o-Quinonoid Compounds. Part VIII.[1] Photodecarbonylation of 1,3-Diphenylinden-2-one Adducts; 1,5-Sigmatropic Shifts in Sterically Stabilised *o*-Quinodimethanes

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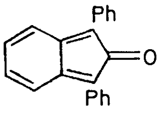
Photodecarbonylation of the 1,3-diphenylinden-2-one–substituted maleimide adducts (9a and b) gave the sterically stabilised *o*-quinodimethanes (3b and c), which undergo 1,5-sigmatropic shift of the imido-group rather than alkyl migration.

1,3-DIPHENYLINDEN-2-ONE (1) is conveniently generated by dissociation of its dimer (2) in boiling xylene.[2] The reversible nature of the dimerisation allows the preparation of adducts from unreactive dienophiles like tetramethylethylene. A study of the photodecarbonylation of adducts derived from (1) was undertaken with a view to preparing an *o*-quinodimethane (3) in which the termini of the normally reactive ring-A diene system are sterically protected by bridges or groups X^1 and X^2.† The properties of such an *o*-quinodimethane should allow an assessment of the contributions of steric and aromatic stabilisation in naphtho(2′,3′:1,2)[1,2]dicarbadodecaborane(12) (4).[4] We were also interested in the photochemistry of the *o*-quinodimethanes (3), which could indicate why inversion of stereochemistry accompanies the photodecarbonylation of (2) to the benzocyclobutane (5).[2]



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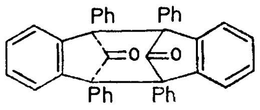

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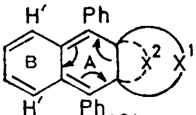

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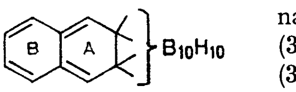
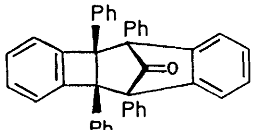


(4)

(3) a; $X^1 = CO{\cdot}NPh{\cdot}CO$, $X^2 = H_2$
b, $X^1 = CO{\cdot}NMe{\cdot}CO$, $X^2 = [CH_2]_4$
c; $X^1 = CO{\cdot}NMe{\cdot}CO$, $X^2 = Me_2$
d; $X^1 = X^2 = Me_2$



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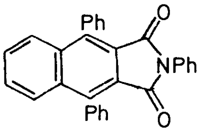

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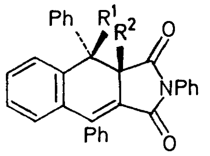
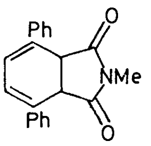


(7) $R^1 = R^2 = H$
(16) $R^1R^2 = [CH_2]_4$
(17) $R^1 = R^2 = Me$



(8)

Irradiation of the *N*-phenylmaleimide–1,3-diphenylinden-2-one adduct gave a mixture of the naphthalene (6) and its dihydro-derivative (7). These products probably arise from the expected *o*-quinodimethane (3a) by dehydrogenation and 1,5-hydrogen shift, respectively. The same *o*-quinodimethane is a presumed intermediate in the reaction of 1,3-diphenylbenzo[*c*]thiophen 2,2-dioxide with *N*-phenylmaleimide, which likewise leads to (6) and (7).[5] The *cis*-stereochemistry of (7) agrees with its formation from (3a) by a suprafacial 1,5-hydrogen shift. This experiment showed that the imide system was sufficiently photo-stable [6] to serve as a bridging group (X^1) in our studies; 1,4-diphenylnaphthalene formed by loss of CO and PhNCO from (3a) was not a significant photoproduct. In contrast to (3a) the model compound (8) undergoes exclusive dehydrogenation on photolysis.

Since 1,5-sigmatropic shift of alkyl groups is slow in comparison with hydrogen migration,[7] the *o*-quinodimethane (3b) should be more stable. Accordingly the adduct (9a) was prepared from (2) and the imide (10). Photolysis of (9a) gave the bright yellow, crystalline *o*-quinodimethane (3b) (80%), which can be handled and stored without special precautions. The tetramethylene bridge included in this structure to prevent electrocyclic ring opening (3; arrows) as well as to provide steric protection, can be replaced by two methyl groups without noticeable loss of stability.

