o-Quinonoid Compounds. Part IX.[1] Photodecarboxylation of 2-Benzopyran-3-one Adducts and Photoreactions of the Derived *o*-Quinodimethanes

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Photodecarboxylation of the 2-benzopyran-3-one–trimethylmaleimide adducts (10; R = H, Me, or Ph) gives the non-isolable *o*-quinodimethanes (2), (4), and (3), respectively; these are air-sensitive and undergo further photoreactions including conversion into cyclobuta[3,4]cyclobuta[1,2]benzenes of types (21) and (31) and cycloprop[*a*]indenes (23). The cyclobutacyclobutabenzenes revert to the *o*-quinodimethanes on heating or on irradiation.

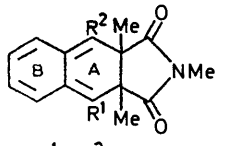
We have described[1a] the preparation of the *o*-quinodimethane (1), which can be handled and stored without special precautions. This remarkable stability appeared to be associated with steric protection of the normally reactive ring-A diene system by non-planar phenyl substituents. It was therefore of interest to prepare derivatives of this system, *e.g.* (2), lacking phenyl substituents.[1b] By analogy with (1), compound (2) might be prepared by photodecarbonylation of the inden-2-one–trimethylmaleimide adduct. However since the trapping of inden-2-one with cyclopentadiene proceeds poorly[2] we considered preparation of the derivatives (2)—(4) by photodecarboxylation of adducts derived from the efficiently generated[3] 2-benzopyran-3-ones (5)—(7). Unlike most esters, those derived from benzyl alcohol[4] and phenylacetic acid[5] undergo fairly smooth photodecarboxylation in solution. The likely utility of photodecarboxylation was established in model experiments. The dihydro-derivative of the isolable 1,4-diphenyl-2-benzopyran-3-one (8)[6] gave on photolysis the known[7] 1,2-dihydrobenzocyclobutene (9; $R^1 = R^2 = Ph$) as a *cis–trans*-mixture, and methyl 3-oxoisochroman-1-carboxylate underwent photodecarboxylation to (9; $R^1 = CO_2Me$, $R^2 = H$).

2-Benzopyran-3-one (5), generated by dehydration of *o*-formylphenylacetic acid with acetic anhydride,[3] reacted smoothly with trimethylmaleimide to give the adduct (10; R = H). The adduct (10; R = Ph) was similarly prepared. However the adduct (10; R = Me) was prepared in reasonable yield (55%) only when the acetic anhydride used was freshly distilled from quinoline; the omission of this step led to appreciable quantities of the *endo*- and *exo*-dimers (11) of 1-methyl-2-benzopyran-3-one. The constitution of

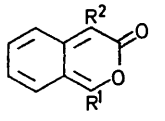
[1] (*a*) Part VIII, D. W. Jones and G. Kneen, preceding paper; (*b*) preliminary communication, D. W. Jones and G. Kneen, *J.C.S. Chem. Comm.*, 1972, 1038.
[2] J. M. Holland and D. W. Jones, *Chem. Comm.*, 1969, 587.
[3] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 536.
[4] R. S. Givens and W. F. Oettle, *Chem. Comm.*, 1969, 1164; *J. Amer. Chem. Soc.*, 1971, **93**, 3301, 3963; H. E. Zimmerman and U. R. Sandel, *ibid.*, 1963, **85**, 915.
[5] T. O. Meiggs and S. I. Miller, *J. Amer. Chem. Soc.*, 1972, **94**, 1989.
[6] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 531.
[7] G. Quinkert, K. Opitz, W.-W. Weisdorff, and M. Finke, *Annalen*, 1966, **693**, 44.

the dimers follows from their spectroscopic properties (see Experimental section) and their thermolysis or photolysis to the naphthalene (12). The *endo*- and *exo*-dimers are distinguished by the appearance of one high-field (τ 4·20) aromatic proton (H′) signal in the n.m.r. spectrum of the *endo*-isomer. Presumably an impurity present in ' normal ' acetic anhydride catalyses conversion of (6) into its tautomer (13) which then competes favourably with trimethylmaleimide for (6). In the absence of added trap the dimers are also obtained by using purified acetic anhydride.

