Intermediates in the Photocyclisation of 1-(*o*-Alkylphenyl)propane-1,2-diones

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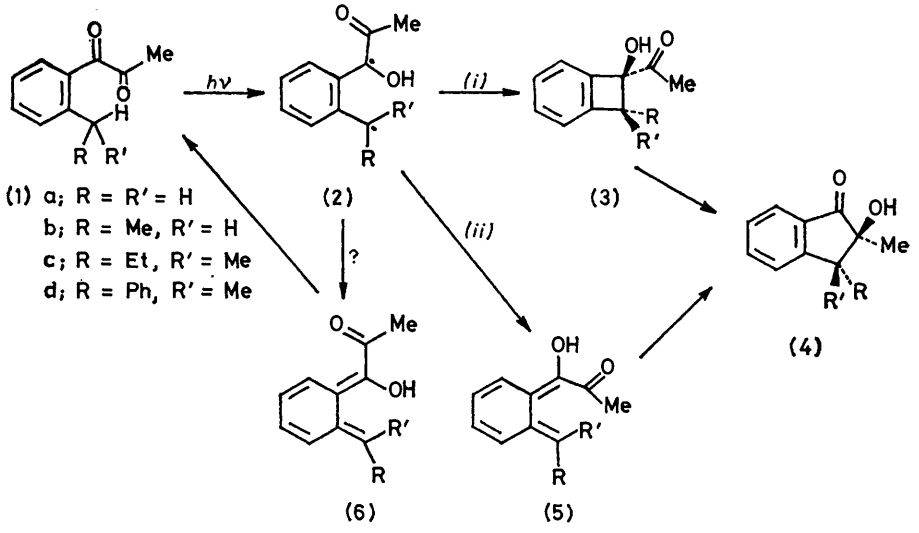
An intermediate in the photocyclisation of 1-(*o*-alkylphenyl)propane-1,2-diones may, in several cases, be efficiently trapped by sulphur dioxide but not by maleic anhydride. Reaction of 1-(*o*-bromoalkylphenyl)propane-1,2-diones with zinc leads to products expected from the photoenols of the parent diketones but there are significant differences between this reaction and the photocyclisation. It is argued that there is no evidence to implicate such enols as intermediates in the photoreaction.

THE photocyclisation of 1-(*o*-alkylphenyl)propane-1,2-diones (1) to 2-hydroxyindanones has been the subject of considerable study both by us [1,2] and by other groups.[3,4] There is a general consensus of opinion that

RESULTS AND DISCUSSION

When (1a) was irradiated ($\lambda > 400$ nm) in benzene containing sulphur dioxide, formation of a crystalline 1 : 1 adduct was observed. With 2.0M sulphur dioxide