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† A variety of otherwise reactive molecules are stabilised by bulky substituents (ref. 3).

[1] Part VII, D. W. Jones and R. L. Wife, *J.C.S. Perkin I*, 1974, 1.

[2] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1971, 608.

[3] J. H. Wieringa, H. Wynberg, and J. Strating, *Tetrahedron Letters*, 1972, 2071 and cited references; E. W. Garbisch, and R. F. Sprecher, *J. Amer. Chem. Soc.*, 1969, **91**, 6785; E. R. Talaty and C. M. Utermoehlen, *Chem. Comm.*, 1970, 473; H. Kimling and A. Krebs, *Angew. Chem. Internat. Edn.*, 1972, **11**, 932; 1971, **10**, 509; J. K. Crandall and S. A. Sojka, *Tetrahedron Letters*, 1972, 1641.

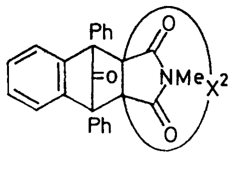
[4] D. S. Matteson and R. A. Davis, *Chem. Comm.*, 1970, 669.

[5] M. P. Cava and J. McGrady, *Chem. Comm.*, 1968, 1648.

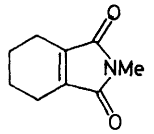
[6] *Cf.* J. B. Bremner and R. N. Warrener, *Chem. Comm.*, 1967, 926; *Angew. Internat. Edn.*, 1966, **5**, 311.

[7] 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.

Thus on photolysis the 1,3-diphenylinden-2-one–trimethylmaleimide adduct (9b) deposited the crystalline *o*-quinodimethane (3c) (80%). This compound is presumably constrained from electrocyclic ring opening by the imide ring; an attempt to prepare (3d) by photodecarbonylation of the tetramethylethylene adduct of (1) gave the valence isomer (11) which was oxidised (CrO_3–HOAc) to *o*-dibenzoylbenzene (83%).



(9) a; $X^2 = [CH_2]_4$
b; $X^2 = Me_2$
c; $X^2 = H_2$



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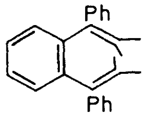

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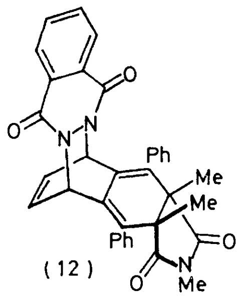

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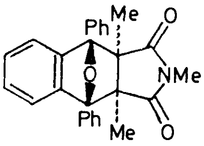

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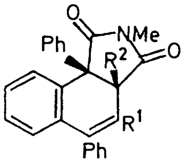

(14) $R^1R^2 = [CH_2]_4$
(15) $R^1 = R^2 = Me$

Steric shielding of the ring-A diene system in (3b and c) is shown by the failure of (3b) to react with dimethyl acetylenedicarboxylate in boiling toluene, and the reaction of (3c) with phthalazine-1,4-dione to give a ring-B adduct (12) and a stereoisomer in which the methyl groups and imide ring are interchanged. The constitution of the adducts follows from their spectroscopic properties (see Experimental section). In contrast reaction of (3c) with bromine and adventitious moisture leads to attack on ring A and affords the product (13), which on heating undergoes reverse Diels–Alder addition to give 1,3-diphenylbenzo[*c*]furan. Steric shielding of ring B is greater for (3b) than for the carbaborane (4); the latter adds dimethyl acetylenedicarboxylate to the ring-B diene system at 110°.

The naphthodicarbadodecaborane (4) absorbs at only slightly shorter wavelength ($\lambda_{max.}$ *ca.* 393 nm) [4] than the derivatives (3b) (*ca.* 415) and (3c) (*ca.* 414 nm). This suggests that the phenyl groups in the latter compounds lie orthogonal to the *o*-quinonoid system. The *ortho*-hydrogen atoms of the phenyl groups will then lie above and below the termini of the ring-A diene system where they provide steric protection. Examination of space-filling models supports this view; interference between the *ortho*-hydrogen atoms of the phenyl rings and the protons H′ and ring-A substituents is minimised when the *o*-quinonoid system and the phenyl rings are orthogonal. Additional evidence is provided by the n.m.r. spectra of (3b and c). For both compounds the resonance of the ring-B protons is centred at τ *ca.* 3·9; these protons are therefore shielded in comparison with the ring-B protons in the carbaborane (4) (τ 3·5) in agreement with their location above the phenyl rings.

