The Photo-oxidation of Tropolone Methyl Ether

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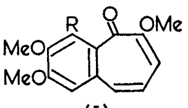
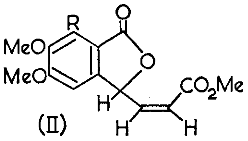
IRRADIATION with a tungsten lamp of the benztropones (I: R = H, OH, and OMe) in a variety of solvents (including ethanol) under oxygen in the presence of a sensitizer (Rose Bengal) gave high yields of the lactones (II: R = H, OH, and OMe).[1] In contrast, we now find that irradiation of tropolone methyl ether under similar conditions results not in a lactone but in diesters (III: R = Me and Et) which incorporate the solvent alcohol.

When tropolone methyl ether was irradiated with a tungsten lamp in a carbon disulphide–ether–alcohol mixture containing Rose Bengal as sensitizer it absorbed one mol. of oxygen. No lactonic material could be detected in the products, which were chiefly the esters (III: R = Me or Et) depending on whether methanol or ethanol had been used as co-solvent. The alcohols are unstable and have not been obtained pure, but spectral data supports the assignment (III). Their infrared spectra show bands at 3500 and 1725 cm.$^{-1}$ ($\alpha\beta$-unsaturated ester) and their ultraviolet spectra show bands at 220 mμ. The ester groups show up nicely in the n.m.r. spectra, *e.g.*, the dimethyl ester shows a singlet at τ 6·2, but the olefinic region is not clear enough to allow a definite assignment to the double bonds.

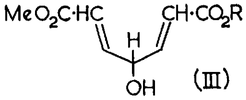
The structure of the esters has been confirmed by oxidising them to the ketones (IV: R = Me and Et), which give bands at 1728 and 1672 (dimethyl ester) and 1729 and 1680 cm.$^{-1}$ (methyl ethyl ester) in the infrared and a band in the ultraviolet at 240 mμ. Their n.m.r. spectra reveal the double bonds to be transoid with the olefinic protons displaying coupling constants of 17 c./sec. (dimethyl ester) and 15 c./sec. (methyl ethyl ester). The dimethyl ester shows a sharp singlet (τ 6·11) for the ester methyls. The structure of the ester (IV: R = Me) has been confirmed by comparison with an authentic specimen prepared by the method of Midorikawa.[2]



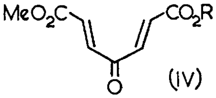
(I)



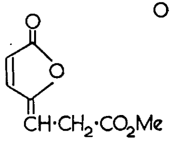
(II)



(III)



(IV)



(V)

The ester (III: R = Me) rearranges on standing to the known compound, $MeO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH{=}CH{\cdot}CO_2Me$, whose n.m.r. spectrum is identical to that reported by Winterfeldt;[3] this indicates a *trans* double bond (olefinic protons τ 2·70 and 3·17, J = 16 c./sec.).

On passage through an alumina column the ester (III: R = Me) is converted into the lactone (V), m.p. 84—85°, whose structure is supported by elemental analysis, mass spectrum, and spectral data. The infrared spectrum shows bands at 1784 (γ-lactone) and 1744 cm.$^{-1}$ (saturated ester) and the n.m.r. spectrum reveals the ring protons at τ 2·5 and 3·72 (J = 6 c./sec.), the exocyclic olefinic proton as a triplet (τ 4·44, J = 8 c./sec.), the methoxyl as a singlet (τ 6·22), and the methylene protons as a doublet (τ 6·42, J = 8 c./sec.). The exocyclic double bond presumably arises as a result of an isomerisation noted earlier in the benztropone series.[1]

With both the benztropolones and the simple tropolone the initial chemical reaction in the photo-oxidation is probably the addition of singlet oxygen across the tropolone ring to form an *endo*-peroxide. The reasons for the apparent subsequent divergence of reaction paths are being investigated.

(*Received, November 4th,* 1966; *Com.* 856.)

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[1] E. J. Forbes and J. Griffiths, *J. Chem. Soc.* (*C*), in the press.
[2] H. Midorikawa, *Bull. Chem. Soc. Japan*, 1953, **26**, 302.
[3] E. Winterfeldt, *Chem. Ber.*, 1954, **87**, 1952.