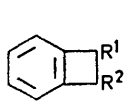
Photodecarboxylation of the adducts (10) produced yellow solutions of the *o*-quinodimethanes (2)—(4). However the yellow colours faded slowly on continued



(1) $R^1 = R^2 = Ph$
(2) $R^1 = R^2 = H$
(3) $R^1 = Ph, R^2 = H$
(4) $R^1 = Me, R^2 = H$



(5) $R^1 = R^2 = H$
(6) $R^1 = Me, R^2 = H$
(7) $R^1 = Ph, R^2 = H$
(8) $R^1 = R^2 = Ph$



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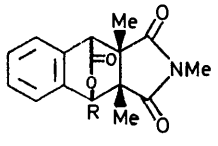

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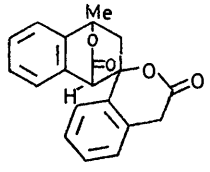

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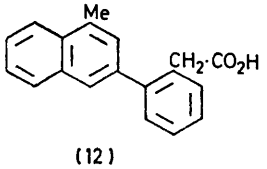

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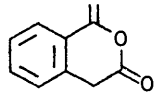


(13)

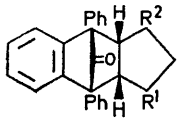
irradiation, and rapidly on exposure to air. Accordingly the u.v. spectra of (2)—(4) were measured by producing them from the adducts (10) in a u.v. cell (under nitrogen). The long-wavelength absorption band shown by these solutions was similar in position and fine structure to the absorption of the isolable diphenyl derivative (1). The latter absorbs at only slightly longer wavelength (415 nm) than the unsubstituted compound (2) (400 nm) whilst both the monophenyl (3) and the methyl derivative (4) absorb at *ca.* 410 nm. The effect of phenyl substituents on the *o*-quinodimethane chromophore in compounds (1)—(4) is only marginally greater than the effect of alkyl substitution predicted by Woodward's rules. Larger bathochromic shifts attend the introduction of phenyl groups into 2-benzopyran-3-one (5),[3,6] and the related isoquinolin-3-one.[8] In the former series (5), (6), (7), and (8) have $\lambda_{max.}$ 441, 448, 459, and 479 nm, respectively. Comparison indicates that the phenyl groups in (1) lie orthogonal to the *o*-quinonoid system, and provide steric rather than conjugative stabilisation. Further adventitious information supports this explanation. At their m.p.s the *endo*-adducts (14) and (15)[9] were observed to evolve gas and provide yellow melts; the yellow colour gradually faded (more rapidly on attemped dissolution). Photolysis (u.v. cell) of the adducts provided strongly yellow solutions of the *o*-quinodimethanes (16) and (17), which showed $\lambda_{max.}$ 444 and 453 nm, respectively. Reduced steric compression in (16) and (17) presumably allows conjugation of the phenyl groups with the *o*-quinonoid system. More rapid dehydrogenation and 1,5-hydrogen shift in the related *o*-quinodimethane (18) prevented its observation.[1] The carbonyl substituents in this compound might be expected to promote dehydrogenation,[10] and, by analogy with the acceleration of the 1,5-shift by phenyl substitution,[11] the 1,5-shift also.

Steric protection of (1) by the phenyl groups also accords with the increased ring-A reactivity of (2)—(4). Whereas phthalazine-1,4-dione adds only to ring B of (1),[1] 1-phenyltriazoline-2,5-dione reacts with (3) to give two adducts derived by addition to the two faces of ring A. The constitution of the adducts follows from their spectroscopic properties (see Experimental section). In particular the adduct (19) shows an NMe group shielded by the phenylene ring (τ 7·4) whereas in the adduct (20) the resonance of the NMe group is normal (τ 6·91) and the CMe groups are shielded (τ 8·85 and 9·05). These adducts presumably arise *via* concerted Diels–Alder reactions with lopsided transition states.

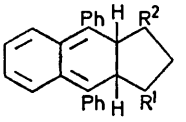
Attempts to isolate the *o*-quinonoid compounds (2)—(4) failed, as, unlike (1), they are air-sensitive. In this respect reactivity increases in the expected order (2) > (4) > (3). They also undergo further photoreactions. Thus preparative photolysis of the adduct (10; R = Ph) gave the *syn*-cyclobutane (21; R = Ph) (28%) as well as the dihydronaphthalene (22; R^1 = Ph, R^2 = Me) (23%), and the cyclopropane (23; R^1 = Ph, R^2 = Me) (3·5%). The constitution (21; R = Ph) is supported by the presence of a shielded NMe group (τ 7·62), unequally shielded CMe groups (τ 8·5 and 9·0), and ready reversion of (21; R = Ph) to the *o*-quinodimethane (3) in boiling xylene. At this temperature the ring opening is followed by a slower 1,5-shift of the acyl groups[1] to give the dihydronaphthalenes (24) and (25). The tertiary methyl group in (24) is shielded (τ 8·97) in comparison with that in (25) (τ 8·44), supporting the assigned stereochemistry and the suprafacial course of the acyl shift. This is consistent with a concerted 1,5-sigmatropic shift, as is the formation of (24) and (25) in about equal quantities.

[8] D. W. Jones, *J. Chem. Soc.* (*C*), 1969, 1729.
[9] D. W. Jones and R. L. Wife, *J.C.S. Chem. Comm.*, 1973, 421.
[10] *Cf.* L. M. Jackman, *Adv. Org. Chem.*, 1960, **2**, 329.
[11] L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, 1969, **91**, 1578; L. L. Miller and R. F. Boyer, *ibid.*, 1971, **93**, 650.

