Photochemical and Thermal Reactions of Heterocycles.   Part 2.[1]   Photolysis of 2,3-Diphenylnaphthoquinone 2,3-Epoxide: Trapping of a Cyclic Carbonyl Ylide and Photoisomerisation

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Photolysis of 2.3-diphenylnaphthoquinone epoxide (1) caused epoxy-carbon–carbon bond cleavage to form a cyclic carbonyl ylide (4), which was trapped by dipolarophiles. The norbornadiene primary adduct (3) underwent further photochemical isomerisation. *via* methylenephthalide derivatives (5). to spiro[oxetan-phthalide] derivatives (7). which reverted thermally to methylenephthalides (5). Thermal fragmentation of an oxabicycloheptadiene adduct (18a) gave a formal acetylene adduct (11) and a furan (21). Carbon-13 n.m.r. spectroscopy was useful in establishing the structures of the products. Photolysis of the epoxide (1) in the absence of a dipolarophile gave 3-(α-benzoylbenzylidene)phthalides (24).

THE photochemistry of epoxy-ketones has been investigated in detail, and the various reaction paths have generally been interpreted as involving an initial cleavage of the carbon–oxygen or the epoxy-carbon–carbon bond, or an α-cleavage.[2] We report here the photochemical behaviour of 2,3-diphenylnaphthoquinone 2,3-epoxide (1) in which an epoxy-ketone partial structure is incorporated. It was initially thought that if the photolysis causes the epoxy-carbon–carbon bond to rupture, then the resultant ylide (4) may be stabilised sufficiently to be isolated or observed by delocalisation of a sextet of electrons balanced by polarised carbonyl groups. As will be described below, the cyclic carbonyl ylide (4) actually had only a fleeting existence. The photochemical reactions of quinone epoxides were not known when we initiated this study. During the course of this investigation,[3] Maruyama *et al.*[4] and Jiménz *et al.*[5] independently studied the photochemical reactions of naphthoquinone epoxides.

Irradiation of naphthoquinone 2,3-epoxide in several solvents both in the presence and absence of dipolarophiles failed to give well-defined products. However, when 2,3-diphenylnaphthoquinone 2,3-epoxide (1)[6] was irradiated in the presence of norbornadiene, a 1 : 1 adduct was isolated. In our preliminary communication,[3] we erroneously assigned structure (3) for the adduct, but later work showed that the reaction is not so simple, and the reaction with a shorter irradiation time afforded as many as five 1 : 1 adducts, which were assigned as the primary adduct (3), methylenephthalide derivatives (5a) and (5b), and spiro[oxetan-phthalide] derivatives (7a) and (7b) based on the spectral properties to be described below. The spiro[oxetan-phthalides] (7a) and (7b) rearranged thermally in refluxing xylene to methylenephthalides (5a) and (5b) respectively, and irradiation of the methylenephthalides (5a) gave the spiro[oxetan-phthalide] (7a) in moderate yield. Monitoring of the photochemical reaction by both t.l.c. and h.p.l.c. (Table) showed that (3) is the primary photoadduct, which later rearranged to the spiro[oxetan-phthalides] (7) *via* the methylenephthalides (5).

The primary photoadduct (3) had a carbonyl absorption at 1 685 cm⁻¹, and its symmetrical structure was supported by both ¹H and ¹³C n.m.r. spectra: the latter

[1] Part 1, H. Kato, T. Shiba, E. Kitajima, T. Kiyosawa, F. Yamada, and T. Nishiyama, *J.C.S. Perkin I*, 1976, 863.

[2] A. Padwa, ' Organic Photochemistry,' ed. O. L. Chapman, Marcel Dekker, Inc., New York, 1967, vol. 1, p. 91; N. R. Bertoniere and G. W. Griffin, *ibid.*, 1973, vol. 3, p. 115.

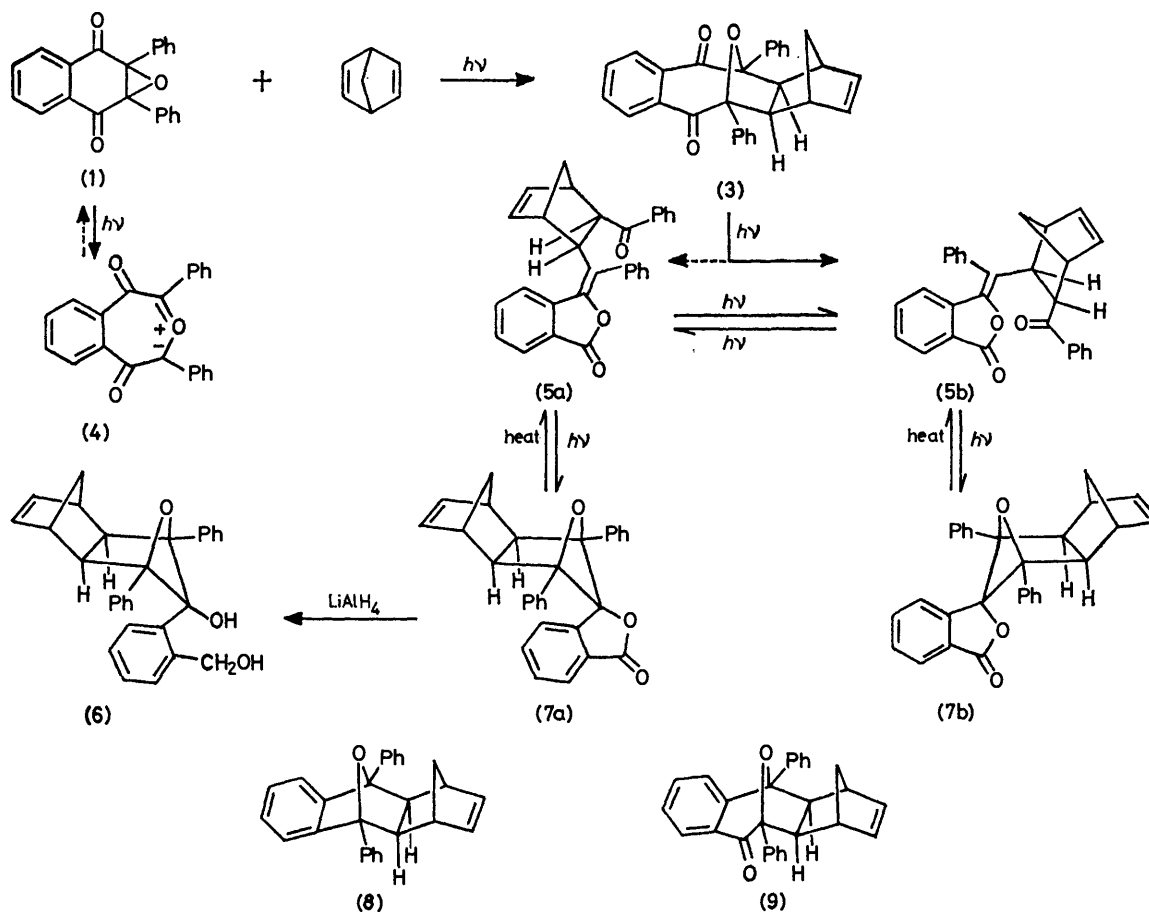[3] Preliminary report: H. Kato, K. Yamaguchi, and H. Tezuka, *Chemistry Letters*, 1974, 1089.

