

Photochemical Reactions of Methyl Benzoate

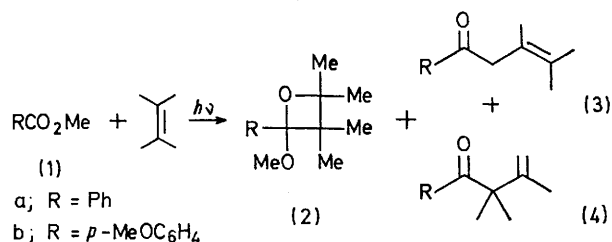
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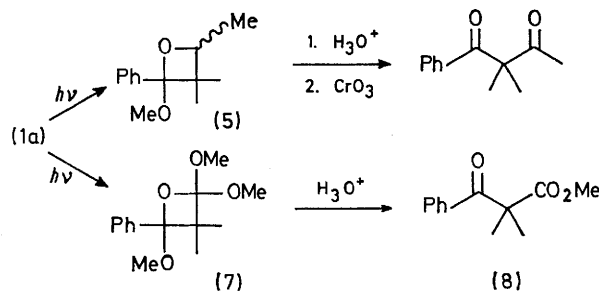
Summary Methyl benzoate and methyl *p*-methoxybenzoate undergo processes of hydrogen abstraction and 2 + 2 cycloaddition with olefins to give, for example, the ketones (3) and (4), and the oxetan (2), respectively; these reactions apparently occur *via* excited singlet states of the esters.

In contrast to the photochemistry of aldehydes and ketones (especially diaryl and aryl alkyl ketones)^{1,2} the photochemical behaviour of simple aromatic acids and their esters has received scant attention. Recently, it has been reported that simple benzoate esters of suitable alcohols slowly undergo type II cleavage. Methyl esters of pyromellitic and the isomeric phthalic and cyanobenzoic acids are known to add to olefins to give oxetans, and to abstract

at the carbonyl group to give oxetans and hydrogen abstraction from allylic positions of the olefins to give ketones and other products.



hydrogen from toluene.⁴ It has been stated that methyl benzoate is photochemically unreactive.^{4a,5} However, benzoic acid itself exhibits a complex and interesting photochemistry.⁶ We report that methyl benzoate and other aromatic esters with chromophores less complex than those studied in ref. 4 can undergo both cycloaddition to olefins



Irradiation[†] through Vycor of hexane solutions of methyl benzoate (1a) and an excess of 2,3-dimethylbut-2-ene until 50% of (1a) was destroyed led to the formation of three primary products, (2a), (3a), and (4a)[‡] (43%, 21%, and 6%, respectively), identified by their spectral properties, and in the case of (2a), m.p. 51°, by its hydrolysis to 2-benzoyl-2,3-dimethylbutan-2-ol. The ketones (3a) and (4a) are consumed by secondary reactions, including oxetan formation, when longer irradiation times are employed; (4a) is efficiently transformed to (3a), but the reverse process does not occur.⁷ The ketone (4a) evidently arises *via* coupling of the two radicals produced by abstraction of an allylic hydrogen from the olefin by the carbonyl oxygen of photoexcited (1a). The initially formed hemiacetal quickly reverts to the ketone. Compound (3a) may be formed by a similar process as well as by isomerization of (4a).

[†] Preparative irradiations were performed using Corex-filtered light from a Hanovia 450-watt medium-pressure mercury arc: for quantum yield measurements a Rayonet reactor with 2537 Å lamps was used.

[‡] The i.r., n.m.r., and mass spectra of all new compounds fully support their assigned structures.

The quantum yields for the formation of (2a) and (3a) at 2537 Å in 5M olefin were 0.034 ± 0.03 and 0.014 ± 0.02 , respectively. Irradiation of (1a) and olefin in solutions up to 0.5 M in *cis*-penta-1,3-diene under conditions such that the quencher absorbed essentially none of the incident light led to formation of all three photoproducts at an undiminished rate. This result suggests that (2)—(4) arise *via* excited singlet states of methyl benzoate, or less likely, a rapidly reacting triplet.

Irradiation of (1b) with an excess of 2,3-dimethylbut-2-ene until 40% of (1b) was consumed gave the analogous products (2b), (3b), and (4b)‡ (8, 27, and 16%). Irradiation in similar fashion of (1a) and an excess of 2-methylbut-2-ene gave the epimeric oxetans (5) (3:1, 36%) and a mixture of the four ketones analogous to (3) and (4) (25%).⁸ Hydrolysis of (5) and subsequent Jones oxidation of the resulting keto-

alcohol gave (6),⁶ identical with an authentic sample. Photolysis of (1a) with 1,1-dimethyl-2,2-dimethoxyethylene afforded the oxetan (7) as the sole product (65%). The unexpected orientation of (7) was established by its rapid hydrolysis in a 4:1 mixture of tetrahydrofuran and 2% aqueous HCl to (8), and by a strong mass spectral fragment ion at *m/e* 162 (loss of dimethyl carbonate).

Irradiation of (1a) in the presence of less electron-rich olefins (*e.g.*, isobutene, cyclohexene) leads to addition to the ring, as shown by the presence of intact ester functions in the product mixtures. Work is in progress on the structures of these compounds and will be reported subsequently.

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⁷ Ketone (4a) is converted into (3a) and other, minor, products on irradiation; T. S. Cantrell and J. I. Seeman, unpublished results.

⁸ The isolation and characterization of the individual products will be described in detail in the full publication.

⁹ A. R. Pinder and R. Robinson, *J. Chem. Soc.*, 1955, 3341.