Photocyclisation of 1-*o*-Alkylphenylpropane-1,2-diones: Stereochemistry

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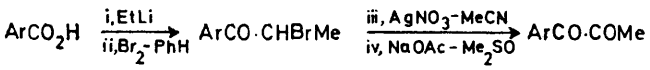
The photoreactions of 1-[*o*-(s-butyl)- and 1-[*o*-(α-methylbenzyl)-phenyl]propane-1,2-diones are reported. In hydroxylic solvents the major products are 2-hydroxyindan-1-ones, whereas in aprotic solvents substantial amounts of substituted isochroman-4-ones are also formed. It is shown that the formation of the hydroxyindinanones may proceed with a high degree of stereospecificity, both epimers possessing the same chirality at C-3, and that the photocyclisation of 1-(*o*-s-butylphenyl)propane-1,2-diones results in predominant inversion of configuration at the alkyl group of the hydroxyindanones. Photoracemisation of the starting diketones is also found to occur, and mechanisms for these processes are discussed.

THE photocyclisation of 1-*o*-alkylphenylpropane-1,2-diones to 2-hydroxyindan-1-ones has been discussed both by us [1] and by Ullman [2] and his co-workers. Similar products have also been obtained by irradiation of 2,2'-dimethylbenzil and related compounds.[3] From the observed epimeric composition of the hydroxyindanones we argued that intramolecular γ-hydrogen abstraction occurred to give a benzocyclobutenol intermediate, which underwent a thermal stereospecific ring expansion to afford the final product.[1] Recent studies on the thermal rearrangement of 2-benzoyl-2-hydroxybicyclo[2.2.1]-heptanes to 2-hydroxy-2-phenylbicyclo[3.2.1]octan-3-ones [4] have shown it to be stereospecific, indicating that our postulated final step is reasonable. Other possible mechanisms, however, cannot be excluded and we have therefore extended our studies to related diketones where the site of hydrogen abstraction is chiral.

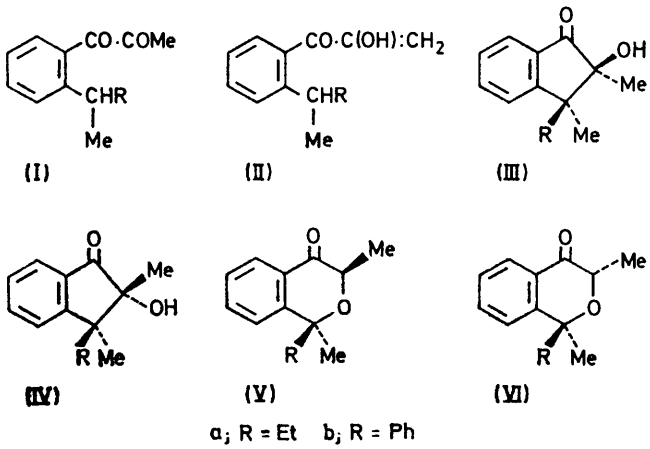
The diketones (Ia and b) were prepared from the appropriate *o*-alkylbenzoic acids by the route shown (Scheme 1). When this procedure was used to prepare



SCHEME 1

optically active samples of the diketones the products were degraded to the parent acid (with alkaline hydrogen peroxide) to verify that no racemisation had occurred. Although the diketone (Ia) and the expected hydroxyindanones may be related to 2-phenylbutane and 4-ethyl-4-methylisochroman-1,3-dione, the chirality of both of which is well established,[5-7] we were not able to achieve satisfactory separations of epimeric photoproducts. Moreover, the large number of overlapping saturated CH signals in the ^{1}H n.m.r. spectra of the products hinders spectroscopic determination of the composition of crude photolysis mixtures. Accordingly the diketone (Ia) was used primarily to determine the stereochemistry of the reaction and (Ib), which did not suffer from the aforementioned drawbacks, for most of the more detailed studies.

