# o-Quinonoid Compounds. Part 18.[1] Stabilised 2,3-Naphthoquinodimethanes via Transient 1,3-Diphenylbenz[f]inden-2-one

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1,3-Diphenylbenz[f]inden-2-one (8) can be reversibly generated by thermolysis of its formal ($_\pi 4_s + _\pi 4_s$)-dimer (11) which is itself available in 5 steps from benz[f]indan-1,3-dione; (8) adds stereospecifically to cis- and trans-but-2-ene. Photodecarbonylation of the adducts (23), (21), and (22) derived by trapping (8) with norbornadiene, trimethylmaleimide, and the dienophile (24) gives the sterically stabilised 2,3-naphthoquinodimethanes (29), (25), and (26) respectively. These are long-lived in fluid solution at 20 °C and were characterised by u.v.–visible spectroscopy and as their adducts with 4-phenyltriazoline-3,5-dione (PTD). 1,3,4,9-Tetraphenylbenz[f]inden-2-one (37) generated by reaction of its dibromide (10; X = O, Y = Br) with sodium iodide forms the formal ($_\pi 6_s + _\pi 6_s$)-dimer (35). Dissociation of (35) in the presence of N-phenylmaleimide gives the adduct (15).
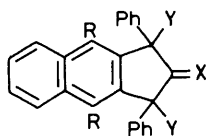
Our interest in inden-2-ones (1) was in part kindled by the possibility that they might be better represented as the biradicals (2) or the related oxyallyls (3).[2] Hückel MO calculations appeared to support this view for they indicated that the HOMO and LUMO of (1) have the symmetries and energies depicted in (4) and (5) respectively. Comparison of these orbitals with the HOMO (6) and LUMO (7) of o-quinodimethane suggests that incorporation of a keto group into o-quinodimethane to give (1; R = H) leaves the HOMO (6) unperturbed but so strongly stabilised the LUMO (7) that it becomes the HOMO (4) of inden-2-one. As in related calculations[3] it is likely that localisation of the double bonds in (1; R = H) prevents this situation from actually arising. The diphenyl derivative (1; R = Ph) adds 1,2- to cyclopentadiene and not 1,4- as would be expected for a molecule with the HOMO (4) and LUMO (5). Contrary to the simple calculation (5) in the HOMO and (4) the LUMO of (1; R = H), but the HOMO–LUMO energy gap will be small as in cyclobutadiene, cyclopentadienone, and related antiaromatic species. Nevertheless (1; R = Ph) shows no biradical character. It adds stereospecifically to dimethyl maleate and dimethyl fumarate and has as its principal eccentricity the tendency to dimerise by a formal ($_\pi 4_s + _\pi 4_s$)-addition.[2] Since the HOMO–LUMO energy gap in 2,3-naphthoquinodimethane is smaller (0.34 β) than that in o-quinodimethane (0.59 β) the HOMO–LUMO gap in the benz[f]inden-2-ones, e.g. (8), would be expected to be very small, so that biradical or zwitterionic character might be more highly developed. We describe the generation and properties of (8) and its use in the preparation of some remarkably stable 2,3-naphthoquinodimethanes.[1b]

The 2-oxime of benz[f]indan-1,2,3-trione was prepared by reaction of benz[f]indan-1,3-dione with nitrous acid. Reaction of this oxime with phenylmagnesium bromide, or better phenyl-lithium, gave a mixture of the stereoisomeric diols (9; X = NOH, Y = OH). Reduction of this mixture with constant boiling hydriodic acid in acetic acid on a steam-bath gave the ketone (9; X = O, Y = H) which, with bromine in carbon tetrachloride (20 °C; 17 h), gave the dibromo-ketone (9; X = O, Y = Br). With sodium iodide in boiling acetone the dibromide afforded the insoluble dimer (11) (96% yield) of (8). The structure of the dimer is proposed by analogy with the dimer of 1,3-diphenylinden-2-one.[2] Like the latter, (11) shows carbonyl absorption at ca. 1 770 cm⁻¹ and no band at ca. 1 700 cm⁻¹ which would be expected for the enone system of a dimer of the Diels-Alder type (12). Moreover the dimer is colourless whereas (12) would be expected to be coloured. As
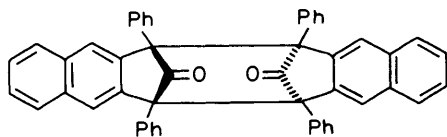