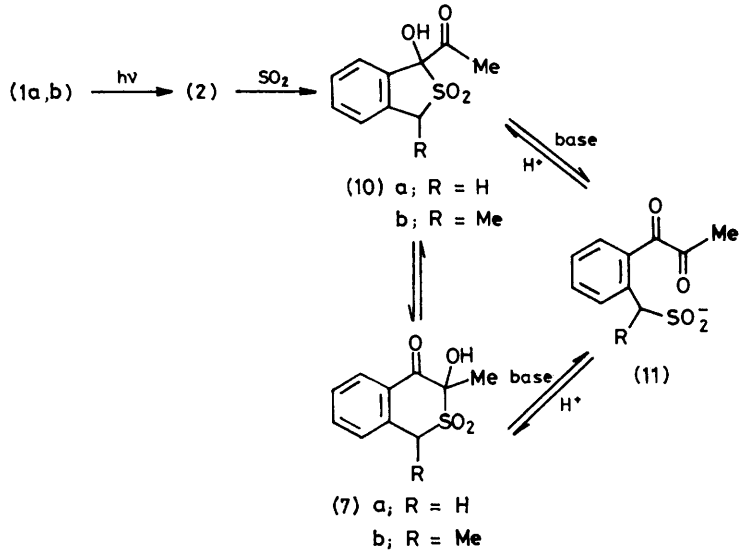
SCHEME

first 1,5-H transfer occurs from the $n \rightarrow \pi^*$ triplet of the diketone giving the diradical (2) but we have proposed [1] that this leads to the product *via* a benzocyclobutenol (3) [path (*i*) of the Scheme] whereas others have argued in favour of the (*E*)-dienol (5) as an intermediate [path (*ii*)]. The photoracemisation [2] observed for (1c and d) may result from hydrogen reversion in (2) or by reketonisation of the (*Z*)-dienol (6) since the existence of these hitherto elusive species [5a] has recently been demonstrated in the photolysis of related alkyl aryl monoketones.[5b] Both routes (*i*) and (*ii*) account satisfactorily for the stereoselectivity observed in the hydroxyindanone formation provided the final proton transfer is intramolecular.[1] However, the situation is complicated by the fact that (3) and (5) may be thermally interconvertible, thus one may be a precursor of the other.[6] A similar problem occurs in the photoenolisation of *o*-alkylacetophenones and related compounds which has been recently reviewed by Sammes [5a] and where the evidence suggests that benzocyclobutenols may well be precursors of the observed (*E*)-dienols. We describe here experiments which strongly support our initial view [1] that path (*i*) is to be preferred for the formation of hydroxyindanones from (1).

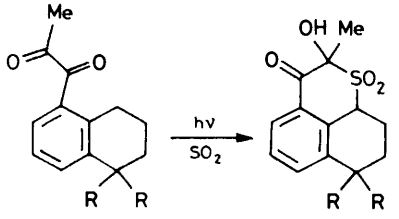
hydroxyindanone formation was almost entirely suppressed in favour of this adduct (92%), but even at 0.1M sulphur dioxide concentration the adduct comprised 47% of the photoproduct along with 53% of (4a). The adduct was soluble in mild aqueous base giving the characteristic u.v. absorbance of the 1,2-diketone moiety and was regenerated on subsequent acidification. This observation taken with the spectral data establishes the structure as 3-hydroxy-3-methylisothiochroman-4-one 2,2-dioxide (7a). Analogous adducts (7b) and (9) were formed in >80% yield from irradiation of (1b) and (8) in 2.0M sulphur dioxide. It was not possible to assign the relative configurations at C-1 and C-3 in (7b) or (9); moreover, the ^{1}H n.m.r. of (7b) in solution at room temperature showed that an equilibrium composed of the two epimers of (7b) and of the five-membered cyclic sulphone (10b) was rapidly established. Addition of base, however, caused the spectrum to simplify to that anticipated for the ring-opened sulphinate (11). As a consequence of this rapid equilibration the epimer composition of the cyclic sulphones (7) and (9), unlike that of the hydroxyindanone products, bears no relationship to the configuration of the precursor.

In contrast no adduct was obtained from irradiation

of (1d) in the presence of sulphur dioxide under similar conditions and only a low yield (*ca.* 10—15%) from (1c). The latter appeared, like (7b), to exist as an equilibrium



mixture and no crystalline isomer could be isolated. It seems probable that this is a result of increased steric

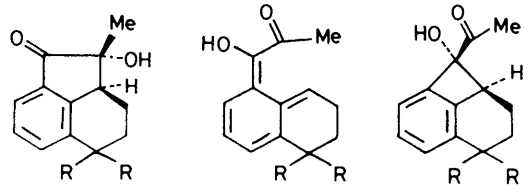


(8) a; R = H
b; R = Me

(9) a; R = H
b; R = Me

hindrance but it is unfortunate since the effect of an efficient trapping agent on the photoracemisation of these latter two diketones would have provided important evidence on the nature of the intermediate involved. Interestingly no α-hydroxysulphone-type adducts were found in the irradiation of heptane-2,3-dione in the presence of sulphur dioxide.