Both diketones appeared to be relatively inert to irradiation at wavelengths above 410 nm, compared with those studied earlier. The quantum yields (Φ_c) for conversion into products were found to be *ca.* 0·01 and *ca.* 0·05 in benzene and methanol, respectively, for both diketones, in contrast with the value (0·83) for



1-*o*-tolylpropane-1,2-dione.[8] These quantum yields are approximate as there was evidence for the formation of small amounts (≯3%) of an intermediate [almost certainly the enol (II) [9,10]] which reverted slowly to the starting diketone. With (Ib) there was additional complication in that the quantum yield for conversion in methanol decreased with increasing concentration of substrate. Since the absorption spectrum of (Ib) in methanol also showed small but consistent variations with concentration there appears to be some degree of molecular association in this solvent. Because of this and of the very low Φ_c value for the unquenched reaction in benzene and other non-hydroxylic solvents, we found that although there was evidence of quenching by pyrene we were unable to make quantitative measurements with the apparatus available. Thus the proportion of the reaction proceeding through the $n \longrightarrow \pi^*$ triplet, which is involved almost exclusively in the more efficient

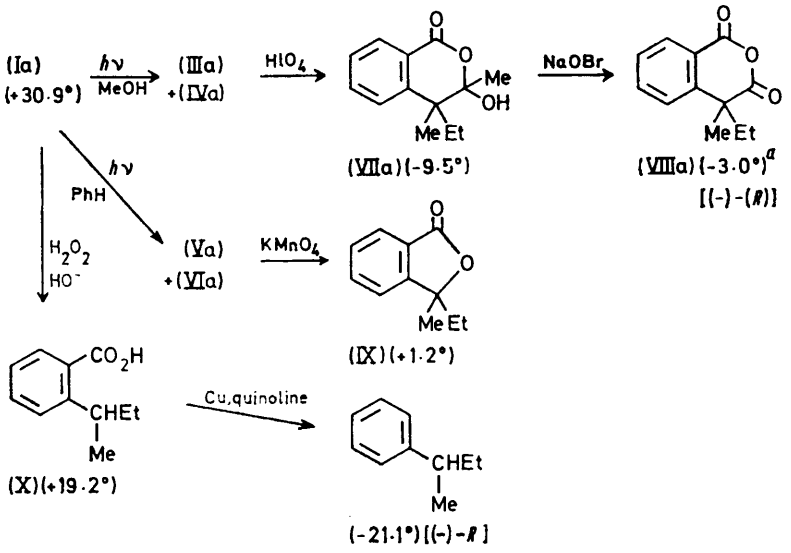
[1] R. Bishop and N. K. Hamer, *J. Chem. Soc.* (*C*), 1970, 1193; N. K. Hamer and C. J. Samuel, *J.C.S. Chem. Comm.*, 1972, 470.
[2] T. L. Burkoth and E. F. Ullman, *Tetrahedron Letters*, 1970, 145.
[3] K. Maruyama, K. Ono, and J. Osugi, *Bull. Chem. Soc. Japan*, 1972, **45**, 847.
[4] C. L. Stevens, T. R. Treat, and P. M. Pillai, *J. Org. Chem.*, 1972, **37**, 2091.
[5] D. J. Cram, *J. Amer. Chem. Soc.*, 1952, **74**, 2149.
[6] R. K. Hill and G. R. Newkome, *Tetrahedron*, 1969, **25**, 1249.
[7] R. B. Longmore and B. Robinson, *Chem. and Ind.*, 1969, 622.
[8] H. Gusten, personal communication.
[9] N. J. Turro and T.-J. Lee, *J. Amer. Chem. Soc.*, 1969, **91**, 5651; 1970, **92**, 7467.
[10] R. G. Zepp and P. J. Wagner, *J. Amer. Chem. Soc.*, 1970, **92**, 7466.

photocyclisations of 1-*o*-tolylpropane-1,2-dione, is not settled.

In hydroxylic solvents (MeOH or AcOH) both diketones gave hydroxyindanones [(III) and (IV)] as the principal products [>90% for (Ib) in AcOH], together with small amounts of several other products. Most of these we were unable to identify, with the exception of the isochromanones (Va and b) and (VIa and b). These latter were formed in much higher proportion (20—40%) from photoreactions carried out in aprotic solvents, and their structures were deduced from spectroscopic data and comparison of these with those of 1,1-diethyl-3-methylisochroman-4-one prepared from 3-methylisochroman.[11] Although the yields of hydroxyindanones were much smaller in aprotic solvents, the epimer ratio was relatively insensitive to the solvent being in the range 2—3 : 1 for (IIIa) : (IVa) and 0·5—1·0 : 1 for (IIIb) : (IVb). As before, the stereochemical assignments are based on the chemical shifts of the two methyl singlets. The epimer ratios of isochromanones were variable but since these probably are formed (see later) from ketonisation of the corresponding enols this is probably not relevant to the photochemical process.

Both ketones underwent photoracemisation (Φ_r) and in all solvents this process was considerably more efficient than those leading to other products. In benzene the measured values of Φ_r/Φ_c were 14 ± 2 for (Ib) and 5 ± 1 for (Ia). As with Φ_c itself we observed that Φ_r/Φ_c for (Ib) in methanol decreased with increasing concentration of substrate, but for small conversions (0·01M) it was *ca.* 6 ± 1. However, the photoracemisation proceeded without incorporation of deuterium into the diketones when conducted in MeOD or AcOD.