[4] (a) K. Maruyama and S. Arakawa, *Chemistry Letters*, 1974, 719; (b) K. Maruyama, S. Arakawa, and T. Oysuki, *Tetrahedron Letters*, 1975, 2433; (c) K. Maruyama and S. Arakawa, *Abstr. Meeting of the Society of Synthetic Organic Chemistry, Japan,* Tokyo, 1976, p. 33.

[5] M. Jiménz, L. Rodrriguez-Hahn, and J. Romo, *Rev. Latino-amer. Quim.*, 1974, **5**, 184

[6] F. M. Beringer and S. A. Galton, *J. Org. Chem.*, 1963, **28**, 3250.

showed a carbonyl carbon and an ether carbon singlet at δ 209.88 and 92.93 respectively, and the entire spectrum consisted of thirteen peaks in accord with the theoretical number expected for this symmetrical structure. The *exo,exo*-configuration was deduced from its ¹H n.m.r. spectrum, which showed no coupling

The spiro[oxetan-phthalide] (7a) which we originally isolated and erroneously assigned structure (3) in our preliminary communication,[3] had an n.m.r. spectrum indicating the existence of a plane of symmetry along the norbornene moiety. However, the i.r. carbonyl band of this adduct appeared at 1 760 cm⁻¹ which is too

Scheme 1

between the methine and the bridgehead protons and indicated that one methylene bridge proton is shielded by the bridge oxygen atom.

The i.r. and n.m.r. spectra of the methylenephthalide derivatives (5a) and (5b) were similar to each other, the former showing a benzoyl and a lactone carbonyl band. The isomer having a high-field n.m.r. signal (δ 5.74) of a benzenoid proton was assigned the *E*-configuration (5b) because the hydrogen atom at the 4-position of the phthalide group can enter into the shielding zone of the *cis*-phenyl group (see later). The ¹³C n.m.r. spectrum of the *E*-isomer supported its structure by two carbonyl singlets at δ 202.87 and 165.81, and reflecting the unsymmetrical structure of (5b), all the theoretically possible twenty-five unequivalent carbon signals could be observed.

high for a carbonyl group of this type, and fits more appropriately to a lactone carbonyl group. The adducts of triphenylpyrylium 3-oxide[7] and diphenylbenzopyrylium 3-oxide[8,9] with olefins show an absorption at 1 690—1 710 and 1 698—1 714 cm⁻¹ respectively. These spectral data, as well as its thermal cleavage and photochemical formation described above, suggest that the structure of the adduct should be revised to the spiro-[oxetan-phthalide] (7). Further support for structure (7) came from its ¹³C n.m.r. spectrum, which showed singlets at δ 167.92, 103.28, and 95.22 assignable to the lactone carbonyl, the spiro carbon, and the oxetan α-carbon atoms respectively. Of the seventeen theoretically possible resonance peaks for (7), sixteen could be

⁷ K. T. Potts, A. J. Elliott, and M. Sorm, *J. Org. Chem.*, 1972, **37**, 3838.

⁸ E. F. Ullmann and J. E. Milks, *J. Amer. Chem. Soc.*, 1964, **86**, 3814.

⁹ J. W. Lown and K. Matsumoto, *Canad. J. Chem.*, 1971, **49**, 3443.

discerned, one sp^2 doublet peak apparently overlapping with another. Chemical support for structure (7) was provided by lithium aluminium hydride reduction of (7) which gave the corresponding diol (6) by reductive cleavage of the lactone ring. The i.r. and n.m.r. spectra of the isomer (7b) were similar to those of (7a), and accordingly, they are configurational isomers. The lack of coupling between the methine and the bridgehead protons shows that the oxetan ring is *exo* to the norbornene unit. The appearance of the n.m.r. signal of one methylene bridge proton at a strongly deshielded region (δ *ca.* 3.1) shows that the methylene bridge is very close to the oxetan oxygen atom. These considerations left two structures (7a) and (7b) out of the eight theoretically possible configurations. Configuration (7a) in which the norbornene unit is *syn* to the phthalide benzene ring was assigned to the isomer which gave the (*Z*)-methylenephthalide (5a) on thermolysis. Another support for this configurational assignment was provided by n.m.r. spectra, which showed that the norbornene protons of the *syn*-isomer (7a) are slightly more deshielded by the benzene ring than those of the *anti*-isomer (7b).

Stereo-models of the adducts (3) and (7) and related compounds (8)[10] and (9)[8] show that the distance between the bridge oxygen atom and the bridge methylene group decreases in the order (3) ⟶ (9) ⟶ (8) ⟶ (7), and this is reflected in the n.m.r. δ values of the methylene bridge protons: the deshielding effect of the oxygen atom on the *syn*-proton increases (1.33 ⟶ 1.74 ⟶ 2.68 ⟶ 3.10 and 3.05) while the shielding effect on the *anti*-proton decreases (0.69 ⟶ 0.75 ⟶ 0.92 ⟶ 1.12 and 1.15) as the ring size decreases.
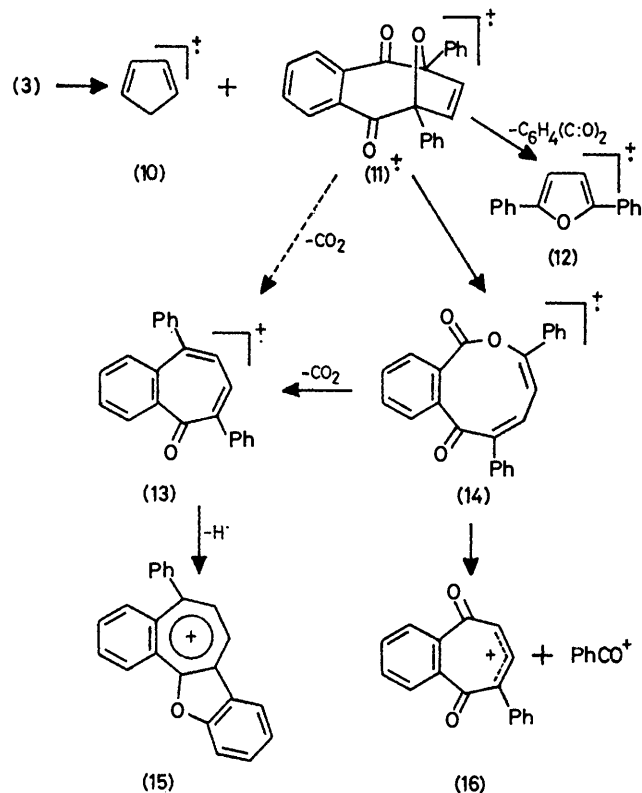
The results presented above show that the carbon–carbon bond of the epoxide (1) is photochemically cleaved to give a cyclic carbonyl ylide intermediate (4). This is trapped by norbornadiene to give the primary cycloadduct (3). Further irradiation of the adduct (3) causes its α-cleavage and recyclisation to the methylenephthalides (5), which finally undergo an intramolecular photo-cycloaddition to afford the spiro[oxetan-phthalides] (7).

