Photocyclisation and Photoracemisation of 1-(*o*-α-Methylbenzyl)-phenylpropane-1,2-dione

By N. K. HAMER* and C. J. SAMUEL

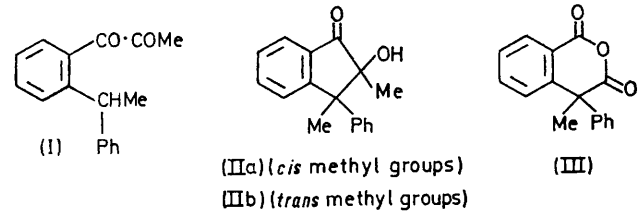
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

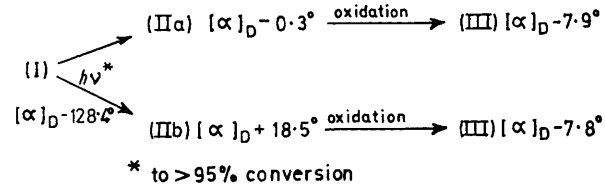
Summary Optically active 1-(*o*-α-methylbenzyl)phenylpropane-1,2-dione undergoes photoracemisation concurrently with photocyclisation to 2-hydroxyindan-1-one derivatives, the epimers of which are formed with the same optical purity.

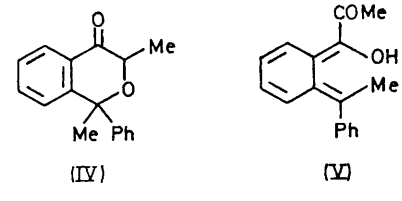
WE have reported the photocyclisation of 1-*o*-alkylphenylpropane-1,2-diones to 2-hydroxyindan-1-one derivatives[1] and, on the basis of the isomer distribution, made some tentative proposals concerning the mechanism. The same reaction has also been observed by Burkoth and Ullman.[2] Since these processes have been discussed in terms of hydrogen abstraction, we present here results on compound (I) in which the site of abstraction is asymmetric.

Irradiation of (I) ($\lambda > 436$ nm) in methanol gave the hydroxyindanones (IIa) and (IIb). The ratio (IIa):(IIb) (1·4:1) was relatively insensitive to solvent, as found earlier for the photocyclisation of 1-*o*-ethylphenylpropane-1,2-dione.[1] In contrast, the efficiency of cyclisation was very sensitive to solvent, and solvents other than methanol gave, in addition to (IIa) and (IIb), substantial quantities of other products including (IV). When optically active (I) was photolysed in methanol, the hydroxyindanone epimers had the rotations shown and oxidative degradation of both (IIa) and (IIb) gave samples of the anhydride (III) with the same rotations (reproducible to ±0·5°). Difficulties encountered in the separation of (IIa) and (IIb), and losses in subsequent steps limited the quantities of (III) available and consequently the precision of the rotation measurements, but care was taken to avoid processes likely to change the enantiomer composition of the products. In addition to the above reaction, (I) underwent racemisation [ϕ (racemisation)/ϕ (conversion) *ca.* 2·7] on irradiation in methanol, but, as with the other diketones studied,[1,2] irradiation in methan[^{2}H]ol gave no detectable incorporation of deuterium.

That both epimers of the 2-hydroxyindan-1-one are formed with the same degree of stereospecificity [this was also observed for the hydroxyindanones from irradiation of (I) in benzene] strongly implies a stereospecific process for the formation of (II). In view of the absence of deuterium incorporation into the benzylic position, which contrasts with the behaviour of *o*-alkyl-acetophenones and -benzophenones,[3] the photoracemisation is somewhat unexpected.







However, it could result from intramolecular reketonisation of the *Z*-photoenol[4] (V) provided this were sufficiently rapid. If, as we suggest, the hydroxyindanones are formed stereo-

specifically they must arise from a precursor which cannot racemise. Thus on the present evidence there is no necessary conflict with our earlier postulate of a benzocyclobutenol intermediate although the detailed relation between this and the racemisation process clearly require further study.

One of us (C.J.S.) acknowledges a maintenance award from the S.R.C.

(*Received*, 28*th February* 1972; *Com.* 319.)

[1] R. Bishop and N. K. Hamer, *J. Chem. Soc.* (*C*), 1970, 1193.
[2] T. L. Burkoth and E. F. Ullman, *Tetrahedron Letters*, 1970, 145.
[3] N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1597.
[4] S. M. Mellows and P. G. Sammes, *Chem. Comm.*, 1971, 21.