The above adducts could, in principle, arise by capture of either the diradical (2) or the (*E*)-dienol (5) by sulphur dioxide to give initially, (10). [The (*Z*)-dienols (6) will not be considered as intermediates as they cannot account for the stereoselectivity shown in hydroxyindanone formation.] However, for the reasons detailed below the former is much to be preferred. First, although sulphur dioxide may function as a dienophile [7] it is less reactive in such a role than maleic anhydride [8] which gives no trace of adduct. [Dimethyl butynedioate however is reported to form an adduct in low yield when (1a) is irradiated in its presence.] [4] It is, however, established as an efficient radical trap and has been shown to trap diradical intermediates in the cycloaddition of benzophenone to olefins [9] and in the intramolecular hydrogen-abstraction reactions of *o*-t-butylbenzoquinone.[10] Further, it is remarkable that a bimolecular addition of sulphur dioxide to (5) should compete successfully at concentrations down to 0.1M with the intramolecular cyclisation to (4), since the latter is extremely favourable both on energetic and stereochemical grounds. The cyclisation of (2) to (3), however, since it involves non-conservation of spin, may be relatively slow. Finally the high yield of the adduct (9) from (8) contrasts with the rather mediocre yields (<40%) of the photocyclisation product (12) formed in the absence of sulphur dioxide and shows that it is not the initial hydrogen-abstraction but the subsequent cyclisation which is responsible. There is no obvious reason why the cyclisation of the dienol (13) here to the



(12) a; R = H
b; R = Me

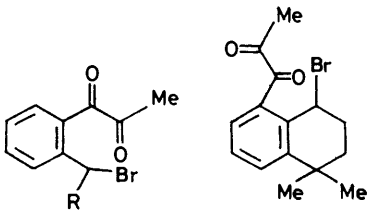
(13)

(14)

acenaphthylenone derivative (12) should be adversely affected by the molecular geometry (see later), whereas the benzocyclobutenol intermediate (14) will have additional angle strain. Support for this last point comes from the photolysis of 5,8-dimethyl-α-tetralone [11] where the initial intramolecular hydrogen-abstraction leads to dimeric products rather than dienols or benzocyclobutenols.

Unlike the (*E*)-dienols of related *o*-alkylaryl ketones whose existence and reactions are well established, there exists very little information on the dienols (5) and (13) which have been suggested as potential intermediates in the present photocyclisation. Padwa and Au [12] have made a very plausible proposal for them as precursors of hydroxyindanones formed in the photolysis of 3-

methoxycarbonylisochromanone but the reaction conditions there do not entirely exclude the possibility that the hydroxyindanones result from re-ketonisation followed by photocyclisation. We have therefore attempted to generate such dienols by a chemical rather than a photochemical route using the reaction of the brominated ketones (15a, b) and (16) with zinc in methanol containing acetic acid. Under these conditions one may reasonably hope to observe reactions of dienols rather than enolates or organozinc derivatives.



(15) a; R = H
b; R = Me

(16)

We find that both hydroxyindanones and debrominated diketones are formed together with reduction products of the latter (hydroxyindanone reduction was not important under the conditions employed). The yields and product composition are given in the Table and show

Products from the reduction of bromodiketones with Zn

Substrate	[AcOH]	Diketone	Hydroxyindanone
(15a)	0.2	(1a) 50%	(4a) 20%
(15a)	2.0	(1a) 40%	(4a) *ca.* 2%
(15b)	0.2	(1b) 10%	(4b) 50%; C-2 epimer 5%
(16)	0.2	(8b) 15%	(12b) 65%; C-2 epimer 0%