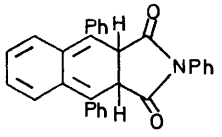
A mechanism involving homolytic cleavage and recombination might be expected to favour the doubly benzylic radical (26) leading to the product (24). A



(14) $R^1 = R^2 = H$
(15) $R^1R^2 = [CH_2]_2$



(16) $R^1 = R^2 = H$
(17) $R^1R^2 = [CH_2]_2$



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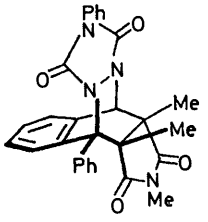

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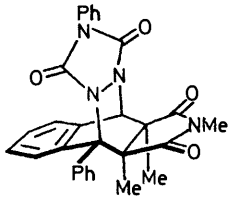

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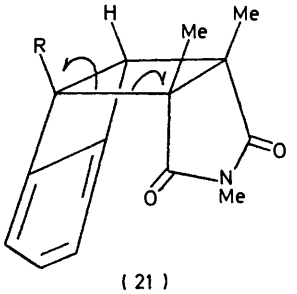

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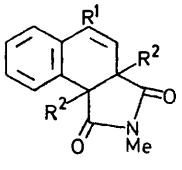

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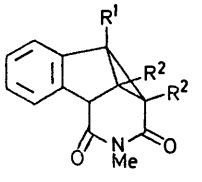
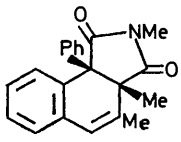


(23)

diradical like (26) might be expected to lose CO and MeNCO to give a 1-phenylnaphthalene; no such product was detected.

The photochemical, orbital-symmetry-allowed ring opening of (21; R = Ph) [⟶(3)] also occurs. Photolysis of (21; R = Ph) gives the photoproducts (22; R^1 = Ph, R^2 = Me) and (23; R^1 = Ph, R^2 = Me) obtained from (10; R = Ph); (22; R^1 = Ph, R^2 = Me) probably arises from (21) *via* the indicated homolysis [(21); arrows] to (27). Related cleavage β to a carbonyl group is known for other small ring compounds,[12] and in the present case benefits from the doubly benzylic nature of the radical site in (27). Radical pairing as shown [(27); arrows] and valence isomerism then gives (22; R^1 = Ph, R^2 = Me). The photoproduct (23; R^1 = Ph, R^2 = Me) may arise from the *o*-quinodimethane (3) by a process related to the oxadi-π-methane rearrangement of βγ-unsaturated



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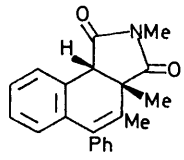

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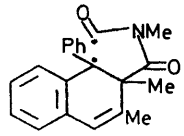

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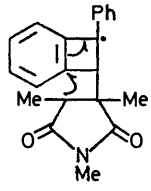

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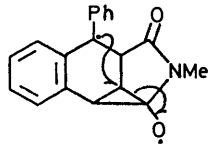
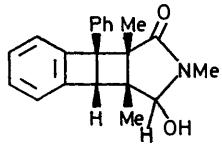


(28)

ketones.[13] In the present case this could lead to the *more stable* diradical intermediate (28), a vinylogue of that proposed for the normal di-π-methane rearrangement;[14] this could then collapse [(28); arrows] to the observed product.

Treatment of (21; R = Ph) with lithium aluminium hydride gave only a partially reduced product which survived further attempted reduction with the reagent. This product is tentatively assigned the structure (29). On heating in xylene a strong yellow colour ($\lambda_{max.}$ 408 nm) developed in accord with ring opening



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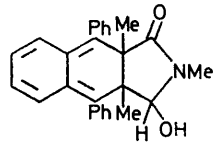

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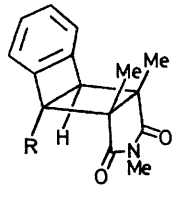

(31)

to (30). The observed $\lambda_{max.}$ value suggests that conjugation between the *o*-quinonoid system and the carbonyl groups in (3) is of little importance.

Photolysis of (10; R = Me) gave mainly (71%) the *syn*- and *anti*-cyclobutanes (21; R = Me) and (31; R = Me), which showed NMe resonance at τ

[12] A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, 1969, **91**, 456; G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, 1965, **87**, 1410.

[13] W. G. Dauben, M. S. Kellog, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, 1970, **92**, 1786, and cited references; S. Wolff and W. C. Agosta, *J.C.S. Chem. Comm.*, 1972, 226.

[14] H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 1409, 6267, 6259; H. E. Zimmerman and A. A. Baum, *ibid.*, 1971, **93**, 3646.

7·68 and 6·9, respectively. On heating in boiling xylene both isomers gave the yellow *o*-quinodimethane (4). The sensitivity of the latter to traces of oxygen precluded a study of the 1,5-acyl shift in (4).