The hydroxyindanones from both diketones were optically active and the degradations (Scheme 2) show that the hydroxyindanones from (Ia) are formed with preferential inversions of configuration. A similar oxidative degradation of the hydroxyindanones from (Ib) demonstrates that both epimers are formed with the same configuration at C-3 and with the same (±5%) degree of stereospecificity. The degree of stereospecificity (λ) of



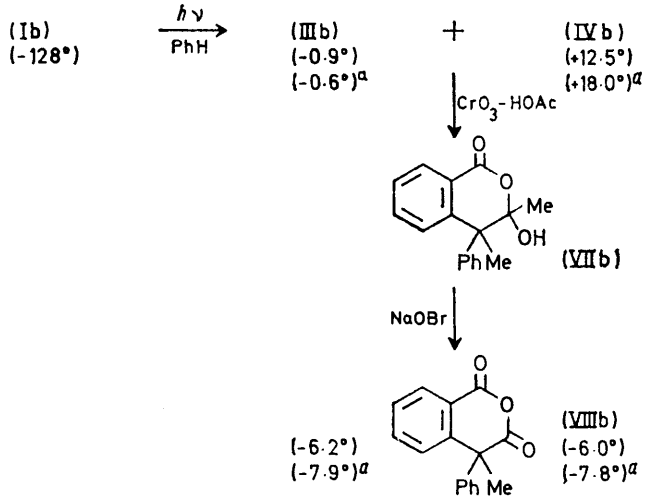
[a] Reported for (+)-(*S*)-(VIIIa), $[\alpha]_D$ +41·2° (*c* 0·09 in MeOH)

SCHEME 2

the reaction can be derived from the relation * (1), which holds at complete conversion (β_0 is the optical

$$\beta'/\beta_0 = \lambda/(1 + \Phi/\Phi_c) \qquad (1)$$

purity of the starting diketone and β' the optical purity of the products). By use of the value (106°) found for the specific rotation of the optically pure anhydride (VIIIb) we find that for the photocyclisation of (Ib) in benzene



[a] From irradiation in MeOH

SCHEME 3

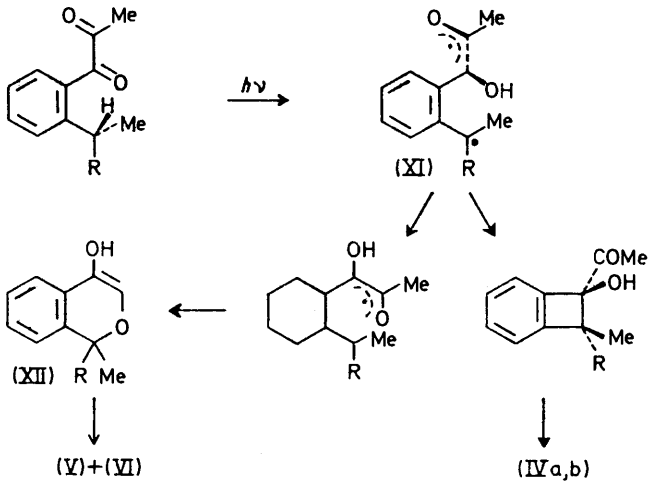
* See Appendix.

[11] P. Maitte, *Compt. rend.*, 1954, **239**, 1508.

λ is 0·9 ± 0·15. For the reasons stated earlier the comparatively large error in λ is not unexpected, but it is clear that for this case the photocyclisation shows a high degree of stereospecificity. The photoreaction of (Ib) in methanol (0·01M) gave λ *ca.* 0·6, indicating a less stereospecific process, and it seems likely that the photocyclisation of (Ia) is also much less stereospecific although, since the rotation of the optically pure anhydride (VIIIa) is uncertain, we cannot give a precise figure for it.

The isochromanone mixture from the photoreaction of (Ia) in benzene was also optically active, and was oxidised to the phthalide (IX). There is evidence from the work of Kramer [12] that (IX) has the same configuration as (X), but since there is no independent proof of the relative assignments of (IX) and (X) and no report of the optical purity of (IX) we shall not consider this aspect further.

