Photoenolization of Dimethyl 2,5-Dimethylterephthalate. Photodienol Trapping by Oxygen

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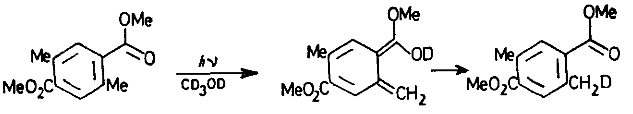
Summary Dimethyl 2,5-dimethylterephthalate undergoes photoenolisation in the presence of oxygen to give the methoxyphthalide (II); the reaction apparently occurs by a process similar to the one observed with *o*-methylbenzophenones.

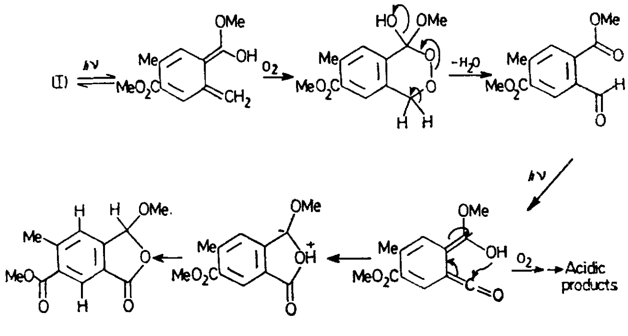
IT has been reported that, by analogy with aromatic ketone photochemistry, benzoate esters substituted by an electron-withdrawing group can undergo hydrogen abstraction from aromatic hydrocarbons[1] and cycloaddition with olefins to form oxetans.[2] It was of interest to see if the *o*-alkyl aromatic ketone photoenolization process[3] would also occur with this type of ester and dimethyl 2,5-dimethylterephthalate (I) was selected as an appropriate substrate.



(I)

The electron-withdrawing substituent effect, and thus photodienol formation possibility, was established by hydrogen-deuterium exchange. Methyl *o*-toluate irradiated† (quartz) in CD_3OD does not incorporate deuterium atoms in the ring methyl group while under the same conditions dimethyl 2,5-dimethylterephthalate exchanges 14% of its hydrogen atoms.

Irradiation† through a Vycor filter of an oxygen flushed 0·02 M methanolic solution of compound (I) until 70% of the ester was consumed gave the methoxyphthalide (II) (12% yield) and acidic products (15% yield), besides polymeric material. The phthalide (II) (m.p. 121 °C) has been identified by satisfactory analytical and spectral data.



(II)

SCHEME

It is reasonable to assume that formation of the methoxyphthalide (II) proceeds through photodienol intermediates (Scheme) by anology with the photo-oxidation of *o*-methylbenzophenones,[4] although with a much reduced efficiency.

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† Hanovia 450 W lamp.

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