Predominant photo-closure of (4) to the *anti*-cyclobutane (31; R = Me) (*syn* : *anti* ratio 1 : 6) contrasts with our failure to observe the *anti*-isomer (31; R = Ph) on photolysis of either the *syn*-isomer (21; R = Ph) or the adduct (10; R = Ph). The predominance of the *anti*-isomer (31; R = Me) is not due to preferential excitation of the *syn*-isomer, for the latter has the lower ε value at 267·5 nm. Similarly neither steric effects in the transition state [15] nor the products [16] appear to provide an adequate explanation of these results. In several cases [15-18] photo-closure appears to provide the more sterically compressed product; the factors determining the preferred closure would merit further attention.

Preparative photolysis of (10; R = H) gave only a 10% yield of an inseparable mixture of the isomers (21; R = H) and (31; R = H); the major product (30%) is assigned the structure (23; R^1 = H, R^2 = Me). This compound surprisingly survived heating at 200° (15 min), and treatment with methanolic hydrogen chloride. In search of precedent for this behaviour and the 1,2-shift of imide carbonyl involved in the formation of the compounds (23) we prepared the model compound (22; $R^1 = R^2$ = H) by the reaction of *N*-methylmaleimide with α-bromostyrene.[19] On photolysis this gave the cyclopropane (23; $R^1 = R^2$ = H), which had n.m.r. and carbonyl i.r. absorption characteristics very similar to those of the photolysis product (23; R^1 = H, R^2 = Me) and likewise survived thermal and acidic treatment. In a similar way irradiation of (25) gave the cyclopropane (23; R^1 = Ph, R^2 = Me).

EXPERIMENTAL

For general details see the preceding paper,[1a]

Preparation of Trimethylmaleimide Adducts.—(a) *With 2-benzopyran-3-one.* *o*-Formylphenylacetic acid (320 mg, 1·95 mmol), trimethylmaleimide (278 mg, 2·00 mmol), and acetic anhydride (6·4 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (45 min). Evaporation under reduced pressure on a water-bath gave 1,4-*dihydro*-N,9,10-*trimethyl*-3-*oxo*-1,4-*ethano*-2-*benzopyran*-9,10-*dicarboximide* (10; R = H) (312 mg, 56%), m.p. 196—198° (from chloroform–ethanol) (Found: C, 67·1; H, 5·35; N, 4·95. $C_{16}H_{15}NO_4$ requires C, 67·4; H, 5·3; N, 4·9%), $\nu_{max.}$ 1787, 1768, and 1695 cm^{-1}, τ 2·66 (4H, s), 4·55 (1H, s), 6·00 (1H, s), 7·57 (3H, s), 8·40 (3H, s), and 8·51 (3H, s).

(b) *With 1-phenyl-2-benzopyran-3-one.* *o*-Benzoylphenylacetic acid (400 mg, 1·66 mmol), trimethylmaleimide (235 mg, 1·69 mmol), and acetic anhydride (10 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (3 h). Evaporation of acetic anhydride left the *adduct* (10; R = Ph) (470 mg, 78%), m.p. 187—190° (from chloroform–ethanol) (Found: C, 73·05; H, 5·15; N, 3·95. $C_{22}H_{19}NO_4$ requires C, 73·2; H, 5·3; N, 3·9%), $\nu_{max.}$ 1768 and 1695 cm^{-1}, τ 1·7—2·0 (2H, m), 2·3—3·0 (7H, m), 5·90 (1H, s), 7·47 (3H, s), 8·50 (3H, s), and 8·72 (3H, s), *m/e* 222, 194, 165, and 138 (42, 100, 24, and 7%).

(c) *With 1-methyl-2-benzopyran-3-one.* *o*-Acetylphenylacetic acid (190 mg, 1·07 mmol), trimethylmaleimide (160 mg, 1·15 mmol), and acetic anhydride (4 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (3 h). Evaporation of acetic anhydride left the *adduct* (10; R = Me) (175 mg, 55%), m.p. 215—216° (from chloroform–ethanol) (Found: C, 68·0; H, 5·7; N, 4·9. $C_{17}H_{17}NO_4$ requires C, 68·2; H, 5·7; N, 4·7%), $\nu_{max.}$ 1763 and 1693 cm^{-1}, τ 2·70br (4H, s), 6·03 (1H, s), 7·62 (3H, s), 7·95 (3H, s), and 8·54 (6H, s), *m/e* 255, 170, 160, 155, and 132 (17, 69·5, 61, 35, and 100%), *m** 141·32 (170 ⟶ 155) and 113·33 (255 ⟶ 170).