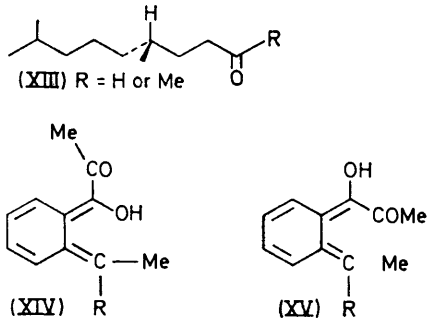
Although isochromanones were not observed in the photoreactions of the *o*-alkylphenylpropane-1,2-diones examined previously, their formation from the diradical intermediate resulting from γ-hydrogen abstraction is conceivable. We suggest that, assuming the two carbonyl groups in the diketone are orientated transoid,[13] this relation will be retained both in the excited state and after the initial H abstraction. Steric effects in these very hindered species (XI) will prevent both radical



SCHEME 4

centres becoming coplanar with the aromatic ring and, of the two, the more stable semidione radical [14] is likely to be forced out of complete conjugation with the aromatic ring. Hence the energy barrier to rotation about the C(1)–aryl bond will be lowered and the necessary rotation followed by collapse of the diradical to the enol (XII) is possible. Hydroxylic solvents are expected to solvate the oxygen atoms and hence hinder C–O bond formation relative to C–C. We emphasise that the formation of isochromanones which, unlike that of the hydroxyindanones, cannot be easily explained on the basis of a δ-hydrogen abstraction provides the most direct support to favour our initial suggestion of γ-H abstraction; however there is much other evidence supporting the latter process.

The preference for inversion at the benzylic centre in the photocyclisation of (Ia) to hydroxyindanones is unexpected. In the absence of any degree of stereoelectronic control we would expect racemisation, with or without some retention of configuration, as has been observed in the photocyclisation of the saturated ketone



(XIII).[15] Taken in conjunction with our earlier observation [1] that the photocyclisation of 1-(5,6,7,8-tetrahydro-1-naphthyl)propane-1,2-dione gives *r*-2a,3,4,5-tetrahydro-2-hydroxy-*t*-2-methylacenaphthen-1(2*H*)-one with no trace of the corresponding *cis*-epimer, this seems to implicate considerable steric control—presumably influenced by orbital symmetry considerations. The fact that both (IIIb) and (IVb) are formed from (Ib) with some chirality and degree of stereospecificity supports this view. Since, unfortunately, we cannot exclude the possibility of both triplet and singlet excited states participating in the present rather inefficient cyclisations it seems premature to attempt a detailed discussion at this stage. However, in our previous paper [1] we favoured an explanation involving disrotatory closure of the initial intermediate analogous to (XII) to give a benzocyclobutenol. If this is followed here then it is clear from the geometry of (XII) that the disrotatory mode leading to the observed inversion at the benzylic position should be preferred. Whether it is legitimate to treat (XII), which here is not coplanar, as an excited state of the corresponding enol is, however, questionable.

Finally we consider the photoracemisation; this is the most efficient process for both diketones yet it seems to us, in conjunction with the absence of deuterium incorporation, the most difficult to explain satisfactorily. Owing to this lack of incorporation there is no means of estimating the quantum yield for the initial H abstraction; thus we cannot say whether the intermediate involved in the racemisation brings it about by a non-stereospecific process or by one which stereospecifically inverts the chiral centre. On the other hand it does

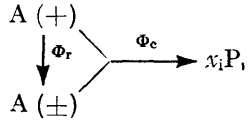
[12] E. C. Kramer Ph.D. Thesis, Rutgers 1959; *Diss. Abs.*, 1959, **20**, 1584.
[13] T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1967, **89**, 4380.
[14] E. T. Kaiser and L. Kevan, 'Radical Ions,' Interscience, New York, 1968.
[15] I. Orban, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, 1963, **85**, 3034.

argue strongly against the involvement of enolic species (XIV) and (XV), since related enols from similar monoketones appear to have comparatively long lifetimes [16] in non-hydroxylic solvents and undergo rapid reketonisation in the presence of alcohols or acetic acid—presumably by external protonation. The H reversion must therefore be extremely fast to exclude proton exchange between the hydroxy-group and the solvent, and thus presumably takes place at the diradical stage (XI). In orbital symmetry terms an antarafacial H transfer in (XI) (again regarded as an excited enol) could give rise to inversion at the benzylic position; however the conformation of (XI) seems unfavourable on steric grounds for such a process.

APPENDIX

The relationship between the variation in optical purities of substrate and products with degree of conversion in a system undergoing concomitant photoreaction and photoracemisation has not been explicitly discussed hitherto; we therefore indicate the derivation of equation (1).

The system may be represented as:



where x_i is the fraction of reactant converted into product P_i.