that the stereoselectivity in hydroxyindanone formation is similar to the photocyclisation and consistent with that expected for a thermally allowed conrotatory cyclisation of the (*E*)-dienol with intramolecular proton transfer. Whether the debrominated diketones arise, in part, by ketonisation of the (*Z*)-dienol is uncertain but the dramatic fall in hydroxyindanone yield with increased acidity of the medium shows that protonation at carbon of the (*E*)-dienol must compete with cyclisation. In contrast, the lack of deuterium incorporated into reactants or products in the photoreaction [1-3] shows that protonation at carbon is unimportant there. Significant too is the fact that the yield of (12b) from debromination of (15) is considerably higher than that from the photocyclisation of (8a, b) and the residue is composed largely of (8b) and its reduction products. Thus it appears that, apart from the competitive protonation at carbon, (13b) cyclises rather efficiently to (12b) and reinforces our conclusion from the trapping experiment that it is not an intermediate in the photocyclisation. Unfortunately, nothing definite can be learned from carrying out the debromination reaction in the presence of sulphur dioxide since neither hydroxyindanones or adducts of the type (7) or (10) are formed, doubtless because of the acidity of the medium.

While no individual observation here or in earlier work specifically excludes the possibility of dienol intermediates in the photocyclisation, the combined weight of evidence against their involvement (except perhaps to a very minor extent) now seems conclusive. Since all the data are well in accord with path (*i*) this is clearly to be preferred. It is however unfortunate that the key benzocyclobutenol intermediates (and those which may be involved in the photoenolisation of *o*-alkylaryl ketones) do not lend themselves readily to observation by flash-photolysis techniques.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained with a Varian HA 100 spectrometer with tetramethylsilane as internal reference. I.r. spectra were recorded on Nujol mulls (solids) or on liquid films. Preparative t.l.c. separations were conducted on Merck Kieselgel 60 PF 254 in acetone–hexane. Photoreactions used a Phillips 400 W medium pressure lamp cooled by a water jacket (Pyrex) with a filter solution (1.0 cm) of aqueous sodium nitrite solution (5%).

3-Hydroxy-3-methylisothiochroman-4-one 2,2-Dioxide (7a).—Into dry, degassed, benzene (80 ml) in a 100-ml standard flask cooled in ice–water was passed a slow stream of sulphur dioxide until 12.8 g had been absorbed, after which the solution was made up to 100 ml. *o*-Tolylpropane-1,2-dione (1a) (450 mg) in 50 ml of this solution was irradiated until it was colourless, then evaporated to dryness under reduced pressure. The solid residue (641 mg) was recrystallised from acetone–carbon tetrachloride to give the product (579 mg), m.p. 147—148 °C; $\nu_{max.}$ 3 230, 1 690, and 1 300 cm^{-1}; δ[$(CD_3)_2CO$] 1.75 (3 H, s), 3.0 (1 H, exchangeable), 4.62, 5.06 (2 H, AB quartet, *J* 16 Hz), 7.3—7.8 (3 H, m), and 8.15 (1 H, m) (Found: C, 52.9; H, 4.4; S, 14.0. $C_{10}H_{10}O_4S$ requires C, 53.1; H, 4.4; S, 14.2%).

In a similar irradiation of (1a) in benzene with sulphur dioxide (0.1M) examination of the crude product by n.m.r. showed that only (4a) and (7a) were present and in the proportions 53 and 47% respectively.

3-Hydroxy-1,3-dimethylisothiochroman-4-one 2,2-Dioxide (7b).—Irradiation of 1-(*o*-ethylphenyl)propane-1,2-dione [1] (1b) (400 mg) in a benzene solution of sulphur dioxide (50 ml, 2M) under similar conditions gave, after evaporation of the solvent, a gum which was taken up in ether (25 ml). This solution was extracted with sodium carbonate solution (4 × 10 ml, 5% aqueous) and the combined aqueous extracts immediately acidified (concentrated HCl). The acid solution was extracted with dichloromethane (3 × 25 ml), and the combined extracts were dried, then evaporated *in vacuo* to give a residual gum (492 mg) which was taken up in ether (3 ml). The solution was set aside for several days at 0 °C, and the product slowly crystallised, m.p. 107—108 °C, $\nu_{max.}$ 3 280, 1 690, and 1 303 cm^{-1}, δ [in a solution made up and run in $(CD_3)_2CO$ at −40 °C] 1.77 (3 H, s), 1.85 (3 H, d, *J* 8 Hz), 5.2 (1 H, q, *J* 8 Hz), 7.4—7.8 (3 H, m), and 8.15 (1 H, m) (Found: C, 54.7; H, 5.1. $C_{11}H_{12}O_4S$ requires C, 55.0; H, 5.0%).