(1)   (2)   (3)

(4) $E = +0.443\beta$ (5) $E = +0.295\beta$

(6) $E = +0.295\beta$ (7) $E = -0.295\beta$ (8)
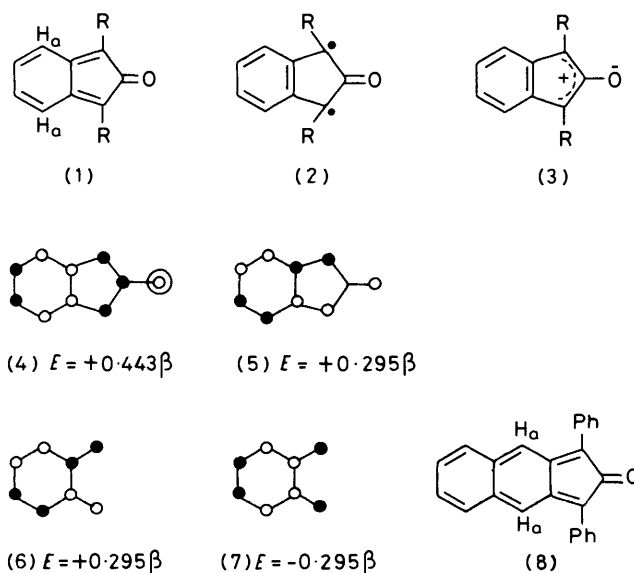
for the dimer of 1,3-diphenylinden-2-one, (11) showed a strong M/2 peak in its mass spectrum and gave adducts derived from the monomer upon heating with various olefins. The insolubility of (11) prevented the measurement of its ¹H n.m.r. and ¹³C n.m.r. spectra. The ¹H n.m.r. spectrum of the more-soluble dimer of 1,3-diphenylinden-2-one suggested an anti-stereochemistry for that compound.[2] Structure (11) is derived by a formal ($_\pi 4_s + _\pi 4_s$)-dimerisation of (8). Such a dimer could arise via the biradical (13) or by initial formation of the Diels–Alder dimer (12) followed by a formal 1,3-shift (12; arrows). The latter shift could either involve the biradical intermediate (13) or be of the concerted-forbidden type.[4] The anti-stereochemistry tentatively assigned to the dimer (11) is that which would arise by a suprafacial–retention rearrangement of the endo-dimer (12).

Although (1; R = Ph) generated by iodide reduction of its dibromide could be intercepted by cyclopentadiene (ratio dimer : adduct : : 1 : 2.33) attempts to trap (8) with cyclopentadiene during analogous reduction of (9; X = O, Y = Br) gave only the dimer (11). If the HOMO–LUMO energy gap in (8) is indeed smaller than that in (1; R = Ph) the former would be expected to dimerise more rapidly. That the anti-
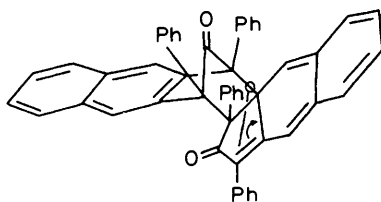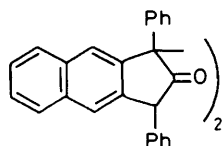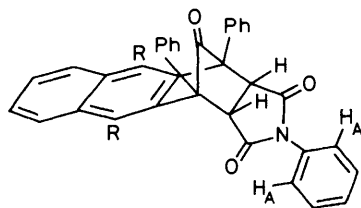
(9) R = H
(10) R = Ph

(11)