After our preliminary report,[3] Maruyama and his co-workers[4b] also reported the isolation of adducts corresponding to (3) from 2,3-dimethylnaphthoquinone epoxide. Their correct structures are probably those corresponding to spiro[oxetan-phthalide] (7) since these adducts show a high-frequency i.r. carbonyl band (1 760—1 770 cm^{-1}). Further, the same authors more recently reported[4c] the photochemical addition and rearrangement reactions of the same type as described above with a closely related system, the adduct corresponding to (3) from 2,3-dimethylnaphthoquinone epoxide and dimethyl fumarate being reported as showing i.r. absorptions at 1 695 and 1 685 cm^{-1}.

The high-resolution mass spectrum of the primary adduct (3) (see Experimental section for assignments of pertinent fragment ions) showed only a weak molecular ion peak, and suggests a double retro-Diels–Alder fragmentation to cyclopentadiene (10) and to a formal adduct of the epoxide with acetylene (11), and thence to diphenylfuran (12). An intense peak at m/e 308 and the base peak at m/e 307 suggest the extrusion of carbon dioxide from (11) or its rearrangement product (14) to give a benzotropone (13) and then the tropylium ion

SCHEME 2

(15). Similar thermal[7,11] and photochemical[12] rearrangements of hetero-bridged bicyclic rings, and extrusion of carbon dioxide from such rearrangement products[7] are known. Attempts at thermally or photochemically reproducing the mass fragmentation pattern failed however: thus the adduct (3) upon photolysis gave the rearrangement products (5) and (7), whilst it was recovered unchanged when heated under reflux in xylene for 31 h. Attempted photochemical formation of a derivative of the acetylene adduct (11) directly from the epoxide (1) and dimethyl acetylenedicarboxylate resulted in the isolation of several 1 : 1 adducts, none of which showed n.m.r. signals attributable to equivalent methoxycarbonyl groups.[13]
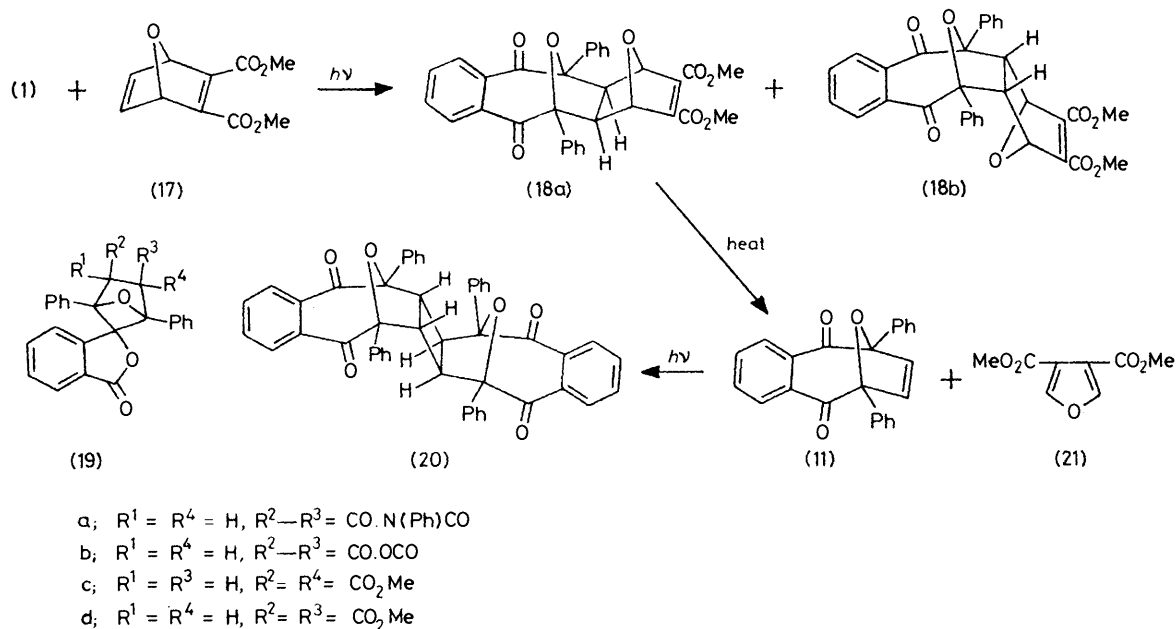
In search of a better leaving group, photocycloaddition of the epoxide (1) with dimethyl 7-oxabicyclo-

[10] M. P. Cava and F. M. Scheel, *J. Org. Chem.*, 1967, **32**, 1304.
[11] N. Dennis, A. R. Katritzky, E. Lunt, M. Ramaiah, R. L. Harlow, and S. H. Simonsen, *Tetrahedron Letters*, 1976, 1569; N. Dennis, A. R. Katritzky, and M. Ramaiah, *J.C.S. Perkin I*, 1976, 2281.

[12] A. Padwa and E. Vega, *J. Org. Chem.*, 1975, **40**, 175.
[13] H. Kato, H. Tezuka, K. Nowada, and Y. Nakamura, unpublished results.