If A represents the total amount of reactant and β its optical purity at any instant then:

$$A = A(+) + A(\pm) \text{ and } A(+) = \beta A$$

After δN quanta have been absorbed,

$$\delta A = -\Phi_c \delta N$$

and $$\delta A(+) = \delta(\beta A) = -\Phi_c \beta \delta N - \Phi_r \beta \delta N$$

giving $$\beta/\beta_0 = (A/A_0)^{\Phi_r/\Phi_c}$$

where A_0 and β_0 are the initial amount and optical purity of reactant.

Similarly, $$P_i = x_i(A_0 - A)$$

$$\delta(\beta' P_i) = \lambda x_i \Phi_c \beta \delta N$$

where β′ is the instantaneous optical purity of product P_i and λ the degree of stereospecificity of the reaction.

After integration this gives

$$\beta'/\beta_0 = [\lambda/(1 + \Phi_r/\Phi_c)]\{[1 + (A/A_0)^{1+\Phi_r/\Phi_c}]/(1 + A/A_0)\}$$

which, at complete conversion reduces to equation (1).

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained with a Varian HA100 (100 MHz) spectrometer for solutions in carbon tetrachloride solution unless otherwise stated, with tetramethylsilane as internal standard. U.v. absorbances were measured for solutions in 95% ethanol on a Cary 14M 40 or a Perkin-Elmer SP 500/2 spectrophotometer. Specific rotations were measured for solutions in 95% ethanol (*c* 0·01—0·05) with a Bendix NPL Automatic Polarimeter 143C. Preparative t.l.c. separations were conducted on Merck Kieselgel GF_{254} by use of multiple run procedures in acetone–hexane unless otherise stated. Column chromatographic separations were performed on Fisons silica gel (100—200 mesh).

M.p.s, unless stated to the contrary, are for racemic materials; in isolating products from optically active starting materials crystallisation procedures were avoided owing to the danger of affecting the enantiomeric composition of mixtures.

o-(α-Methylbenzyl)benzoic acid,[17] from catalytic hydrogenation of 3-methyl-3-phenylphthalide,[18] was resolved by fractional crystallisation of the (−)-1-phenylethylamine salt from aqueous methanol. The pure enantiomer had $[\alpha]_D$ −186°, m.p. 47—48°, but samples of >95% optical purity were also used in the subsequent experiments. Photoreactions were conducted by use of a Phillips 400 W medium-pressure lamp cooled by a water jacket, with a filter solution (8 mm) of *o*-nitrophenol (5×10^{-3}M) in 95% ethanol; they were carried out under nitrogen in previously degassed solvents. Quantum yields were determined (1-phenylpentane-1,2-dione in benzene [10] as actinometer) on a merry-go-round by use of a 125 W medium-pressure mercury lamp with filter solutions of iodine in carbon tetrachloride and aqueous quinine hydrochloride [19] to isolate the 406 nm line. The disappearance of starting material was followed spectrophotometrically. To determine quantum yield ratios (Φ_r/Φ_c) samples were withdrawn at various degrees of conversion and the starting diketone was isolated by column chromatography.

1-(o-*s-Butylphenyl)propane*-1,2-*dione* (Ia).—To a solution of *o*-s-butylbenzoic acid [12] (7·1 g) in dry ether (50 ml) under nitrogen was added an ethereal solution of ethyl-lithium (90 ml; 0·90M). After stirring for 1 h the water was added and the organic layer was separated, washed with sodium hydrogen carbonate solution (2 × 25 ml), dried ($MgSO_4$), and evaporated to give *o*-s-butylpropiophenone (7·2 g, b.p. 106—110° at 4 mmHg). This was taken up in benzene (50 ml) and bromine (2·0 ml) was added dropwise while nitrogen was blown through the solution. After 30 min water was added; the benzene layer was separated, washed with sodium hydrogen carbonate solution (3 × 30 ml), dried, and evaporated *in vacuo* to give the crude bromoketone, which was treated with silver nitrate (9·0 g) in dry acetonitrile (50 ml) for 3 days at room temperature. As described by Kornblum and Frazier,[20] the crude nitratoketone was taken up in dimethyl sulphoxide (50 ml) and stirred with sodium acetate for 30 min. Addition of ice, extraction with petroleum (b.p. 30—40°), and evaporation of the extract gave the crude product which was purified by column chromatography [carbon tetrachloride–dichloromethane (1 : 1) as eluant]. The pure *material* (5·5 g), b.p. 90—92° at 0·5 mmHg had $\lambda_{max.}$ (pentane) 258 and 411 nm (log ε 3·71 and 1·40), $\nu_{max.}$ 1718 and 1680 cm^{-1}, τ 2·5—3·0 (4H, m), 6·91 (1H, sextet, *J* 7 Hz), 7·61 (3H, s), 8·2—8·6