Since the compounds (3b and c), and the carbaborane (4) all have very similar properties it is unlikely that (4) has significant aromatic character. In agreement, the properties of benzodicarbadodecaborane have now been reinterpreted as characteristic of a sterically protected cyclohexadiene.[8] Like (3b and c), 1,3-dimesitylbenzo[*c*]furan [9] is probably sterically stabilised by non-planar aromatic substituents; it fails to react with dienophiles and shows little colour.

On heating, compounds (3b and c) undergo smooth rearrangement. The conversion of (3b) into (14) proceeds slowly at 140°, and rearrangement of (3c) to (15) proceeds quickly at 110°. Both rearrangement products have $\lambda_{max.}$ *ca.* 270 nm. This excludes their formulation as alkyl shift products (16) and (17), which by analogy with compound (7) would absorb at *ca.* 313 nm. These rearrangements are probably concerted 1,5-sigmatropic acyl shifts and show the greater migratory aptitude of the imido-group in comparison with alkyl. Acheson [10] has discussed possible sigmatropic rearrangements of alkoxycarbonyl groups and noted that an ester group can migrate in preference to phenyl. For sigmatropic shifts in certain indenes phenyl migrates more readily than alkyl.[7] Subsequent to the preliminary communication of our own [11] and contemporary work,[12,13] a large number of ready 1,5-acyl shifts have been reported.[14]

The failure of (3b and c) to undergo closure to benzo-

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[8] D. S. Matteson and N. K. Hota, *J. Amer. Chem. Soc.*, 1971, 2893.

[9] M. S. Newmann, *J. Org. Chem.*, 1961, **26**, 2630.

[10] R. M. Acheson, *Accounts Chem. Res.*, 1971, 177.

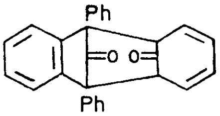
[11] D. W. Jones and G. Kneen, *Chem. Comm.*, 1971, 1356.

[12] J. A. Berson and R. G. Solomon, *J. Amer. Chem. Soc.*, 1971, **93**, 4620.

[13] R. A. Baylouny, *J. Amer. Chem. Soc.*, 1971, **93**, 4621.

[14] P. Schiess and P. Fünfschilling, *Tetrahedron Letters*, 1972, 5195 and references cited therein; P. Schmidt, R. W. Hoffmann, and J. Backes, *Angew. Chem. Internat. Edn.*, 1972, **11**, 13; H. Dürr, B. Heu, B. Ruge, and G. Scheppers, *J.C.S. Chem. Comm.*, 1972, 1257; M. Franck-Neumann and C. Buchecker, *Tetrahedron Letters*, 1972, 937; R. E. Bernard and H. Schechter, *ibid.*, p. 4529; T. Yamazaki and H. Schechter, *ibid.*, p. 4533; C. L. Habraken and P. Cohen-Fernandes, *J.C.S. Chem. Comm.*, 1972, 37; T. Yamazaki and H. Shechter, *Tetrahedron Letters*, 1973, 1417; M. Franck-Neumann and C. Buchecker, *Angew. Chem. Internat. Edn.*, 1973, **12**, 240.

cyclobutenes on irradiation thwarted our intention of obtaining information relating to the stereochemical inversion attending the decarbonylation (2) ⟶ (5). We therefore attempted to prepare the $[_{\pi}6 + _{\pi}4]$ adduct (18) which on monodecarbonylation would afford an *o*-quinonoid system more similar in geometry to the putative *o*-quinodimethane intermediate involved in the conversion (2) ⟶ (5). There was also the possibility that bisdecarbonylation of (18) would give a benzocyclodecene or a valence isomer derived therefrom. However reaction of tropone with (1) gave the naphthalene (19), presumably derived by initial $[_{\pi}4 + _{\pi}2]$ addition to give (20) which by 1,5-shifts of H^1 and H^2 and decarbonylation would give (19).