(d) *Dehydration of o-acetylphenylacetic acid in the absence of a trap.* *o*-Acetylphenylacetic acid (89 mg, 0·5 mmol), and acetic anhydride (2 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (1 h). Evaporation of acetic anhydride gave endo-1,4-*dihydro*-1-*methylspiro*-{1,4-*ethano*-2-*benzopyran*-9,1′(4′H)-[2]*benzopyran*}-3,3′-*dione* (11) (45 mg, 56·5%), m.p. 242—246° (decomp.) (from chloroform–ethanol) (Found: C, 74·95; H, 4·85. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%), $\nu_{max.}$ 1755 cm^{-1}, τ 2·4—3·3 (7H, m), 4·20 (1H, d, *J* 8 Hz), 5·95 (1H, s), 6·07br (2H, s), 7·04 (1H, d, *J* 15 Hz), 7·42 (1H, d, *J* 15 Hz), and 7·96 (3H, s).

Chromatography of the mother liquors on silica in ether–benzene (1 : 3) afforded the exo-*isomer* (11) (26 mg, 32·5%), m.p. 199—203° (decomp.) (from chloroform–ethanol) (Found: C, 74·8; H, 5·1%), $\nu_{max.}$ 1759 cm^{-1}, τ 2·3—3·0 (8H, m), 5·84 (1H, s), 6·16 (2H, s), 6·83 (1H, d, *J* 15 Hz), 7·66 (1H, d, *J* 15 Hz), and 7·98 (3H, s).

Continued elution afforded more (6 mg, 7·5%) of the *endo*-dimer (11).

Pyrolysis of the endo-*Dimer* (11).—The *endo*-dimer (11) (110 mg, 0·344 mmol) was pyrolysed at 260 °C under nitrogen until no more gas was evolved (*ca.* 5 min). The product was taken up in sodium hydrogen carbonate solution, acidified with hydrochloric acid, and extracted into ether. The extract was washed with water, dried ($MgSO_4$), and evaporated to give [2-(4-*methyl*-2-*naphthyl*)-*phenyl*]*acetic acid* (12) (75 mg, 79%), m.p. 108—109° (from benzene–petroleum) (Found: C, 82·7; H, 5·9. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%), $\nu_{max.}$ 1695 cm^{-1}, τ 0·09br (1H, s, exch. D_2O), 1·80—2·80 (10H, m), 6·36 (2H, s), and 7·31 (3H, s).

Photolysis of the endo-*Dimer* (11).—The *endo*-dimer (11) (250 mg, 0·782 mmol) was photolysed in benzene (500 ml) (20 h) as described in (*a*) below. Evaporation, and isolation of the acid as described above, gave the naphthalene (12) (200 mg, 93%), identical (mixed m.p. and i.r. spectrum) with the sample previously prepared.

Photolysis of the Adduct (10; R = Ph).—(*a*) The adduct (1·0 g) was irradiated in a Hanovia 1 l photochemical reactor in deoxygenated benzene (800 ml) with a medium-pressure (100 W) mercury lamp, while a slow nitrogen

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stream was bubbled through the solution (mercury bubbler at exit) (117 h). Evaporation, and chromatography on silica in ether–benzene (5 : 95) gave 1,1a,6,6a-*tetrahydro*-N,1,6a-*trimethyl*-1a-*phenylcycloprop*[a]*indene*-1,6-*dicarboximide* (23; R^1 = Ph, R^2 = Me) (31 mg, 3·5%), m.p. 171—172° (from chloroform–ethanol) (Found: C, 79·25; H, 5·85; N, 4·2. $C_{21}H_{19}NO_2$ requires C, 79·5; H, 6·0; N, 4·4%), $\nu_{max.}$ 1721 and 1672 cm^{-1}, τ 2·4—3·4 (9H, m), 5·79 (1H, s), 6·94 (3H, s), 8·62 (3H, s), and 8·83 (3H, s), *m/e* 317 (M^+), 233, 232, 217, 215, 202, and 101 (33, 28, 100, 31, 22, 19, and 15%), *m** 202·97 (232 ⟶ 217), 188·04 (217 ⟶ 202), and 169·79 (317 ⟶ 232).

