A New Photo-Fries Rearrangement of Methyl Aryl Oxalates

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Summary Irradiation of methyl aryl oxalates induces the photo-Fries rearrangement of the α-ketoester to give hydroxyarylglyoxylates.

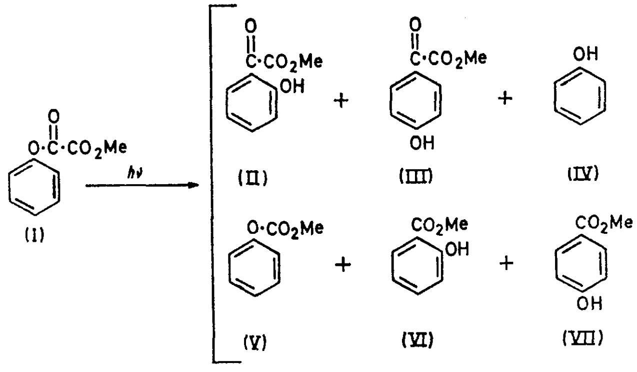
WHILE the photo-Fries rearrangement of various functional groups has been extensively studied in recent years,[1] that of an α-ketoester has not yet been reported. We report that the photoreaction of methyl aryl oxalates induces the photo-Fries rearrangement of the α-ketoester group to give hydroxyarylglyoxylates.

Irradiation (500 W high pressure Hg arc, 15 h) of a solution of methyl phenyl oxalate (I) in Bu^{t}OH, AcOH, or Et$_2$O through quartz gave (II),† (III) (12·9%),‡ (IV) (9·4%), (V) (4·7%), (VI) (4·9%), and (VII) (3·9%).

Irradiation of the 2,6-dimethyl derivative of (I) gave methyl 4-hydroxy-3,5-dimethylphenylglyoxylate (10·5%), methyl 4-hydroxy-3,5-dimethylbenzoate (12%), and small amounts of 2,6-xylenol, and the 2,4-dimethyl derivative of (I) gave, upon irradiation, methyl 2-hydroxy-3,5-dimethylphenylglyoxylate.

Compound (III) was unchanged upon irradiation in Bu^{t}OH, therefore the other products did not arise from further reactions of (III).

Treatment, in the dark, of (I) with Lewis acids such as AlCl$_3$ gave phenol (63%) without any of the Fries-rearranged products.



The photoreaction of (I) may proceed by a similar mechanism to that suggested for the photo-Fries rearrangement of phenyl acetate.[2]

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† (II) was identified, but its yield could not be determined by g.l.c. because of thermal instability.

‡ Yields based on reacted (I).

[1] Recent review: D. Bellus, *Adv. Photochem.*, 1971, **8**, 109.

[2] H. Shizuka, T. Morita, Y. Mori, and I. Tanaka, *Bull. Chem. Soc. Japan*, 1969, **42**, 1831, and references cited therein.