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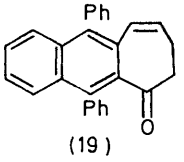

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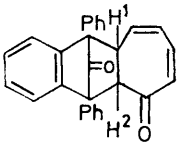

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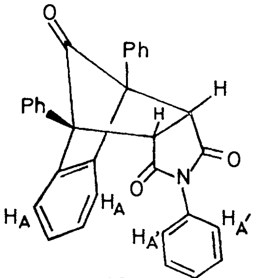

(21)

Configuration of N-*Phenyl- and* N-*Methyl-maleimide Adducts*.—The n.m.r. spectra of the adduct (21) [2] and related *N*-phenylmaleimide adducts [15-17] show a two-proton signal (τ *ca.* 3·6) attributed to the aromatic protons H_A which are located over the imide carbonyl groups. However the adduct (9b) and the related *endo*-*N*-methylmaleimide adduct (9c) have no shielded aromatic protons. Instead the NMe group which is located over the phenylene ring resonates at high field (τ 7·5) {*cf.* the methyl resonance in *N*-methylmaleimide (τ 6·93) and the *exo*-benzo[*c*]furan–*N*-methylmaleimide adduct (τ *ca.* 7)}.[18] These observations suggested that the shielded aromatic protons in the *N*-phenylmaleimide adducts were either the protons H_A' which lie over the phenylene ring, or the protons H_A which were shielded by the *N*-phenyl group rather than the carbonyl groups. To settle this point *N*-2,4,6-trideuteriophenylmaleimide was prepared from the corresponding deuteriated aniline [19] by the usual procedure,[20] and treated with 1,3-diphenylinden-2-one, 1-methyl-2-benzopyran-3-one, and 1-methylisoquinolin-3-one. The n.m.r. spectra of the derived adducts lacked the usual high-field resonance, showing that this is due to the protons H_A'. For these and other *N*-phenylmaleimide adducts the *endo*-configuration previously assigned is confirmed by correct identification of the signals due to the shielded aromatic protons. However the *N*-methylisoquinolin-3-one–maleic anhydride adduct was assigned the *exo*-configuration since its n.m.r. spectrum *lacked* signals corresponding to shielded aromatic protons.[21] In view of the present results and the exclusive *endo*-addition observed for closely related dienes it is likely that this assignment is erroneous.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified, i.r. spectra refer to Nujol mulls, u.v. spectra to ethanolic solutions, and n.m.r. spectra to solutions in deuteriochloroform measured with a Varian A60 spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light petroleum, b.p. 60—80°, and chromatography on silica to short-column chromatography [22] over Kieselgel G (Merck).

N-*Methylcyclohex*-1-*ene*-1,2-*dicarboximide* (10).—Cyclohex-1-ene-1,2-dicarboxylic anhydride [23] (1 g), xylene (30 ml), benzene (6 ml), and methylamine (1 ml; 33% w/w in ethanol) were boiled under reflux with azeotropic removal of water (4 h). Evaporation on a water-bath under reduced pressure gave a yellow oil which was distilled bulb-to-bulb (bath temp. 175°) at 14 mmHg to give the *imide* (10) (700 mg, 65%), m.p. 46—49° (from petroleum) (Found: M^+, 165·079. $C_9H_{11}NO_2$ requires *M*, 165·079), $\nu_{max.}$ 1759 and 1700 cm^{-1}, τ 6·99 (3H, s, NMe), 7·4—7·9 (4H, m), and 7·9—8·4 (4H, m), *m/e* 165 (M^+), 108, 80, and 79 (54, 100, 50, and 41%), m^* 70·65 (165 ⟶ 108) and 59·3 (108 ⟶ 80).