Continued elution afforded 1,2-*dihydro*-N,1,2-*trimethyl*-4-*phenylnaphthalene*-1,2-*dicarboximide* (22; R^1 = Ph, R^2 Me) (200 mg, 23%), m.p. 138—139° (from chloroform–ethanol) (Found: C, 79·6; H, 6·05; N, 4·7%), $\nu_{max.}$ 1703 and 1776 cm^{-1}, $\lambda_{max.}$ 272 nm (ε 8150), τ 2·15—3·05 (9H, m), 4·27 (1H, s), 7·02 (3H, s), 8·42 (3H, s), and 8·59 (3H, s), *m/e* 317 (M^+), 233, 232, 217, 215, 202, and 101 (39, 29, 100, 31, 24, 19, and 21%), *m** 202·97 (232 ⟶ 217), 188·04 (217 ⟶ 202), and 169·79 (317 ⟶ 232). Further elution gave syn-1,2,2a,6b-*tetrahydro*-N,1,2-*trimethyl*-2a-*phenylcyclobuta*[3,4]*cyclobuta*[1,2]*benzene*-1,2-*dicarboximide* (21; R = Ph) (248 mg, 28%), m.p. 166—168° (from chloroform–methanol) (Found: C, 79·65; H, 6·0; N, 4·45%), $\nu_{max.}$ 1763 and 1690 cm^{-1}, $\lambda_{max.}$ 256sh, 261·5, 268, and 275 nm (ε 2042, 2475, 2820, and 2620), τ 2·45—2·9 (9H, m), 5·92 (1H, s), 7·62 (3H, s), 8·50 (3H, s), and 9·00 (3H, s), *m/e* 317 (M^+), 233, 232, 217, 215, 202, and 101 (33, 28, 100, 31, 22, 19, and 15%), *m** 202·97 (232 ⟶ 217), 188·04 (217 ⟶ 202), and 169·79 (317 ⟶ 232).

(*b*) When the photolysis of the adduct (200 mg) was conducted in acetone (175 ml; freshly distilled from calcium sulphate) with exclusion of oxygen as described above (5 h), isolation by chromatography on silica in benzene–ether (94 : 6) gave the dihydronaphthalene (22; R^1 = Ph, R^2 = Me) (19 mg, 11%) as the only isolable product.

Trapping the o-*Quinodimethane* (3) *with* 4-*Phenyl*-1,2,4,*triazoline*-3,5-*dione*.—The adduct (10; R = Ph) (180 mg, 0·5 mmol) was photolysed as described in (*a*) above in benzene (500 ml) (10 min) and the deep yellow solution produced was titrated to a colourless end-point with a solution of the dienophile in benzene. This irradiation–titration sequence was repeated over 8 h with extension of the irradiation periods to 30 min in the later stages. Evaporation, and chromatography on silica in ether–benzene (1 : 4) gave the adducts (19) and (20) as a mixture (151 mg, 62%). Crystallisation from chloroform–methanol gave first the *adduct* (20) (65 mg, 27%), m.p. 322—324° (Found: C, 70·9; H, 5·0; N, 11·1. $C_{29}H_{24}N_4O_4$ requires C, 70·7; H, 4·9; N, 11·4%), $\nu_{max.}$ 1780, 1768, 1720, and 1700 cm^{-1}, τ 2·0—3·2 (14H, m), 4·53 (1H, s), 6·91 (3H, s), 8·85 (3H, s), and 9·05 (3H, s). The mother liquor left after removal of the adduct (20) deposited the isomeric *adduct* (19) (80 mg, 33%), m.p. 269·5—272° (Found: C, 70·35; H, 5·0; N, 11·35%), $\nu_{max.}$ 1759, 1714, and 1695 cm^{-1}, τ 1·9—2·85 (14H, m), 4·50 (1H, s), 7·40 (3H, s), 8·32 (3H, s), and 8·51 (3H, s).

Photolysis of the Cyclobutane (21; R = Ph).—Compound (21; R = Ph) (120 mg) was photolysed in benzene (800 ml) (25 h) as described in (*a*) above. Evaporation, and chromatography on silica in ether–benzene (1 : 19) gave the cyclopropane (23; R^1 = Ph, R^2 = Me) (4·3 mg, 3·6%), m.p. 170—172° (from chloroform–ethanol), identical (mixed m.p. and i.r. spectrum) with the sample prepared previously. Continued elution gave the dihydronaphthalene (22; R^1 = Ph, R^2 = Me) (31 mg, 26%), m.p. 138—139° (from chloroform–ethanol) identical (mixed m.p. and i.r. spectrum) with material already prepared. Further elution gave starting material (21; R = Ph) (40 mg, 33%).

Photolysis of the Adduct (10; R = Me).—The adduct (1·86 g) was photolysed in benzene (1 l) as described in (*a*) above (120 h). Evaporation, and chromatography on silica (100 g) in ether–benzene (2 : 23) gave first a fraction (68 mg), $\nu_{max.}$ 1675 and 1722 cm^{-1}, not further characterised, and then the anti-*cyclobutacyclobutabenzene* (31; R = Me) (1·0 g, 63%), m.p. 95—97° (from petroleum) (Found: C, 75·2; H, 6·7; N, 5·55. $C_{16}H_{17}NO_2$ requires C, 75·3; H, 6·7; N, 5·5%), $\nu_{max.}$ 1763 and 1695 cm^{-1}, $\lambda_{max.}$ 255sh, 260·5, 267·5, and 274 nm (ε 1638, 2084, 2455, and 2530), τ 2·5—3·0 (4H, m), 6·44 (1H, s), 6·91 (3H, s), 8·60 (3H, s), and 9·06 (6H, s), *m/e* 255 (M^+), 170, 155, and 115 (26, 100, 74, and 17%), *m** 141·32 (170 ⟶ 155), and 113·33 (255 ⟶ 170).