[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (17) was performed, and this reaction gave two 1 : 1 adducts. Both had similar i.r. and n.m.r. spectra, the former showing the presence of an ester carbonyl and an oxo carbonyl group, and the latter having singlet signals for the methine and the bridgehead protons. These spectral data, as well as their mass spectra which showed a

maximum value of ten. Its mass spectrum was quite similar below m/e 352 to that of the norbornadiene adduct (3). However, attempts at effecting thermal rearrangement and decarboxylation of (11) to the benzotropone derivative (13) gave polymeric material, and irradiation of (11) resulted in the formation of a dimer, to which an unsymmetrical $[2_\pi + 2_\pi]$ adduct

a; $R^1 = R^4 = H$, $R^2-R^3 = CO.N(Ph)CO$
b; $R^1 = R^4 = H$, $R^2-R^3 = CO.OCO$
c; $R^1 = R^3 = H$, $R^2 = R^4 = CO_2Me$
d; $R^1 = R^4 = H$, $R^2 = R^3 = CO_2Me$

Scheme 3

similar fragmentation pattern to that of the norbornadiene adduct (3), indicated that the naphthoquinone moiety is incorporated in an *exo* fashion to the unsubstituted double bond of the oxanorbornadiene (17) to give adducts (18a) and (18b). The isomer with the bridgehead protons resonating in a lower magnetic field was assigned the *endo,exo*-configuration (18b) on the basis that the bridgehead protons of this configuration are more strongly deshielded by the carbonyl group than those of the *exo,exo*-isomer (18a). The [13]C n.m.r. spectrum of the *endo,exo*-isomer (18b) showed singlet signals of the ketone and the ester carbonyl carbon atoms at δ 204.78 and 162.03, a singlet and a doublet of the two types of bridgehead carbon atoms at δ 91.11 and 82.02, and a doublet signal of the methine carbon atom at δ 60.18. The entire spectrum consisted of fourteen peaks in accord with structure (18b).

Although attempted thermolysis of the *endo,exo*-isomer (18b) resulted in either recovery of (18b) or excessive decomposition, heating of the *exo,exo*-isomer (18a) in xylene afforded the expected fragmentation product (11) and furandicarboxylate (21). The i.r. ($\nu_{C=O}$ 1 683 cm^{-1}) and the [1]H n.m.r. spectra of the formal acetylene adduct (11) were consistent with the proposed structure, and the [13]C n.m.r. spectrum showed two singlets at δ 203.37 (C=O) and 98.34 (C-O-C), and consisted of nine peaks in contrast to the theoretical

structure (20) was assigned on the basis of the appearance of the methine proton n.m.r. signal as an AB pattern.
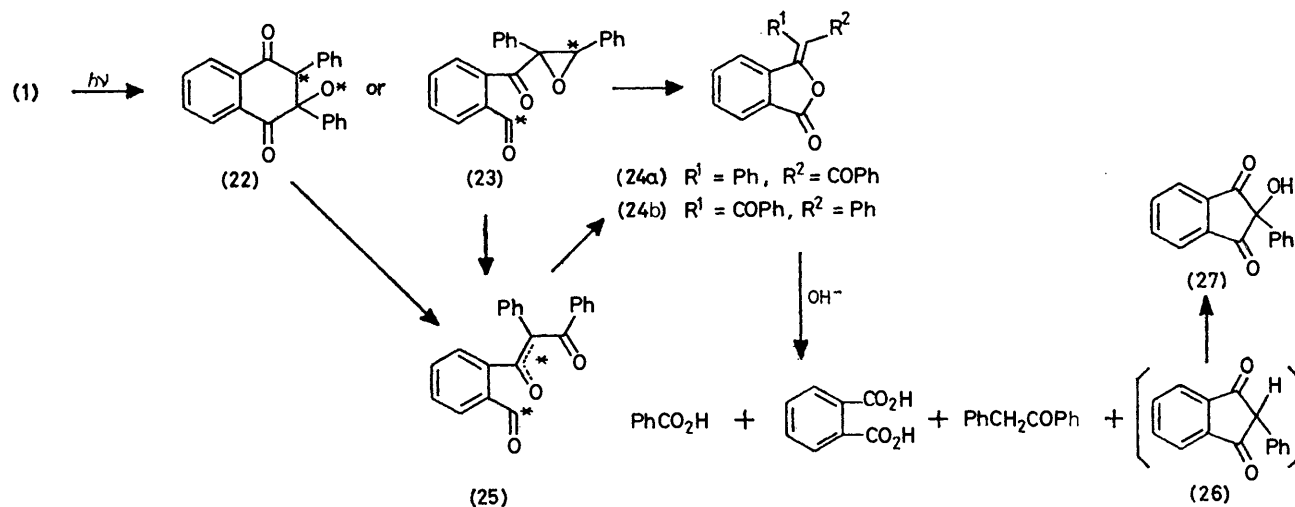
Irradiation of the epoxide (1) in the presence of N-phenylmaleimide, maleic anhydride, and dimethyl fumarate under arbitrarily chosen conditions gave, in every case, the spiro[oxetan-phthalide] (19a—c) with an unestablished configuration, while dimethyl maleate failed to give the expected adduct (19d).* The maleate adduct (19d) could be obtained indirectly by treatment of the maleic anhydride adduct (19b) with diazomethane.

Although the intermediate ylide (4) was not trapped by acetonitrile, both in this solvent and in benzene in the absence of a dipolarophile, isomers of the epoxide (1) were slowly formed; these were assigned as (Z)- and (E)-3-(α-benzoylbenzylidene)phthalide (24a) and (24b). Isomers (24a) and (24b) both had i.r. carbonyl bands at 1 780 and 1 660 cm^{-1} and similar n.m.r. signals except that the major product had a signal for an aromatic proton in a highly shielded region (δ 6.98—6.85). Equilibrium between the two isomers occurred photochemically and thermally. Alkaline hydrolysis of one isomer gave benzoic acid, phthalic acid, deoxybenzoin,

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and a component having identical R_F values on t.l.c. with authentic 2-phenylindane-1,3-dione (26); the latter was isolated as 2-hydroxy-2-phenylindane-1,3-dione (27) after t.l.c. separation on silica. A separate experiment showed that 2-phenylindanedione (26) was converted into 2-hydroxy-2-phenylindanedione (27) during preparative t.l.c. treatment. The structures of the isomers (24a) and (24b) were conclusively established by their syntheses from a base-catalysed condensation of deoxy-

Similar dual photocleavage reactions have been observed with an indenone epoxide [14] and cyclopentadienone epoxide.[15] Unlike the structurally related diphenylindenone epoxide and similar systems,[8,9,12,16] the epoxide (1) did not undergo thermal (disallowed) valence isomerisation to the ylide (4). It appears that the photochemical behaviour of naphthoquinone epoxides depends considerably on the substituents, and photoaddition to a carbonyl group, photo-dimerisation,

SCHEME 4

benzoin with phthaloyl chloride. The major isomer showing the high-field n.m.r. signal was assigned the Z-configuration on the basis that the hydrogen atom at the 4-position can enter into the shielding zone of the cis-phenyl substituent. This interpretation was supported by comparison of the n.m.r. spectra of 3-(diphenylmethylene)phthalide (24; $R^1 = R^2 = $ Ph) and 3-(dibenzoylmethylene)phthalide (24; $R^1 = R^2 = $ Bz): the former showed an n.m.r. multiplet corresponding to one proton at δ 6.15—6.30 whereas the latter had no signal below δ 7.20. Maruyama et al.[4a] reported the photoisomerisation of 2-acyl-3-methylnaphthoquinone 2,3-epoxide to seven-membered lactones. This result which conflicts with ours was recently rectified when these workers reassigned 3-(diacylmethylene)phthalide structures to their products.