Diels–Alder Adducts of 1,3-*Diphenylinden*-2-*one*.—(i) *With* N-*methylcyclohex*-1-*ene*-1,2-*dicarboximide*. The dimer (2) (150 mg, 0·266 mmol), the imide (10) (96·5 mg, 0·585 mmol), and xylene (10 ml) were boiled in a nitrogen atmosphere (5 h). Evaporation under reduced pressure on a water-bath gave 1,2,3,4,4a,9,9a,10-*octahydro*-N-*methyl*-11-*oxo*-9,10-*diphenyl*-9,10-*methanoanthracene*-4a,9a-*dicarboximide* (9a) (180 mg, 79%), m.p. 225—226° (from dichloromethane–ethanol) (Found: C, 80·4; H, 5·65; N, 3·0. $C_{30}H_{25}NO_3$ requires C, 80·5; H, 5·6; N, 3·1%), $\nu_{max.}$ 1765 and 1700 cm^{-1}, τ 1·35—1·75 (4H, m, aromatic), 2·1—3·2 (10H, m, aromatic), 7·3—7·8 (5H, m, including NMe at 7·41), and 8·1—9·0 (6H, m), *m/e* 419, 334, and 282 (65, 100, and 26%), m^* 266·24 (419 ⟶ 334).

(ii) *With trimethylmaleimide*. The dimer (2) (200 mg), trimethylmaleimide [24] (150 mg), and xylene (10 ml) were boiled under reflux in a nitrogen atmosphere (18 h). Evaporation, and chromatography on silica in benzene gave 1,2,3,4-*tetrahydro*-N,2,3-*trimethyl*-9-*oxo*-1,4-*diphenyl*-1,4-*methanonaphthalene*-2,3-*dicarboximide* (9b) (250 mg, 86%), m.p. 178—180° (from ethanol) (Found: C, 80·0; H, 5·6; N, 3·6. $C_{28}H_{23}NO_3$ requires C, 79·8; H, 5·5; N,

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[15] M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, 1966, **88**, 4112.

[16] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 530, 536.

[17] D. W. Jones, *J. Chem. Soc.* (*C*), 1969, 1729.

[18] R. N. Warrener, *J. Amer. Chem. Soc.*, 1971, **93**, 2346.

[19] G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, *J. Amer. Chem. Soc.*, 1967, **89**, 3821.

[20] M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, *Org. Synth.*, 1961, **41**, 93.

[21] N. J. Mruck and H. Tieckelmann, *Tetrahedron Letters*, 1970, 1209.

[22] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

[23] M. E. Bailey and E. D. Amstutz, *J. Amer. Chem. Soc.*, 1956, **78**, 3828.

[24] D. E. Ames and T. F. Grey, *J. Chem. Soc.*, 1955, 631.

3·3%), $\nu_{max.}$ 1785, 1775, and 1705 cm^{-1}, τ 1·40—1·80 (4H, m, aromatic), 2·1—3·2 (10H, m, aromatic), 7·43 (3H, s, NMe), and 8·64 (6H, s), *m/e* 393, 309, 308, 282, 254, 252, and 215 (67, 28, 100, 69·5, 28, 28, and 25%), *m** 241·38 (393 $\longrightarrow$ 308).

(iii) *With* N-*methylmaleimide*. The dimer (2) (100 mg, 0·177 mmol), *N*-methylmaleimide (44 mg, 0·4 mmol), and xylene (7 ml) were boiled under reflux in a nitrogen atmosphere (15 h). Evaporation left a pink solid which after chromatography on silica in benzene–ether (97·5 : 2·5) gave 1,2,3,4-*tetrahydro*-N-*methyl*-9-*oxo*-1,4-*diphenyl*-1,4-*methanonaphthalene*-2,3-*dicarboximide* (9c) (75 mg, 56%), m.p. 240—242° (from dichloromethane–ethanol) (Found: C, 79·55; H, 4·85; N, 3·85. $C_{26}H_{19}NO_3$ requires C, 79·4; H, 4·9; N, 3·6%), $\nu_{max.}$ 1781 and 1704 cm^{-1}, τ 2·0—2·5 (10H, m, aromatic), 2·5—3·1 (4H, m, aromatic), 5·75 (2H, s), and 7·51 (3H, s), *m/e* 365, 281, 280, 279, 203, and 202 (64, 27, 100, 29·5, 20·5, and 28%).