[16] G. Porter and M. F. Tchir, *Chem. Comm.*, 1970, 1372.
[17] S. Mitsui and T. Kamaishi, *Nippon Nagaku Zasshi*, 1961, **82**, 1382.
[18] F. N. Jones and C. R. Hansen, *J. Org. Chem.*, 1962, **27**, 3364.
[19] J. G. Calvert and J. N. Pitts, ' Photochemistry,' Wiley, New York, 1966, p. 736.
[20] N. Kornblum and H. W. Frazier, *J. Amer. Chem. Soc.*, 1966, **88**, 865.

(2H, m) 8·80 (3H, d, *J* 7 Hz), and 9·23 (3H, t, *J* 7 Hz) (Found: C, 76·3; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%).

From acid of $[\alpha]_D$ +19·2° was obtained diketone of $[\alpha]_D$ +30·9° (*c* 0·05 in 95% EtOH). A sample was treated with alkaline hydrogen peroxide as described for (Ib) to give *o*-s-butylbenzoic acid, $[\alpha]_D$ +19·1°.

1-o-(α-*Methylbenzyl*)*phenylpropane*-1,2-*dione* (Ib).—Similarly, *o*-(α-methylbenzyl)benzoic acid [17] (8·7 g) gave the *dione* (Ib), b.p. 126—128° at 0·05 mmHg (7·9 g), $\nu_{max.}$ 1716 and 1680 cm^{-1}, $\lambda_{max.}$ (pentane) 259 and 413 nm (log ε 3·71 and 1·49), τ 2·5—3·1 (9H, m), 5·23 (1H, q, *J* 7 Hz), 7·82 (3H, s), and 8·54 (3H, d, *J* 7 Hz) (Found: C, 80·9; H, 6·7. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

Acid of $[\alpha]_D$ +182·5° gave product of $[\alpha]_D$ +131°, which slowly crystallised (m.p. 60·5—62°). To this (0·5 g) in warm ethanol (20 ml) was added 10% hydrogen peroxide (5 ml) in sodium hydroxide (10%; 5 ml), dropwise until the colour of the diketone was discharged. After cooling and acidification the mixture was extracted with ether (3 × 30 ml); the solvent was removed and the residue distilled to give *o*-(α-methylbenzyl)benzoic acid, $[\alpha]_D$ +183°.

Irradiation Products from the Dione (Ia).—The solution from irradiation of the dione (Ia) (0·5 g) in benzene (250 ml) to >98% conversion was evaporated and subjected to preparative t.l.c. Several products were formed, of which we isolated and identified the two major components. That which ran the slower on t.l.c. was a mixture of the epimers of 3-ethyl-2-hydroxy-2,3-dimethylindan-1-one [(IIIa) and (IVa)] which could not be separated; $\nu_{max.}$ 3450 and 1721 cm^{-1}, τ 2·2—2·9 (m), 6·3br, 7·9—8·5 (m), 8·64 (s), 8·76 (s), 8·84 (s), 8·98 (t, *J* 7·5 Hz), and 9·45 (t, *J* 7 Hz) (insufficiently resolved for integration). To a solution of this mixture of hydroxyindanones (197 mg) in ether (10 ml) was added a saturated solution of periodic acid in ether (200 ml), and the mixture was left for 3 days. After washing with water to remove iodine compounds the product was extracted into 10% sodium hydroxide solution (2 × 10 ml) and the extract was acidified to give crystals (142 mg) of 4-*ethyl*-3-*hydroxy*-3,4-*dimethylisochroman*-1-*one* (VIIa), m.p. 155—157°, $\nu_{max.}$ 3310 and 1699 cm^{-1}, τ ($CDCl_3$) 1·8—2·8 (4H, m), 6·9br (1H, s), 8·1—8·4 (2H, m), 8·59 (3H, s), and 9·40 (3H, t, *J* 8 Hz) (Found: C, 70·7; N, 7·2. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). The second major product was a mixture of epimers [(Va) and (VIa)] of 1-ethyl-1,3-dimethylisochroman-1-one which again could not be separated; $\nu_{max.}$ 1698 cm^{-1}, τ 2·11 (2H, dd, *J* 2 and 7 Hz), 2·5—3·0 (6H, m), 5·64 (2H, dq, *J* 6·5 Hz), 7·8—8·4 (4H, m), 8·49 and 8·52 (each 3H, s), 8·63 (6H, d, *J* 7 Hz), 9·03 (3H, t, *J* 7 Hz), and 9·27 (3H, t, *J* 7 Hz 3H). The *dinitrophenylhydrazone* had m.p. 122—124° (Found: C, 59·4; H, 5·4; N, 14·5. $C_{19}H_{20}N_4O_5$ requires C, 59·4; H, 5·2; N, 14·5%).