The results presented above show that two competing photochemical paths of the epoxide (1) exist. One is cleavage of the epoxy-carbon–carbon bond to form the carbonyl ylide (4). The intermediate (4) is trapped by dipolarophiles to give the adducts corresponding to (3), and reverts to the epoxide (1) in the absence of a dipolarophile. The other slower route may be either the carbon–oxygen bond cleavage or α-cleavage to give intermediate (22) or (23), which recyclises probably via (25) at the carbonyl oxygen atom to give the phthalides (24).

-reduction, and -fragmentation of lower alkyl-substituted naphthoquinone epoxides are reported.[4b,c,5]

EXPERIMENTAL

M.p.s were determined with a Yanagimoto hot-stage apparatus. U.v. spectra were recorded with a Hitachi EPS-3T, and i.r. (KBr) spectra with Hitachi EPI-SII and 345 spectrophotometers. Proton and proton-decoupled and off-resonance [13]C n.m.r. spectra were obtained on JEOL JNM-4H-100 (100 MHz) and JNM-FX-100 (25 MHz) spectrometers respectively for solutions in deuteriochloroform (tetramethylsilane internal standard). Spin-coupling constants of < 1.5 Hz are not recorded here. Mass spectra were measured with Hitachi RMU-6 (low resolution) and JEOL JMS-O1SG-2 (high resolution) spectrometers (direct inlet technique), and metastable transitions were determined by scanning the acceleration voltage. H.p.l.c. and g.l.p.c. were run with a Shimadzu–DuPont model 830 and a Shimadzu GC-4BPF model, and t.l.c. separation was performed on Merck Kieselgel 60 PF_{254}. Photolysis was conducted on a deaerated solution under nitrogen with either a 100 or a 400 W immersion type high-pressure mercury lamp through a Pyrex filter below 25 °C. Compounds stated to be identical were so with respect to m.p., mixed m.p., and i.r. and n.m.r. determinations.

Photocycloaddition of 2,3-Diphenylnaphthoquinone 2,3-Epoxide (1) with Norbornadiene.—A solution of the epoxide (1) [$\lambda_{max.}$(EtOH) 235 (log ε 4.57) and 360 nm (3.38)] and a 50 molar excess of norbornadiene in benzene was irradiated,

[14] H. E. Zimmerman and R. D. Simkin, *Tetrahedron Letters*, 1964, 1847.

[15] J. M. Dunston and P. Yates, *Tetrahedron Letters*, 1964, 505.

[16] J. W. Lown and K. Matsumoto, *J. Org. Chem.*, 1971, **36**, 1405.

and the products were separated by t.l.c. (benzene). The products described below were isolated, and some examples are listed in the Table.

exo,exo-3,12-*Diphenyl*-18-*oxapentacyclo*[12.2.1.1.^{3,12}-0.^{2,13}0^{5,10}]*octadeca*-5,7,9,15-*tetraene*-4,11-*dione* (3). Prisms (from cyclohexane), m.p. 157 °C (Found: C, 83.25; H, 5.3. $C_{29}H_{22}O_3$ requires C, 83.25; H, 5.3%), ν_{max} 1 685 cm^{-1}; δ 8.00—7.85 (4 H, m, ArH), 7.60—7.20 (10 H, m, ArH), 6.22 (2 H, s, =CH), 3.18 (2 H, s, methine CH), 2.68 (2 H, s, bridgehead CH), and 1.33 and 0.69 (each 1 H, d, J 9 Hz, CH$_2$), 209.88 (s, C=O), 136.63 and 136.45 (each s, =C), 139.63, 132.17, 127.88, 127.65, 127.17, and 126.97 (each d, =CH), 92.93 (s, C-O), 55.78 and 44.32 (each d, CH), and 41.55

=CH), 3.10 (2 H, s, methine CH), 2.70 (2 H, s, bridgehead CH), and 3.05 and 1.15 (each in 1 H, d, J 9 Hz, CH$_2$); mass spectrum similar to that of (3).

9-*Hydroxy*-9-(*hydroxymethylphenyl*)-1,8-*diphenyl*-10-*oxa-tetracyclo*[6.1.1.1.^{3,6}0^{2,7}]*undec*-4-*ene* (6).—Lithium aluminium hydride (30 mg) was added to a solution of the spiro-[oxetan-phthalide] (7a) (200 mg) in ether (25 ml) and the mixture was stirred at room temperature for 2 h. Usual work-up and recrystallisation from benzene–hexane gave prisms (21%), m.p. 190—191 °C (Found: C, 82.65; H, 6.25. $C_{29}H_{26}O_3$ requires C, 82.45; H, 6.2%), ν_{max} 3 580 and 3 370 cm^{-1}; δ 7.90—7.14 (16 H, m, ArH and OH), 6.21 (2 H, s, =CH), 3.91 (2 H, s, O-CH$_2$), 2.98 (2 H, s, bridgehead

Photoreaction of the epoxide (1) with norbornadiene

(1) (g)/lamp (W)	1.6/400	0.23/100	0.23/100					
Time (min)	35	240	10	20	30	60	120	240
Product	Isolated yield (%)		H.p.l.c. peak area ratio ^{a}					
(1)	b		30	3				
(3)	44		60	53	39	9	2	
(5a)	13	b	4	8	14	17	17	17
(5b)	10	b	6	32	37	30	17	18
(7a)	b	24	1	2	11	27	32	
(7b)	b	25	3	8	33	37	33	

^{a} Permaphase ODS/MeOH–H$_2$O [4 : 6 (v/v) ⟶ 6 : 4 (v/v)] 2.1 mm × 1 m; not corrected for the difference in the extinction coefficients. ^{b} Detected by t.l.c. but not isolated.

(t, CH$_2$); m/e 418.1570 (1%, M^+), 352.1085 [32, (11)$^{+\cdot}$], 308.1188 [32, (13)], 307.1133 [100, (15)], 247.0754 [13, (16)], 220.0895 [8, (12)], 105.0368 (63, PhCO$^+$), 104.0259 (15, C$_6$H$_4$CO$^+$), 77.0419 (35, Ph$^+$), 76.0326 (7, C$_6$H$_4^+$), 66.0487 [14, (10)], and 65.0418 (9, C$_5$H$_5^+$), metastable transitions: 418 ⟶ 352 and 352 ⟶ 308.