(iv) *With* 2,3-*dimethylbut*-2-*ene*. The dimer (2) (150 mg), 2,3-dimethylbut-2-ene (150 mg), and degassed xylene (10 ml) in an evacuated tube were heated at 140° (48 h). Evaporation gave 1,2,3,4-*tetrahydro*-2,2,3,3-*tetramethyl*-1,4-*diphenyl*-1,4-*methanonaphthalen*-9-*one* (70 mg), m.p. 222—224° (from dichloromethane–ethanol) (Found: C, 88·15; H, 7·05. $C_{27}H_{26}O$ requires C, 88·5; H, 7·1%), $\nu_{max.}$ 1765 cm^{-1}, τ 1·6—1·9 (4H, m, aromatic), 2·2—2·8 (10H, m, aromatic), 9·01 (6H, s), and 9·05 (6H, s). More of this adduct (20 mg) was obtained by chromatography of the material obtained by evaporation of the mother liquor on silica in benzene–petroleum (7 : 3).

Photodecarbonylation of 1,3-*Diphenylinden*-2-*one Adducts*.—(i) *The* N-*phenylmaleimide adduct*. The adduct (100 mg) in dichloromethane (10 ml) in a quartz flask was irradiated with a medium-pressure mercury lamp (Osram MBW/V; 125 W with outer cover removed) at a distance of *ca.* 7 cm (9 h). Oxygen was excluded by boiling under reflux in a nitrogen atmosphere prior to photolysis, and by maintaining a slow nitrogen flow through the solution during photolysis (mercury bubbler at exit). Evaporation of the product and chromatography on silica in benzene–petroleum (3 : 1) gave the naphthalene (6) (30 mg, 32%), m.p. 294—295° (from dichloromethane–petroleum) (lit.,[25] 296—297·5°), $\nu_{max.}$ 1760 and 1715 cm^{-1}, $\lambda_{max.}$ 266, 305, 350, and 359 nm (ε 50,500, 12,050, 4200, and 4500). Continued elution with the same solvent gave the dihydronaphthalene (7) (45 mg, 48%), m.p. 203—207° (from dichloromethane–petroleum) (lit.,[25] 210—214°; lit.,[5] 180—185°), $\nu_{max.}$ 1754 and 1715 cm^{-1}, $\lambda_{max.}$ 238 and 313 nm (ε 20,320 and 15,260), τ 2·3—3·1 (19H, m, aromatic), 5·04 (1H, d, *J* 7 Hz), and 5·65 (1H, d, *J* 7 Hz).

(ii) *The* N-*methylcyclohex*-1-*ene*-1,2-*dicarboximide adduct* (9a). The adduct (9a) (130 mg) in benzene (15 ml) was irradiated as above with a water-cooled 100 W medium-pressure mercury lamp (Hanovia) (28 h). Evaporation under reduced pressure at 20° gave 1,2,3,4,4a,9a-*hexahydro*-N-*methyl*-9,10-*diphenylanthracene*-4a,9a-*dicarboximide* (3b) as yellow crystals (98 mg, 80%), m.p. 213—215° (from dichloromethane–ethanol) (Found: C, 82·7; H, 5·95; N, 3·35. $C_{29}H_{25}NO_2$ requires C, 83·0; H, 6·0; N, 3·3%), $\nu_{max.}$ 1755 and 1694 cm^{-1}, $\lambda_{max.}$ 278, 370, 392, 415, and 438 nm (ε 5600, 3000, 6000, 9450, and 8150), τ 2·48 (10H, m), 3·6—4·2 (4H, AA′BB′ system), 6·90 (3H, s), 8·0—8·50 (4H, m), and 8·50—9·00 (4H, m).

(iii) *The trimethylmaleimide adduct* (9b). The adduct (500 mg) was photolysed as above in benzene (15 ml) (24 h). Evaporation gave 2,3-*dihydro*-N,2,3-*trimethyl*-1,4-*diphenylnaphthalene*-2,3-*dicarboximide* (3c) (330 mg, 80%), m.p. 176—179° (from dichloromethane–ethanol) (Found: C, 82·5; H, 6·0; N, 3·6. $C_{27}H_{23}NO_2$ requires C, 82·4; H, 5·9; N, 3·6%), $\nu_{max.}$ 1765 and 1698 cm^{-1}, $\lambda_{max.}$ 438, 414, 392, 370, 272, and 220 nm (ε 7450, 8450, 5600, 2800, 5500, and 14,400), τ 2·47br (10H, s), 3·89 (4H, s), 6·85 (3H, s), and 8·78 (6H, s), *m/e* 393 (M^+), 308, 284, 282, and 215 (53, 100, 34, 34, and 28%).