A sample of the isochromanone mixture (85 mg), $[\alpha]_D$ −1·8°, was stirred with potassium permanganate (132 mg) and potassium carbonate (230 mg) in water (4 ml) and t-butyl alcohol (2 ml) for 12 h. After acidification and treatment with sulphur dioxide the mixture was extracted with ether to give 3-ethyl-3-methylphthalide (32 mg), $[\alpha]_D$ +1·2° (*c* 0·015 in 95% EtOH), identical with an authentic sample.[21]

Oxidation of the Isochromanone (VIIa).—To a solution of the lactol (VIIa) (150 mg) in aqueous sodium hydroxide (10%; 2 ml) was added a freshly prepared solution of sodium hypobromite (1·6M; 5 ml) and the mixture was stirred for 0·5 h. Aqueous sodium hydrogen sulphite (10%; 10 ml) was added to reduce the excess of oxidant, and the solution was then acidified and extracted with ether (5 × 20 ml). The combined extracts were dried ($MgSO_4$) and evaporated, and the residual gum was heated at 100° to effect complete conversion into the anhydride. After t.l.c. the anhydride was sublimed onto a cold finger at 10^{-3} mmHg from a bath at 80—90° to give material identical with an authentic sample of (VIIIa).[6]

1,1-*Diethyl*-3-*methylisochroman*.—To 3-methylisochroman [11] (14 g) in xylene (50 ml) was added selenium dioxide (30 g), and the mixture was refluxed for 2 days. After cooling, dry ether (200 ml) was added; the mixture was filtered and most of the solvent was removed *in vacuo*. The residue was added dropwise with stirring to the Grignard reagent from ethyl bromide (30 g) and magnesium (7·5 g) in ether (150 ml), and after 4 h at 25° the mixture was treated with saturated ammonium chloride and worked up in the usual way. The product (6 g) was taken up in ether (100 ml) and shaken with concentrated hydrochloric acid (10 ml) for 2 days. Water was added and the organic layer was separated and washed with sodium hydrogen carbonate solution. The product was purified on a column (3 × 40 cm) (carbon tetrachloride as eluant) and distilled to give pure material (3·0 g), b.p. 123—125° at 10 mmHg, τ 3·04 (4H, m), 6·19 (1H, sextet, *J* 6 Hz), 7·48 (2H, d, *J* 7 Hz), 7·9—8·6 (2H, m), 8·74 (3H, d, *J* 6 Hz), 9·08 (3H, t, *J* 7 Hz), and 9·43 (3H, t, *J* 7 Hz).

1,1-*Diethyl*-3-*methylisochroman*-4-*one*.—To a solution of the foregoing isochroman (4·2 g) in acetic acid (25 ml) at 100°, lead tetra-acetate was added in portions until t.l.c. showed that >80% of the starting material had disappeared (a large excess was needed). The mixture was then diluted with water, ether (50 ml) was added, and the ethereal layer was separated, washed with sodium hydrogen carbonate, and evaporated. The residue, containing the crude 4-acetoxy-derivative, was hydrolysed by refluxing with potassium carbonate (2·0 g) in aqueous methanol (1 : 1; 40 ml) for 2 h to give, after extraction into ether, the crude isochromanol (3·0 g), which was oxidised with Jones reagent (0·015 mol).[22] The isochromanone was isolated by preparative t.l.c. to give an *oil*, $\nu_{max.}$ 1702 cm^{-1}, τ 2·0 (1H, dd, *J* 2 and 7 Hz), 2·4—3·0 (3H, m), 6·62 (1H, q, *J* 6 Hz, 1H), 7·7—8·5 (4H, m), 8·58 (3H, d, *J* 6 Hz), 8·99 (3H, t, *J* 8 Hz), and 9·28 (3H, t, *J* 8 Hz) (Found: C, 77·6; H, 8·4%; M^+, 218·1312. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%; *M*, 218·1307).