The ^{1}H n.m.r. spectrum of the crystals in $(CD_3)_2CO$ or CD_3OD at room temperature was extremely complex owing to isomerisation; however, addition of sodium benzoate to a solution in CD_3OD gave an immediate yellow colouration accompanied by simplification of the spectrum

to δ 1.68 (3 H, d, *J* 7 Hz), 2.18 (3 H, s), and 4.48 (1 H, q, *J* 7 Hz). Analogous behaviour was shown by the gum obtained prior to crystallisation.

7,8,9,9a-*Tetrahydro*-2-*hydroxy*-2-*methylnaphtho*[1,8-bc]-*thian*-3-*one* 1,1-*Dioxide* (9).—From 1-(5,6,7,8-tetrahydro-1-naphthyl)propane-1,2-dione (300 mg) irradiated and worked up as in the previous case, there was obtained after crystallisation from ether the product (328 mg), m.p. 148—149 °C; $\nu_{max.}$ 3 285, 1 691, and 1 305 cm^{-1}; δ[$(CD_3)_2$-CO] 1.75 (3 H, s), 2.0—2.6 (5 H, m), 3.0 (2 H, m), 5.05 (1 H, m), 7.45 (2 H, m), and 8.0 (1 H, dd, *J* 6.5 and 2 Hz) (Found: C, 58.9; H, 5.5. $C_{13}H_{14}O_4S$ requires C, 58.6; H, 5.2%).

Photolysis of (1a) *in the Presence of Maleic Anhydride.*—A solution of (1a) (850 mg) and maleic anhydride (2.45 g) in dry benzene (25 ml) was purged with nitrogen, and then irradiated until colourless. Examination of the solution by t.l.c. and ^1H n.m.r. showed that no photoproduct other than (4a) was produced.

Photolysis of (1c) *and* (1d) *in the Presence of Sulphur Dioxide.*—These were carried out on samples (200 mg) in exactly the same way as for (1b). From (1c) there was obtained, after base extraction followed by re-acidification, a gum (34 mg) which could not be crystallised but whose reaction and i.r. spectra paralleled those of the crude product from (1b). No adduct was obtained from (1d) under these conditions.

1-(o-*Bromomethylphenyl*)*propane*-1,2-*dione* (15a).—To a solution of (1a) (325 mg) in dry carbon tetrachloride (10 ml) was added *N*-bromosuccinimide (360 mg) and dibenzoyl peroxide (15 mg) and the mixture refluxed for 45 min, after which time t.l.c. showed that *ca.* 80% of the product was present. The mixture was diluted with carbon tetrachloride (30 ml), washed with cold sodium hydrogencarbonate solution (10 ml, 1%), and dried ($MgSO_4$). After removal of the solvent *in vacuo* below 25 °C the yellow residue was purified by preparative t.l.c. to give the product as a lachrymatory yellow oil (322 mg) which decomposed readily on standing at room temperature with the evolution of hydrogen bromide; $\lambda_{max.}$ (CCl_4) 415 nm (log ε 1.6); $\nu_{max.}$ 1 715 and 1 680 cm^{-1}; δ(CCl_4) 2.5 (3 H, s), 4.77 (2 H, s), and 7.2—7.8 (4 H, m).

Owing to its instability the product was stored in benzene solution (0.3M) at 5 °C for not more than 24 h prior to use.

1-(o-1-*Bromoethylphenyl*)*propane*-1,2-*dione* (15b).—From (1b) (300 mg) and *N*-bromosuccinimide (305 mg) was prepared similarly the product (290 mg); $\lambda_{max.}$ (CCl_4) 413 (log ε 1.58); δ(CCl_4) 2.0 (3 H, d, *J* 7 Hz), 2.4 (3 H, s), 5.88 (1 H, q, *J* 7 Hz), and 7.2—7.4 (4 H, m).