(iv) *The tetramethylethylene adduct*. The adduct (70 mg) in benzene (10 ml) was irradiated as in (i) (6 h). Evaporation, and chromatography on silica in benzene–petroleum (1 : 3), gave o-*bis*-(2-*methyl*-1-*phenylprop*-1-*enyl*)*benzene* (11) (48 mg, 75%), m.p. 92—95° (from methanol at low temperature) (Found: C, 92·5; H, 7·6. $C_{26}H_{26}$ requires C, 92·3; H, 7·7%), τ 2·5—2·9 (14H, m), 8·33 (6H, s), and 9·23 (6H, s).

Oxidation of the Dipropenylbenzene (11).—The product (11) (5 mg), chromium trioxide (20 mg), and acetic acid (1·0 ml) were heated on a water-bath for 2 h. The mixture was then set aside for 14 h, diluted with water, and extracted with ether. The extract was washed with saturated sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated to give *o*-dibenzoylbenzene (3·5 mg, 83%), m.p. 144—146° (from ethanol), identical with an authentic sample [26] (mixed m.p. and i.r. spectrum).

Addition of Phthalazine-1,4-*dione to the* o-*Quinodimethane* (3c).—2,3-Dihydrophthalazine-1,4-dione (243 mg, 1·5 mmol) in acetonitrile (10 ml) at 0° was oxidised by addition of lead tetra-acetate (0·66 g, 1·5 mmol) added in portions with stirring (15 min). The filtered solution was added at 0° to a solution of the *o*-quinodimethane (3c) (90 mg, 0·23 mmol) in acetonitrile. After the green colour had faded (1 h), the solvent was evaporated off and the product chromatographed on silica in ether–benzene (1 : 3) to give 2,3,5,6,11,12-*hexahydro*-N,2,3-*trimethyl*-6,11-*dioxo*-1,4-*diphenyl*-5a,11a-*diaza*-5,12-*ethenonaphthacene*-2,3-*dicarboximide* [(12) or its stereoisomer] (63 mg, 50%), m.p. >310° (from dichloromethane–ethanol) (Found: C, 75·85; H, 4·95; N, 7·9. $C_{35}H_{27}N_3O_4$ requires C, 75·9; H, 4·9; N, 7·6%), $\nu_{max.}$ 1775, 1708, and 1640 cm^{-1}, $\lambda_{max.}$ 282·5 and 340 nm (ε 13,400 and 4290), τ 1·5 (2H, m), 2·10 (2H, m), 2·40 (10H, m), 3·28 (2H, m, HCN), 3·66 (2H, m, olefinic), 6·90 (3H, s), and 8·78 (6H, s), *m/e* 553 (M^+), 393, and 308 (24, 59, and 100%).

Continued elution gave the *isomeric adduct* (15 mg, 12%), m.p. >310° (from dichloromethane–ethanol) (Found: C, 76·05; H, 5·1; N, 7·65%), $\nu_{max.}$ 1785, 1715, and 1643 cm^{-1}, τ (90 MHz), 1·78 (2H, m), 2·3 (2H, m), 2·55 (10H, m), 3·34 (2H, m, HCN), 3·85 (2H, m, olefinic), 7·01 (3H, s), and 8·81 (6H, s).

Reaction of the o-*Quinodimethane* (3c) *with Moist Bromine*.—Compound (3c) (30 mg) in methylene chloride (10 ml) at −75° (CO_2–Me_2CO bath) was treated with bromine (13 mg) without exclusion of moisture (2 h). Evaporation gave 1,2,3,4-*tetrahydro*-N,2,3-*trimethyl*-1,4-*diphenyl*-1,4-*epoxynaphthalene*-2,3-*dicarboximide* (13) (18 mg, 48%), m.p. 178—180° (from chloroform–methanol) (Found: C, 79·1; H, 5·7; N, 3·45. $C_{27}H_{23}NO_3$ requires C, 79·4; H, 5·6; N, 3·4%), $\nu_{max.}$ 1765 and 1700 cm^{-1}, τ 2·1—2·9 (14H, m), 7·22 (3H, s), 8·87 (6H, s), *m/e* 270 and 139. Pyrolysis of

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[25] G. Quinkert, K. Opitz, W.-W. Weisdorff, and M. Finke, *Annalen*, 1966, **693**, 44.

