solvent as well as on the nature of the substituents in the aromatic ring.[3]

The amount of compound (IV) was found to decrease with increasing irradiation time, particularly in solvents as isopropyl alcohol, ether, and dioxan. Therefore, it was concluded that (IV) itself, being a diaryl ether, is converted into other products (*e.g.* ether-bond fission and photo-Claisen rearrangement). The higher rate of conversion of (IV) in these solvents is corroborated by earlier results.[1] As final proof, (IV) was irradiated in ether and in dioxan. The major products were isolated and identified by spectroscopic methods. These products (VI) and (VII;

TABLE

The irradiation of 4-(-2,6-dimethylphenoxy)-2,6-dimethylphenol acetate[a]

			Product yields (%)[b]					
Solvent	Irradiation time (hr.)	Conversion (%)	(III)[c]	(IV)	(V)	(VI)	(VII)	Total[d,e] decarboxylation
$\mathrm{Pr^{i}OH}$ ..	1	81	4·4	16·5		4·4	2·6	23·5
	5	100	4·5	2·9		8·4	5·2	16·5
Ether	1	80	8·9	41·3		4·9	1·0	47·3
	5	100	4·0	12·0		14·3	2·7	29·0
Dioxan ..	1	77	5·5	34·7		3·5	1·8	40·0
	5	100	4·2	8·9		9·3	7·5	25·7
MeCN ..	1	67	5·3	17·6		2·7	0·9	21·2
	5	88	5·1	13·9		3·1	1·7	18·7
	8	91	5·1	12·8		3·4	1·8	18·0
Cyclohexane ..	1	63	8·2	48·1	4·6	1·0	0·9	54·6
	5	89	4·9	38·1	2·7	1·8	1·8	44·4
	8	91	4·9	41·4	2·9	2·1	2·1	48·5
Benzene ..	1	47	10·8	48·6		0·8		49·4
	5	68	9·1	52·3		0·9	0·6	53·8
	8	73	8·9	50·3		1·2	0·6	52·1

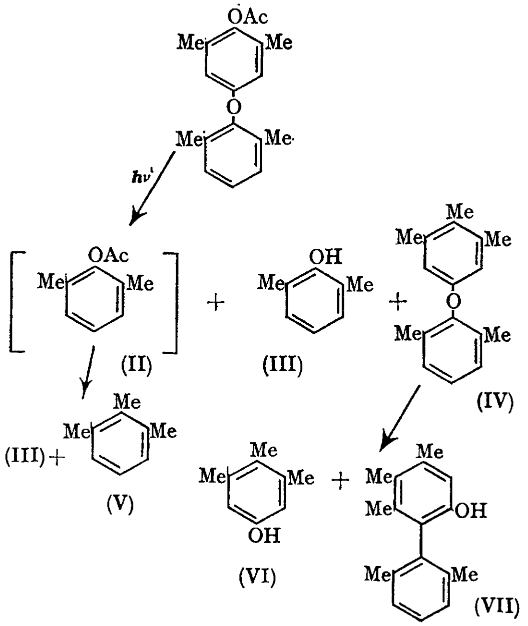
[a] A H.P. Mercury (Hanau Q 81) was used throughout. All irradiations were carried out in a nitrogen atmosphere at 25 ± 1°.

[b] The results were obtained by g.l.c. on a 6 ft. 4 in. o.d. stainless steel column with Silicone GE XE-60 as the stationary phase coated on Gaschrom Z 60/70 as the solid support. The temperature was programmed with 10° min. from 70—210°. For further details see forthcoming paper.[3] The percentages are based on consumed starting material.

[c] Calculated on the basis of 2 moles of phenol per mole of starting material.

[d] Total of compounds (IV—VII).

[e] The decrease in decarboxylation percentage with time is due to the fact that not all of the irradiation products resulting from (IV) have been accounted for.



m.p. 79—81°) proved to be identical with some products which appeared in the irradiation mixture of (I).

From the Table it can be concluded that the photodecarboxylation (total of compounds IV—VII) proceeds with low efficiency in isopropyl alcohol and acetonitrile and with relatively high efficiency in ether, cyclohexane, and benzene.

The photoreactions of compound (I) are represented in the scheme. Primary products of the irradiation of compound (I) are 2,6-dimethylphenol (III) (ether-bond fission) and compound (IV) (decarboxylation). Although 2,6-dimethylphenyl acetate (II) could not be detected, the presence of 1,2,3-trimethylbenzene (V) indicates that (II) must have been an intermediary product, since neither (V) nor (III) resulted from the irradiation of (IV).

The photoreactions of 4-methoxy-2,6-dimethylphenyl acetate are presently being studied[3] in order to exclude the complications encountered above, due to the presence of the aryloxy-group (ether-bond fission).

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[1] H. J. Hageman and W. J. Mijs, to be published.

[2] R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 1965, **21**, 1015; R. A. Finnegan and D. Knutson, *Chem. and Ind.*, 1965, 1837; *Chem. Comm.*, 1966, 182; *J. Amer. Chem. Soc.*, 1967, **89**, 1970.

[3] H. J. Hageman, to be published.