Further elution gave the syn-*isomer* (21; R = Me) (125 mg, 8%), m.p. 107—109° (from petroleum) (Found: C, 75·0; H, 6·7; N, 5·5%), $\nu_{max.}$ 1760 and 1690 cm^{-1}, $\lambda_{max.}$ 255sh, 261, 267·5, and 274 nm (ε 1074, 1370, 1703, and 1666), τ 2·6—3·0 (4H, m), 6·60 (1H, s), 7·68 (3H, s), 8·43 (3H, s), 8·56 (3H, s), and 8·62 (3H, s), *m/e* 255 (M^+), 170, 155, 132, 115, and 78 (21, 100, 54, 25, 25, and 42%), *m** 141·32 (170 ⟶ 155) and 113·33 (255 ⟶ 170).

Photolysis of the anti-*Cyclobutane* (31; R = Me).—The *anti*-cyclobutane (100 mg) was photolysed in benzene (150 ml) (15 h) as described in (*a*) above. Evaporation, and chromatography on silica in ether–benzene (2 : 23) gave the same non-crystalline mixture as obtained above (22 mg, 22%), the *anti*-cyclobutane (31; R = Me) (61 mg), and the *syn*-cyclobutane (21; R = Me) (9 mg).

Photolysis of the Adduct (10; R = H).—The adduct (400 mg) was photolysed in benzene (500 ml) as described in (*a*) above (26 h). Evaporation, and chromatography on silica in ether–benzene (2 : 23) gave the *cyclopropane* (23; R^1 = H, R^2 = Me) (101 mg, 30%), m.p. 128—129° (from benzene–petroleum) (Found: C, 74·9; H, 6·4; N, 6·0. $C_{15}H_{15}NO_2$ requires C, 74·7; H, 6·3; N, 5·8%), $\nu_{max.}$ 1661 and 1704 cm^{-1}, τ 2·5—3·0 (4H, m), 5·88 (1H, s), 7·08 (3H, s), 7·58 (1H, s), 8·44 (3H, s), and 8·50 (3H, s), *m/e* 241 (M^+), 157, 156, 155, 141, 140, 139, 128, and 115 (59, 36, 100, 22·5, 81, 35, 24, 25, and 29%), *m** 100·98 (241 ⟶ 156) and 127·44 (156 ⟶ 141). Continued elution gave, as a mixture, the cyclobutanes (21; R = H) and (31; R = H) (39 mg, 10%).

1,2-*Dihydro*-N-*methylnaphthalene*-1,2-*dicarboximide*.—α-Bromostyrene (8·0 g, 0·044 mol), *N*-methylmaleimide (6·0 g, 0·054 mol), hydroquinone (500 mg), and toluene (35 ml) were boiled under reflux (36 h). Removal of solvent and chromatography on silica (250 g) in ether–benzene (3 : 17) gave the *dihydronaphthalene* (22; R^1 = R^2 = H) (2·0 g, 21·5%), m.p. 132—134° (from chloroform–ethanol) (Found: C, 73·55; H, 5·3; N, 6·45. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·6%), $\nu_{max.}$ 1695 and 1768 cm^{-1}, τ 2·3—3·1 (4H, m), 3·53 (1H, dd, *J* 10 and 2 Hz), 4·11 (1H, dd, *J* 10 and 3·5 Hz), 5·86 (1H, d, *J* 10·5 Hz), 6·17 (1H, dq, *J* 10·5, 3·5, and 2 Hz), and 7·01 (3H, s).

Photolysis of the Dihydronaphthalene (22; R^1 = R^2 = H).—The dihydronaphthalene (1·0 g) was photolysed in benzene (175 ml) (112 h) as described in (*a*) above. Evaporation, and chromatography on silica (100 g) in ether–

benzene (2 : 23)gave N-*methylnaphthalene*-1,2-*dicarboximide* (18 mg, 2%), m.p. 163—166° (from benzene–petroleum) (Found: C, 74·0; H, 4·0; N, 6·9. $C_{13}H_9NO_2$ requires C, 73·9; H, 4·3; N, 6·6%), $\nu_{max.}$ 1771, 1759, 1712, and 1698 cm^{-1}.

Continued elution gave an unidentified formamide (62 mg, 6%), m.p. 91—96° (from petroleum) (Found: C, 73·5; H, 5·15; N, 6·55. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·6%), $\nu_{max.}$ 1722 and 1647 cm^{-1}, τ 0·92 and 1·26 (each 0·5H, HCO), 1·8—3·0 (7H, m), and 6·67 and 6·69 (each 1·5H, s, NMe), *m/e* 213 (M^+), 185, 156, 155, 128, 127, and 126 (33, 21, 19, 100, 19, 62, and 17%), *m** 104·1 (155 ⟶ 127). Continued elution gave starting material (311 mg, 31%).