1-(5,6,7,8-*Tetrahydro*-5,5-*dimethyl*-1-*naphthyl*)*propane*-1,2-*dione* (8b).—This was prepared from 5,6,7,8-tetrahydro-5,5-dimethyl-1-naphthoic acid [13] (9.0 g) by the general procedure given previously [2] and was purified *via* its bisulphite adduct. The product was obtained as a yellow oil (5.65 g), b.p. 133—136 °C at 1.0 mmHg; $\lambda_{max.}$ (pentane) 4.04 (log ε 1.53); $\nu_{max.}$ 1 716 and 1 672 cm^{-1}; δ(CCl_4) 1.27 (6 H, s), 1.4—1.9 (4 H, m), 2.38 (3 H, s), 2.9 (2 H, t, *J* 5.5 Hz), and 7.0—7.55 (3 H, m) (Found: C, 78.6; H, 7.9. $C_{15}H_{18}O_2$ requires C, 78.3; H, 7.8%).

c-2a,3,4,5-*Tetrahydro*-r-2-*hydroxy*-2,5,5-*trimethyl*-2H-*acenaphthylen*-1-*one* (12b).—Irradiation of (8b) (230 mg) in methanol (50 ml) gave, after evaporation of the solvent and crystallisation of the residue from ether, the product (76 mg), m.p. 113—114 °C; $\nu_{max.}$ 3 410 and 1 710 cm^{-1}; δ(CCl_4) 1.22 (6 H, s), 1.42 (3 H, s), 1.8—2.2 (4 H, m), 2.9 (1 H, exchangeable), 3.22 (1 H, dd, *J* 12 and 6 Hz), and 7.2—7.6 (3 H, m) (Found: C, 78.2; H, 7.9. $C_{15}H_{18}O_2$ requires C, 78.3; H, 7.8%).

1-(5,6,7,8-*Tetrahydro*-8-*bromo*-5,5-*dimethyl*-1-*naphthyl*)-*propane*-1,2-*dione* (16).—From (8b) (275 mg) and *N*-bromosuccinimide (220 mg), using the above procedure, the product was obtained as a yellow oil (252 mg), $\lambda_{max.}$ (CCl_4) 416 nm (log ε 1.61); $\nu_{max.}$ 1 717 and 1 680 cm^{-1}; δ(CCl_4) 1.26 (3 H, s), 1.42 (3 H, s), 1.5—2.4 (4 H, m), 2.5 (3 H, s), 6.22 (1 H, dd, *J* 3 and 1 Hz), and 7.0—7.55 (3 H, m).

Reaction of Bromodiketones (15a, b) *and* (16) *with Zinc.*—To a vigorously stirred suspension of zinc dust (85 mg) in methanol (4.0 ml) containing acetic acid (0.2M) was added, in one portion, the appropriate bromoketone (1.0 ml of a benzene solution containing *ca.* 0.3 mmol). After 3 min, when t.l.c. showed that all the starting material had reacted, the solution was decanted from excess of zinc and poured into water (20 ml). The mixture was extracted with benzene (3 × 10 ml), the combined extracts washed with dilute HCl (10 ml) and sodium hydrogencarbonate solution (10 ml), and then dried ($MgSO_4$). After evaporation of the solvent the yields of diketone and hydroxyindanones were determined (*a*) from the integrated ^1H n.m.r. of the mixture using added 1,4-dimethoxybenzene as an internal standard; and (*b*) by h.p.l.c. on a Waters ALC202 chromatograph. The results from different experiments were reproducible to within ±5%.

In one experiment the acetic acid concentration was increased to 2M. In similar experiments the diketones (1a, b) and (8b) also the hydroxyindanones (4a, b) and (12b) were allowed to react with zinc under identical conditions. Some reduction products of the 1,2-diketones were formed and these were qualitively similar (t.l.c.) to unidentified products formed in the debromination reaction: very little reduction of (4) and (12b) was observed.

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