3-[α-(6-exo-*Benzoylnorbornen*-5-*yl*)-exo-*benzylidene*]-*phthalide*. (a) The Z-isomer (5a): prisms (from benzene–hexane), m.p. 195—196 °C (Found: C, 82.8; H, 5.45%), ν_{max} 1 765 and 1 668 cm^{-1}; δ 7.83—6.85 (14 H, m, ArH), 6.33 (2 H, s, =CH), 3.93 and 3.70 (each 1 H, AB d, J 6 Hz, methine CH), 3.02 (2 H, s, bridgehead CH), and 1.69 and 1.23 (each 1 H, d, J 9 Hz, CH$_2$); mass spectrum similar to that of (3). (b) The E-isomer (5b): prisms (from benzene–hexane), m.p. 141.5—143 °C (Found: C, 83.2; H, 5.25%), ν_{max} 1 772 and 1 670 cm^{-1}; δ 8.10—6.95 (13 H, m, ArH), 6.30 (2 H, s, =CH), 5.74 (1 H, m, ArH), 3.99 and 3.70 (each 1 H, AB d, J 9 Hz, methine CH), 2.99 and 2.85 (each 1 H, s, bridgehead CH), and 1.76 and 1.21 (each 1 H, d, J 9 Hz, CH$_2$), 202.87 and 165.81 (each s, C=O), 143.40, 138.32, 138.17, 135.26, 126.23, and 124.57 (each s, =C), 139.03, 138.51, 133.66, 132.45, 130.20, 130.11, 128.74, 128.63, 128.28, 128.14, 124.71, and 122.80 (each d, =CH), 51.21 (d, CH), and 45.67, 45.32, 45.18, and 44.52 (superimposed d and t, CH and CH$_2$); mass spectrum similar to that of (3).

1,8-*Diphenylspiro*[10-*oxatetracyclo*[6.1.1.1.^{3,6}0^{2,7}]*undec*-4-*ene*-9,3'-*phthalide*]. (a) The syn-isomer (7a): prisms (from ethanol), m.p. 157 °C (Found: C, 83.0; H, 5.4%), ν_{max} 1 760 cm^{-1}; δ 8.00—7.20 (14 H, m, ArH), 6.46 (2 H, s, =CH), 3.22 (2 H, s, methine CH), 2.99 (2 H, s, bridgehead CH), and 3.10 and 1.12 (each 1 H, d, J 9 Hz, CH$_2$); 167.92 (s, C=O), 139.97, 133.11, and 130.25 (each s, =C), 140.72, 134.03, 128.37, 128.14, 126.31, 125.74, and 124.03 (each d, =CH), 103.28 and 95.22 (each s, C-O), 50.75 and 42.98 (each d, CH), and 43.89 (t, CH$_2$); mass spectrum similar to that of (3). (b) The anti-isomer (7b): prisms (from ethanol), m.p. 158—159 °C (Found: C, 82.95; H, 5.25%), ν_{max} 1 770 cm^{-1}; δ 7.80—6.80 (14 H, m, ArH), 6.24 (2 H, s,

CH), 2.82 (2 H, s, methine CH), and 2.79 and 0.93 (each 1 H, d, J 9 Hz, CH$_2$); m/e 404 (3%, $M^{+\cdot}$ − H$_2$O) and 105 (100).

Thermal Rearrangement of the Spiro[oxetan-phthalide] (7). —A solution of the syn-spiro[oxetan-phthalide] (7a) (100 mg) in xylene (5 ml) was refluxed for 3 h, and the product was recrystallised from benzene–hexane to give the (Z)-methylenephthalide (5a) (60%), identical with an authentic specimen. Similar pyrolysis (xylene; 3 h) of the anti-isomer (7b) gave the E-isomer (5b) as judged by t.l.c. and h.p.l.c.

Photocyclisation of the (Z)-*Methylenephthalide* (5a).—A solution of the (Z)-methylenephthalide (5a) (40 mg) in benzene (400 ml) was irradiated with a 400 W lamp for 13.5 h. The solution was concentrated and the residue purified by preparative t.l.c. to give the syn-spiro[oxetan-phthalide] (7a) (17%), identical with an authentic specimen.

Photocycloaddition of the Epoxide (1) *with Dipolarophiles.* —*With dimethyl* 7-*oxabicyclo*[2.2.1]*heptadiene*-2,3-*dicarboxylate* (17). A solution of the epoxide (1) (1.66 g) and the oxanorbornadiene (17) (1.89 g) in benzene (200 ml) was irradiated with a 100 W lamp for 2 h 40 min. The mixture was concentrated and a small amount of methanol added to it; the component which separated rapidly was collected and recrystallised from benzene–hexane to give prisms of dimethyl endo,exo-4,11-*dioxo*-3,12-*diphenyl*-17,18-*dioxapentacyclo*[12.2.1.1.^{3,12}0.^{2,13}0^{5,10}]*octadeca*-5,7,9,15-*tetraene*-15,16-*dicarboxylate* (18b) (37%), m.p. 230 °C (Found: C, 71.8; H, 4.4. $C_{32}H_{24}O_8$ requires C, 71.65; H, 4.5%), ν_{max} 1 757, 1 700, and 1 642 cm^{-1}; δ 7.76—7.27 (14 H, m, ArH), 5.78 (2 H, s, bridgehead CH), 3.88 (6 H, s, Me), and 3.52 (2 H, s, methine CH); 204.78 and 162.03 (each s, C=O), 144.43, 140.95, and 135.97 (each s, =C), 132.77, 128.65, 128.26, 127.97, and 125.91 (each d, =CH), 91.11 (s, C-O), 82.02 (d, O-CH), 60.18 (d, CH), and 52.53 (q, Me); m/e 505 (1%, $M^{+\cdot}$ − OMe), 352 [28, (11)$^{+\cdot}$], 308 [36, (13)], 307 [100, (15)], 247 [14, (16)], 220 [18, (12)], 153 [22, (21)$^{+\cdot}$ − OMe], 105 (72, PhCO$^+$), 104 (30,

