Photoreactions of Hydroxyindanones

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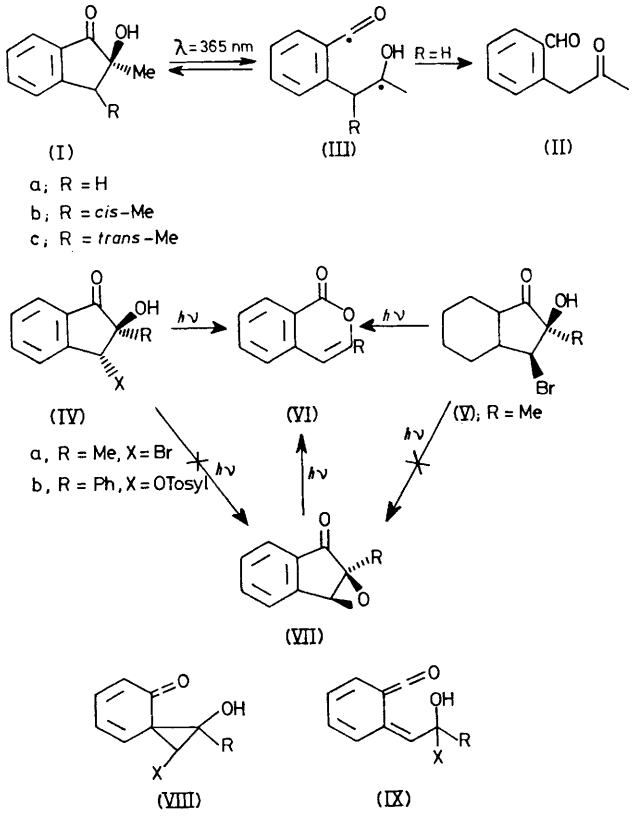
Summary 2-Hydroxyindan-1-one derivatives undergo clean photochemical reactions by initial 1,2-bond cleavage but the subsequent course of the reaction is largely determined by the nature of the substituent on the 3-position.

DURING our earlier studies on the photocyclisation of 1-*o*-alkylphenylpropane-1,2-diones to 2-hydroxyindanone derivatives[1] we observed that the latter underwent further transformations with light, $\lambda < 400$ nm. In a recent paper Padwa has shown that 2-ethoxycarbonyl-2-hydroxy- and 2-phenyl-2-hydroxy-indanones undergo photochemical reaction by initial cleavage of the 1,2-bond followed by intramolecular hydrogen transfer.[2] We show here that the nature of the substituent on the 3-position plays an important part in determining the course of photoreactions of 2-hydroxyindan-1-one derivatives.

Irradiation of 2-hydroxy-2-methylindan-1-one (Ia) in benzene gives clean formation of (II) in yields $> 90\%$ for conversion $< 30\%$. The identity of (II) followed from its spectra and its conversion into 2-naphthol with sodium hydroxide. In contrast, irradiation of the 2,3-dimethyl derivatives (Ib) and (Ic) under similar conditions caused rapid interconversion but no ring-opened products were formed. The reaction of (Ia) differs also from the apparently similar reaction of 2-ethoxycarbonyl-2-hydroxyindan-1-one[2] in that (Ia) is inert to photolysis in methanol [the interconversion of (Ib) and (Ic) is also very inefficient in this solvent] and in that when the hydroxy-proton of (Ia) is deuteriated, D is incorporated into the aldehyde proton of the photoproduct. These differences are understandable on the view that intramolecular transfer of neither a benzylic nor hydroxy hydrogen in (III) [both of which may lead to (II)] can proceed *via* the favoured six-membered cyclic transition state; hence, solvation and conformational effects determine which, if either, may compete with the recyclisation to hydroxyindanone.



When the substituent in the 3-position is a potential leaving group as in (IVa), (IVb), and (V), no aldehyde analogue of (II) is formed and the *cis–trans* isomerisation reaction is largely suppressed. Instead, photoelimination of HX occurs, both in the presence or absence of added base (2,6-lutidine), leading to isocoumarins (VI) (70—85%). Epoxyindanones (VII) were not detected at any stage although, when prepared independently, they underwent the expected photorearrangement[3] to (VI). They are, in any event, unlikely intermediates since neither the reaction conditions nor the stereochemistry of (V) are favourable for their formation. This reaction also appears to be inhibited by increasing polarity of solvent indicating that a photoionisation process with release of X^-, similar to that observed for certain benzylic esters,[4] may be discounted.

Photosensitisation studies suggest that, unlike the reactions of (Ia, b, c), the formation of isocoumarins from (IVa, b) and (V) results from a singlet state. Although isocoumarins could plausibly arise *via* 1,4-Br transfer in an intermediate of the type (III), there are no precedents for an analogous transfer of the tosyloxy group. We therefore suggest that the primary photochemical process gives (VIII), which has been shown to occur with several cyclopentenones,[5] and a 6-hydroxycyclohex-2-enone.[6]

Another possibility,† somewhat preferable on purely stereochemical grounds, would involve a 1,2-Br (or tosyloxy) shift on the analogue of (III) leading to (IX). Similar intermediates may be involved also in the recently reported photochemical formation of 2-pyrones from sulphate esters of hydroxycyclopentenones.[7]

(*Received*, 22*nd December* 1976; *Com.* 1393.)

† Suggested by a referee.

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