[26] W. Baker, J. F. W. McOmie, G. A. Pope, and D. R. Preston, *J. Chem. Soc.*, 1961, 2965.

this product at 180° gave 1,3-diphenylbenzo[*c*]furan, identical (t.l.c.) with authentic material.[27]

Thermolysis of the o-*Quinodimethane* (3b).—The title compound (40 mg) and xylene (10 ml) were boiled under reflux in a nitrogen atmosphere (24 h). Evaporation gave 1,2,3,4,4a,10-*hexahydro*-N-*methyl*-9,10-*diphenylanthracene*-4a,10-*dicarboximide* (14) (30 mg, 75%), m.p. 188—189° (from dichloromethane–methanol) (Found: C, 82·8; H, 6·0; N, 3·4. $C_{29}H_{25}NO_2$ requires C, 83·0; H, 6·0; N, 3·3%), $\nu_{max.}$ 1772 and 1709 cm^{-1}, $\lambda_{max.}$ 275 nm (ε 9050), τ 2·1—3·4 (14H, m), 6·86 (3H, s), 7·2—7·7 (2H, m), and 8·1—9·2 (6H, m).

Thermolysis of the o-*Quinodimethane* (3c).—Compound (3c) (20 mg) and toluene (5 ml) were boiled under reflux in a nitrogen atmosphere (6 h). Evaporation gave 1,2-*dihydro*-N,2,3-*trimethyl*-1,4-*diphenylnaphthalene*-1,2-*dicarboximide* (15) (18 mg, 90%), m.p. 146—147° (from dichloromethane–methanol) (Found: C, 82·45; H, 6·05; N, 3·3. $C_{27}H_{23}NO_2$ requires C, 82·4; H, 5·9; N, 3·6%), $\nu_{max.}$ 1761 and 1697 cm^{-1}, $\lambda_{max.}$ 220, 234, and 270 nm (ε 19,000, 20,600, and 9290), τ 2·2—3·4 (14H, m), 6·87 (3H, s), 8·12 (3H, s), and 8·83 (3H, s).

Addition of 1,3-*Diphenylinden*-2-*one to Tropone*.—The dimer (2) (100 mg), tropone (140 mg), and xylene (10 ml) were boiled under reflux in a nitrogen atmosphere (100 h). Evaporation gave 7,8-*dihydro*-5,11-*diphenylcyclohepta*[b]-*naphthalen*-6-*one* (19) (70 mg, 50%), m.p. 257—258° (from chloroform–ethanol) (Found: C, 89·95; H, 5·6. $C_{27}H_{20}O$ requires C, 90·0; H, 5·6%), $\nu_{max.}$ 1693 cm^{-1}, $\lambda_{max.}$ 248, 300, and 308sh nm (ε 40,378, 11,456, and 10,435), τ 2·3—3·1 (14H, m), 3·68 (1H, d, *J* 11 Hz), 4·08 (1H, dt, *J* 11 and 5·5 Hz), and 6·95—7·75 (4H, m).

Photolysis of Compound (8).—Compound (8)[28] (40 mg, 0·106 mmol), in benzene (15 ml) was irradiated as for the adducts (9) with a water-cooled 100 W medium-pressure mercury lamp (Hanovia) (68 h). Evaporation under reduced pressure and chromatography of the residue on silica in benzene gave N,3,6-*triphenylphthalimide* (25 mg, 63%), m.p. 183—185° (from benzene–petroleum) (Found: C, 83·1; H, 4·55; N, 3·65. $C_{26}H_{17}NO_2$ requires C, 83·2; H, 4·6; N, 3·7%), $\nu_{max.}$ 1773 and 1717 cm^{-1}, τ 2·15—2·80 (m, aromatic).

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[27] M. P. Cava, M. J. Mitchell, and A. H. Deana, *J. Org. Chem.*, 1960, **25**, 1481.

[28] D. W. Jones, *J.C.S. Perkin I*, 1973, 1951.