$C_6H_4CO^{+\cdot}$), 77 (76, Ph$^+$), and 76 (24, $C_6H_4^{+\cdot}$). More methanol was added to the mother liquor, and the precipitate which slowly separated out was recrystallised from benzene–cyclohexane to give needles of dimethyl exo,exo-4,11-dioxo-3,12-diphenyl-17,18-dioxapentacyclo[12.2.1.1.^{3,12}-0.^{2,13}0^{5,10}]octadeca-5,7,9,15-tetraene-15,16-dicarboxylate (18a) (18%), m.p. 199—200 °C (Found: C, 71.65; H, 4.4%), $v_{max.}$ 1 740, 1 708, and 1 640 cm^{-1}; δ 7.93—7.80 (4 H, m, ArH), 7.60—7.26 (10 H, m, ArH), 4.87 (2 H, s, bridgehead CH), 3.84 (6 H, s, Me), and 3.51 (2 H, s, methine CH); m/e 505 (<1%, $M^{+\cdot}$ − OMe), 352 [16%, (11)$^{+\cdot}$], 308 [30, (13)], 307 [88, (15)], 247 [14, (16)], 220 [28, (12)], 184 [22, (21)$^{+\cdot}$], 153 [100, (21)$^{+\cdot}$ − OMe], 123 [53, (21)$^{+\cdot}$ − OMe − CH$_2$O], 115 (17, PhC$_3$H$_2^+$), 105 (52, PhCO$^+$), 104 (32, $C_6H_4CO^{+\cdot}$), 77 (30, Ph$^+$), and 76 (15, $C_6H_4^{+\cdot}$). The following cycloadducts were isolated by similar methods. 4-Phenylspiro[4-aza-9-oxatricyclo[5.1.1.0^{2,6}]nonane-8,3'-phthalide]-3,5-dione (19a) [72% from 200 mg of (1) by 5 h irradiation with N-phenylmaleimide], leaflets (from butanol), m.p. 238 °C (Found: C, 77.15; H, 4.3; N, 2.75. $C_{32}H_{21}NO_5$ requires C, 76.95; H, 4.25; N, 2.8%), $v_{max.}$ 1 780 and 1 720 cm^{-1}, δ 7.90—7.10 (19 H, m, ArH) and 4.38 (2 H, s, CH). Spiro[4,9-dioxatricyclo[5.1.1.0^{2,6}]nonane-8,3'-phthalide]-3,5-dione (19b) [27% from 1 g of (1) by 5 h irradiation with maleic anhydride], prisms (from benzene–cyclohexane), m.p. 247—249 °C (Found: C, 73.25; H, 3.55. $C_{26}H_{16}O_6$ requires C, 73.6; H, 3.8%), $v_{max.}$ 1 870 and 1 795 cm^{-1}; δ 7.73—7.10 (14 H, m, ArH) and 4.45 (2 H, s, CH); m/e 424 (14%, $M^{+\cdot}$), 352 [11, (11)$^{+\cdot}$], 308 [14, (13)], 307 [41, (15)], 275 [60, (11)$^{+\cdot}$ − Ph], 247 [12, (16)], 220 [11, (12)], 105 (100, PhCO$^+$), 104 (15, $C_6H_4CO^{+\cdot}$), 77 (43, Ph$^+$), and 76 (12, $C_6H_4^{+\cdot}$). Dimethyl spiro[6-oxabicyclo[2.1.1]hexane-5,3'-phthalide]-2,3-trans-dicarboxylate (19c) [79% from 1 g of (1) by 8 h irradiation with dimethyl fumarate], prisms (from methanol), m.p. 174.5—175.5 °C (Found: C, 71.45; H, 4.5. $C_{28}H_{22}O_7$ requires C, 71.5; H, 4.7%), $v_{max.}$ 1 786 and 1 745 cm^{-1}; δ 7.82—7.70 (1 H, m, ArH), 7.43—6.97 (13 H, m, ArH), 4.46 and 4.19 (each 1 H, d, J 5 Hz, CH), and 3.68 and 3.42 (each 3 H, s, Me); m/e 470 (<1%, $M^{+\cdot}$), 438 (31, $M^{+\cdot}$ − MeOH), and 105 (100, PhCO$^+$).

Dimethyl Spiro[6-oxabicyclo[2.2.1]hexane-5,3'-phthalide]-2,3-cis-dicarboxylate (19d).—An excess of ethereal diazomethane was added to a suspension of the maleic anhydride adduct (19b) (0.21 g) in methanol (10 ml). The solution was concentrated and the residue was recrystallised from methanol to give prisms (22%), m.p. 226.5—228 °C (Found: C, 71.35; H, 4.55. $C_{28}H_{22}O_7$ requires C, 71.5; H, 4.7%), $v_{max.}$ 1 780 and 1 745 cm^{-1}; δ 7.73—7.50 (2 H, m, ArH), 7.40—7.02 (12 H, m, ArH), 4.45 (2 H, s, CH), and 3.47 (6 H, s, Me); m/e 438 (19%, $M^{+\cdot}$ − MeOH) and 105 (100, PhCO$^+$).

1,10-Diphenyl-13-oxatricyclo[8.2.1.0^{3,8}]tridec-11-ene-2,9-dione (11).—A solution of the exo,exo-oxanorbornadiene adduct (20a) (1.36 g) in xylene (30 ml) was heated under reflux for 20 h. The solution was concentrated and the residue was recrystallised from benzene to give prisms (86%), m.p. 200—201 °C (Found: C, 81.95; H, 4.35. $C_{24}H_{16}O_3$ requires C, 81.8; H, 4.6%), $v_{max.}$ 1 683 and 1 580 cm^{-1}; δ 7.92—7.25 (14 H, m, ArH) and 6.51 (2 H, s, =CH); 203.37 (s, C=O), 138.09 and 133.33 (each s, =C), 133.16, 132.04, 129.92, 128.28, and 126.35 (each d, =CH), and

98.34 (s, C–O); m/e 352 (5%, $M^{+\cdot}$), 308 [34, (13)], 307 [100, (15)], 247 [11, (16)], 220 [33, (12)], 115 (23, PhC$_3$H$_2^+$), 105 (63, PhCO$^+$), 104 (48, $C_6H_4CO^{+\cdot}$), 77 (47, Ph$^+$), and 76 (27, $C_6H_4^{+\cdot}$). The mother liquor of recrystallisation was concentrated and the residue extracted with methanol and concentrated to give a pale yellow oily material which slowly deposited slightly impure dimethyl furan-3,4-dicarboxylate (21) (43%, m.p. 43—45 °C). Recrystallisation from ether afforded prisms, m.p. 46.5—47 °C (lit.,[17] 47.5 °C), identical with an authentic specimen.[18]

Photodimerisation of the 'Acetylene Adduct' (11).—A solution of the 'acetylene adduct' (11) (0.2 g) in benzene was irradiated with a 100 W lamp for 1 h 45 min. The solution was chromatographed on silica (dichloromethane) and recrystallised from propan-1-ol to give needles of the dimer (20) (32%), m.p. 239—240.5 °C (Found: C, 81.75; H, 4.45. $C_{48}H_{32}O_6$ requires C, 81.8; H, 4.6%), $v_{max.}$ 1 682 cm^{-1}; δ 8.42—7.30 (28 H, m, ArH), and 4.14 and 3.95 (each 2 H, AB d, J 4.6 Hz, CH); m/e 352 [14%, (11)$^{+\cdot}$] and 307 [100, (15)].