r-2-*Hydroxy*-2,c-3-*dimethyl*-t-3-*phenylindan*-1-*one* (IVb).—A solution of racemic dione (Ib) (1·0 g) in methanol (500 ml) under nitrogen was irradiated until no starting material remained. The solvent was then removed *in vacuo*. N.m.r. spectroscopy showed that 85—90% of the product was a mixture of (IVb) and its epimer (IIIb). Preparative t.l.c. gave the *product* (302 mg), m.p. 132—133° (from ether), $\nu_{max.}$ 3440 and 1723 cm^{-1}, τ 2·1—3·3 (9H, m), 6·6br (1H), 8·47 (3H, s), and 9·29 (3H, s) (Found: C, 80·9; H, 6·2. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

r-2-*Hydroxy*-2,t-3-*dimethyl*-c-3-*phenylindan*-1-*one* (IIIb).—From the foregoing photolysis this was obtained as the slower running *isomer* (370 mg), m.p. 118—119° (from ether–pentane), $\nu_{max.}$ 3440 and 1723 cm^{-1}, τ 2·1—3·3 (9H, m), 7·9br (1H), 8·30 (3H, s), and 8·75 (3H, s) (Found: C, 80·7; H, 6·4%).

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1,3-*Dimethyl*-3-*phenylisochroman*-4-*one*.—From irradiation (complete conversion) of the dione (Ib) (1·0 g) in carbon tetrachloride (500 ml) (this solvent gives the highest proposition of isochromanone products) were obtained (after preparative t.l.c.) the isochromanones (Vb) and (VIb). One was an oil (180 mg), $\nu_{max.}$ 1704 cm^{-1}, τ 1·96 (1H, dd, *J* 2 and 8 Hz), 2·3—2·9 (8H, m), 6·05 (1H, q, *J* 7 Hz), 8·12 (3H, s), and 8·64 (3H, d, *J* 7 Hz) (Found: C, 80·9; H, 6·6. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%). The other formed crystals (197 mg) (from methanol), m.p. 104—105°, $\nu_{max.}$ 1700 cm^{-1}, τ 1·9—3·4 (9H, m), 5·40 (1H, q, *J* 7 Hz), 8·04 (3H, s), and 8·56 (3H, d, *J* 7 Hz).

On treatment with sodium methoxide (0·05M) in methanol both isomers gave an equilibrium mixture of which the crystalline epimer constituted 15%. On this basis we suggest that the oil is 1,*c*-3-dimethyl-*r*-1-phenylisochroman-4-one (Vb), whereas the crystalline isomer is 1,*t*-3-dimethyl-*r*-1-phenylisochroman-4-one (VIb).

Oxidation of the Indanones (IIIb) *and* (IVb) *to* 4-*Methyl*-4-*phenylisochroman*-1,3-*dione*.—Solutions of the dione (Ib), $[\alpha]_D$ −128°, were irradiated in the appropriate solvents and the isomers of (IIIb) and (IVb) were separated but not recrystallised. Each of these isomers (400 mg) was taken up in acetic acid (10 ml) and chromium trioxide (1·0 g) in aqueous acetic acid (1 : 1; 10 ml) was added. After 6 h at room temperature sodium hydrogen sulphite solution was added to reduce the excess of oxidant and the solution was extracted with ether. Evaporation of the extract gave a solid which was oxidised with sodium hypobromite as described for (VIIa). The product was purified by sublimation at 10^{-4} mmHg (bath at 90—100°) and was used directly for the rotation measurements.

(+)-4-*Methyl*-4-*phenylisochroman*-1,3-*dione*.— 2-*o*-Carboxyphenyl-2-phenylpropionic acid [23] (12 g) was taken up in a mixture of water (200 ml) and triethylamine (15 ml) and the solution was concentrated at 50° *in vacuo* to remove most of the excess of base. To this was added a solution of quinine hydrochloride (30 g) in water (200 ml), whereupon a sticky crystalline salt separated. This was recrystallised from aqueous methanol to constant rotation and then treated with acid and extracted with ether. The mixture of the diacid and anhydride was sublimed at 90—110° and 10^{-3}—10^{-4} mmHg to give the product,[24] $[\alpha]_D$ 106·6°, m.p. 97·5—98·5°.

Decarboxylation of o-*s*-*Butylbenzoic Acid*.—To a solution of *o*-s-butylbenzoic acid (2·0 g; $[\alpha]_D$ −16·0°) in quinoline (10 ml) was added copper powder (0·5 g), and the mixture was refluxed for 1 h, cooled, filtered, diluted with ether (50 ml), and washed with dilute hydrochloric acid (4 × 50 ml). The residue was distilled to give 2-phenylbutane (0·8 g), b.p. 174—175°, $[\alpha]_D$ 17·7° (*c* 0·3 in C_6H_6).

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