Further elution gave the *cyclopropane* (23; $R^1 = R^2 =$ H) (134 mg, 14%), m.p. 150—152° (from benzene–petroleum) (Found: C, 73·25; H, 5·55; N, 6·4%), $\nu_{max.}$ 1665 and 1710 cm^{-1}, τ 2·45—2·90 (4H, m), 5·60 (1H, d, *J* 7 Hz, HC·CO), 6·92 (1H, dd, *J* 8 and 6·5 Hz, benzylic cyclopropyl), 7·07 (3H, s), 7·22 (1H, m), and 7·54 (1H, t, *J* 8 Hz, HC·CO), *m/e* 213 (M^+), 156, 155, 129, 128, 127, and 78 (22·5, 6, 7, 17, 100, 14, and 11%).

Thermolysis of the syn-*Cyclobutane* (21; R = Ph).—Compound (21; R = Ph) (35 mg) and xylene (5 ml) were boiled under reflux in a nitrogen atmosphere (10 h). Evaporation, and chromatography on silica in ether–benzene (1 : 19) gave the *dihydronaphthalene* (24) (15 mg, 43%) (Found: M^+, 317·1413. $C_{21}H_{19}NO_2$ requires *M*, 317·1416), $\nu_{max.}$ 1770, 1703, and 1690 cm^{-1}, τ 2·8 (9H, m), 3·42 (1H, q, *J* 1·5 Hz), 6·94 (3H, s), 7·88 (3H, d, *J* 15 Hz), and 8·97 (3H, s).

Continued elution gave the *dihydronaphthalene* (25) (13 mg, 37%), m.p. 153—154° (from benzene–petroleum) (Found: C, 79·7; H, 6·0; N, 4·3%), $\nu_{max.}$ 1777, 1710, and 1700 cm^{-1}, τ (90 MHz), 2·75 (8H, m), 3·46 (1H, m, aromatic), 6·16 (1H, s), 6·95 (3H, s), 8·28 (3H, s), and 8·44 (3H, s), *m/e* 317 (M^+), 233, 232, 217, 215, 202, and 101 (39, 29, 100, 31, 24, 19, and 21%), *m** 202·97 (232 ⟶ 217), 188·03 (217 ⟶ 202), and 169·79 (317 ⟶ 232).

Reduction of the Cyclobuta[3,4]*cyclobuta*[1,2]*benzene* (21; R = Ph).—Compound (21; R = Ph) (50 mg, 0·158 mmol), lithium aluminium hydride (20 mg), and ether (10 ml) were boiled under reflux (3 h). After stirring with water (5 drops) the ether layer was washed with sodium hydroxide (2N) and with water, dried ($MgSO_4$), and evaporated to give 2,3,3a,3b,7b,7c-*hexahydro*-3-*hydroxy*-2,3a,7c-*trimethyl*-7b-*phenylbenzo*[3′,4′]*cyclobuta*[1′,2′:3,4]*cyclobuta*-[1,2-c]*pyrrol*-2-*one* (29) (42 mg, 84%), m.p. 166—168° (from chloroform–ether) (Found: C, 79·0; H, 6·6; N, 4·2. $C_{21}H_{21}NO_2$ requires C, 79·0; H, 6·6; N, 4·4%), $\nu_{max.}$ 3250 and 1653 cm^{-1}, τ 2·5—2·85 (10H, m, aromatic and HC·N), 5·4br (1H, s, OH), 6·11 (1H, s), 7·6 (3H, s), 8·58 (3H, s), and 9·10 (3H, s). This product was unchanged after further treatment with lithium aluminium hydride. After heating in xylene it showed $\lambda_{max.}$ 408 nm, characteristic of the derived *o*-quinodimethane (30).

Photolysis of the Dihydronaphthalene (25).—Compound (25) (8 mg) in deoxygenated benzene (15 ml) in a quartz flask under nitrogen was irradiated with a 100 W water-cooled medium-pressure mercury lamp (Hanovia) at a distance of *ca.* 7 cm (4·5 h). Evaporation, and chromatography on silica in ether–benzene (1 : 19) gave the cyclopropane (23; R^1 = Ph, R^2 = Me) (4·5 mg, 56%), identical (t.l.c. in a number of solvent systems) to material previously prepared.

Photolysis of 1,4-*Dihydro*-1,4-*diphenyl*-2-*benzopyran*-3-*one*.—The benzopyranone (100 mg) was photolysed in benzene (800 ml) (6 days) as described in (*a*) above. Evaporation, and passage down a short column of alumina (neutral Woelm, grade III) gave an oil (87 mg) of which the n.m.r. spectrum showed *cis*- and *trans*-1,2-dihydro-1,2-diphenylbenzocyclobutene to be present in the ratio 2 : 3.

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