3-(α-Benzoylbenzylidene)phthalides (24).—(a) A solution of the epoxide (1) (1.93 g) in benzene (500 ml) was irradiated with a 400 W lamp for 23 h. The solution was concentrated and the products separated by t.l.c. (benzene) to give the Z-isomer (24a) (23%) as prisms (from benzene–hexane), m.p. 145.5—146 °C * (Found: C, 80.85; H, 4.2. $C_{22}H_{14}O_3$ requires C, 81.0; H, 4.3%), $v_{max.}$ 1 780 and 1 660 cm^{-1}; δ 8.10—7.75 (3 H, m), 7.70—7.20 (10 H, m), and 6.98—6.85 (1 H, m); m/e 326 (4%, $M^{+\cdot}$) and 105 (100, PhCO$^+$); and the E-isomer (24b) (11%) as prisms (from benzene–hexane), m.p. 160—161 °C (Found: C, 81.2; H, 4.25%), $v_{max.}$ 1 780 and 1 660 cm^{-1}; δ 8.10—7.75 (3 H, m) and 7.70—7.20 (11 H, m); m/e 326 (4%, $M^{+\cdot}$) and 105 (100, PhCO$^+$).

(b) A solution of phthaloyl chloride (1 g) in ether (10 ml) was added to a mixture of deoxybenzoin (1 g) and sodium hydride (0.5 g; 50% NaH content) in ether (20 ml), and the mixture was stirred for 4 days at room temperature. Purification by t.l.c. and recrystallisation from methanol afforded the phthalides (24a) (13%) and (24b) (10%), both identical with the samples obtained by procedure (a).

Photochemical and Thermal Isomerisation of the Methylenephthalides (24).—(a) Irradiation of a benzene solution of the Z-isomer (24a) (52 mg) with a 400 W lamp for 11 h, followed by t.l.c. (benzene) separation gave the Z-isomer (24a) (30 mg) and the E-isomer (24b) (16 mg).

(b) Similar irradiation and t.l.c. separation of the E-isomer (24b) (49 mg) gave the Z-isomer (24a) (25 mg) and the E-isomer (24b) (17 mg).

(c) A solution of the Z-isomer (24a) (50 mg) and a catalytic amount of iodine in o-chlorotoluene (5 ml) was heated under reflux for 13 h, and the products were separated by t.l.c. to give the Z-isomer (24a) (25 mg) and the E-isomer (24b) (18 mg).

(d) The E-isomer (24b) (52 mg) was similarly heated and separated to give the Z-isomer (24a) (28 mg) and the E-isomer (24b) (17 mg).

Hydrolysis of the (Z)-Methylenephthalide (24a).—The Z-isomer (24a) (49 mg) was dissolved in methanolic sodium hydroxide (0.16N; 2 ml). After 2 h at room temperature, the solvent was removed in vacuo, and the residue was extracted with dichloromethane. Sublimation of the

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* A m.p. of 123—125 °C is reported for (24) of unspecified configuration: J. Rotbergs, I. Lukina, and V. Oskaja, Lativ. PSR Zinat. Akad. Vestis, Kim. Ser., 1969, 465.

[17] S. Oae, N. Furukawa, T. Watanabe, Y. Otsuji, and M. Hamada, Bull. Chem. Soc. Japan, 1965, 38, 1247.
[18] H. Matsukubo and H. Kato, J.C.S. Perkin I, 1976, 2565.

extract afforded a slightly impure deoxybenzoin (2.1 mg), m.p. 52.4—54 °C (lit., 55—56 °C), undepressed on admixture with an authentic sample; i.r. and mass spectra and g.l.p.c. retention times were identical with those for an authentic sample. The residue insoluble in dichloromethane was dissolved in water, acidified, extracted with dichloromethane, and separated on t.l.c. (dichloromethane) to give 2-hydroxy-2-phenylindane-1,3-dione (27) (18 mg), m.p. 105.5—106.5 °C (lit.,[19] 106—108 °C) (Found: C, 75.75; H, 4.3. Calc. for $C_{15}H_{10}O_3$: C, 75.6; H, 4.25%), $\nu_{max.}$ 3 520, 3 200, 1 740, and 1 700 cm^{-1}; δ 8.10—7.74 (4 H, m, ArH), 7.40—7.14 (5 H, m, ArH), and 3.93 (1 H, s, OH, exchangeable by D_2O), m/e 238 (87%, $M^{+\cdot}$). Another t.l.c. fraction gave a mixture of benzoic acid and phthalic acid, which were treated with ethereal diazomethane and analysed by g.l.p.c. (PEG-20M and Apiezone Grease L on Chromosorb W AW; 4 mm × 2 m) and had identical retention times with authentic methyl benzoate and dimethyl phthalate (50 and 14% yields respectively based on g.l.p.c. evaluation).

2-*Hydroxy-2-phenylindane*-1,3-*dione* (27).—T.l.c. treatment (silica–dichloromethane) of 2-phenylindane-1,3-dione (26) (315 mg) afforded 2-hydroxy-2-phenylindane-1,3-dione (27) (199 mg), identical with the specimen described above.

3-(*Diphenylmethylene*)*phthalide*.—A mixture of diphenyl-acetic acid (1.71 g), phthalic anhydride (1 g), and fused sodium acetate (30 mg) was heated at 220 °C for 13 h. The products were separated by t.l.c. (benzene) and recrystallised from benzene–hexane to give prisms (4%), m.p. 150—151 °C (lit.,[20] 147—148 °C) (Found: C, 84.45; H, 4.55. Calc. for $C_{21}H_{14}O_2$: C, 84.55; H, 4.75%), $\nu_{max.}$ 1 775 and 1 760 cm^{-1}; δ 7.90—7.70 (1 H, m, ArH), 7.55—7.10 (12 H, m, ArH), and 6.30—6.15 (1 H, m, H-4); m/e 298 (100%, $M^{+\cdot}$).

3-(*Dibenzoylmethylene*)*phthalide*.—This compound was prepared in 26% yield according to the reported procedure,[21] m.p. 163—164 °C (lit., 162 °C,[21] 158—160 °C [22]) (Found: C, 77.8; H, 3.95. Calc. for $C_{23}H_{14}O_4$: C, 77.95; H, 4.0%), $\nu_{max.}$ 1 780, 1 660, and 1 640 cm^{-1}; δ 8.20—7.80 (5 H, m) and 7.60—7.20 (9 H, m), m/e 354 (18%, $M^{+\cdot}$) and 105 (100).

[19] L. Horner, K. H. Weber, and W. Duerckheimer, *Chem. Ber.*, 1961, **94**, 2881.

[20] J. Rigaudy and P. Derible, *Bull. Soc. chim. France*, 1965, 3047. They prepared this compound by photo-rearrangement of 2,2-diphenylindane-1,3-dione.

[21] J. Scheiber, *Annalen*, 1912, **389**, 121. This compound is described as 2,2-dibenzoylindane-1,3-dione.

[22] J. Rotbergs, I. Lukina, V. Oskaja, and G. Vanags, *Lativ. PSR Zinat. Akad. Vestis, Kim. Ser.*, 1966, 358 (*Chem. Abs.*, 1966, **65**, 15,265).