(16) $R^1 = R^4 = CO_2Me$; $R^2 = R^3 = H$
(17) $R^1 = R^3 = CO_2Me$; $R^2 = R^4 = H$
(18) $R^1 = R^3 = Me$; $R^2 = R^4 = H$
(19) $R^1 = R^3 = H$; $R^2 = R^4 = Me$
(20) $R^1 = R^4 = Me$; $R^2 = R^3 = H$
(21) $R^2 = R^4 = Me$; $R^1, R^3 = CO.NMe.CO$
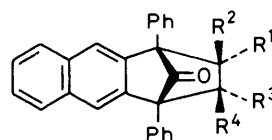(22) $R^2, R^4 = -[CH_2]_4^-$; $R^1, R^3 = CO.NMe.CO$

(12)

(13)

(14) R = H
(15) R = Ph

cipated lowering of the LUMO of (8) does not equally accelerate its addition to cyclopentadiene can be attributed to *two* enhanced HOMO–LUMO interactions for the dimerisation of (8) but only one such improved interaction in its addition to cyclopentadiene. It is hard to assess the possible role of steric effects in this competition as non-coplanar phenyl substituents may retard *endo*-addition to 2,3-naphthoquinodimethanes more than *endo*-addition to the corresponding *o*-quinodimethanes.[5] However steric effects might be expected to be more acutely felt in the dimerisation whatever the mechanism of that process.

As judged by trapping experiments with various olefins (11) reversibly dissociates into (8) in *o*-dichlorobenzene at *ca.* 160 °C. In this way the *N*-phenylmaleimide adduct (14) was prepared in 66% yield. The ^{1}H n.m.r. spectrum of the adduct showed two strongly shielded aromatic protons (H_A) at δ 6.0—6.2 in agreement with the assigned *endo*-configuration. In search of any biradical character for (8) the stereospecificity of its addition to olefins was carefully examined. Trapping with dimethyl fumarate was stereospecific giving (16) and no trace of the maleate adduct (17). Initial trapping experiments with dimethyl maleate suggested a marked non-stereospecificity, the adducts (16) and (17) being produced in approximately equal quantities. However this apparent non-stereospecificity was traced to the presence of *ca.* 1.5% dimethyl fumarate in the dimethyl maleate which was

employed in very large excess in the trapping experiment. The implied much faster addition of (8) to dimethyl fumarate than to dimethyl maleate was substantiated by dissociation of (11) in the presence of equal quantities of the two dienophiles; only the fumarate adduct (16) was detected in the 300 MHz ^{1}H n.m.r. spectrum of the product. Even dimethyl maleate purified by preparative g.l.c. and containing <0.2% of the fumarate ester gave rise to a noticeable quantity of the fumarate adduct (16). It is usual for fumarate esters to react *ca.* 100 times faster than maleate esters in the Diels-Alder reaction;[6] steric factors in the *cis*-diester impede simultaneous conjugation of *both* activating carbonyl groups with the dienophilic double bond. Dimethyl maleate purified by preparative g.l.c. adds stereospecifically to (1; R = Ph) so that k_{trans}/k_{cis} is larger for (8) than (1; R = Ph). This is understandable if the transition state for addition to (8) is more sterically hindered than that for addition to (1; R = Ph). The phenyl groups in (8) may depart from the plane of the enone system to a greater extent than those in (1; R = Ph) since the hydrogens H_A occupy *peri*-positions on a naphthalene-like ring (buttressing effect). In related phenyl substituted *o*-quinonoid dienes departure of the phenyl substitutes from the plane of the rest of the molecule has been shown to lead to *exo*-selective additions[5b] and the *exo*-selectivity increases in going from *o*-quinodimethane to 2,3-naphthoquinodimethane systems.[5a] Increased departure of phenyl groups from the molecular plane in going from (1; R = Ph) to (8) will therefore lead to a reduced rate of *endo*-addition to the latter. This effect will presumably be most acute for the more sterically demanding dimethyl maleate; *exo*-addition of dimethyl maleate to (1; R = Ph) and (8) has not been observed.

After preliminary experiments had shown that (1; R = Ph) adds to *cis*- and *trans*-but-2-ene stereospecifically and at *similar rates* these olefins were employed in the stereospecificity test. Dissociation of (11) in the presence of *cis*-but-2-ene gave the *endo*- and *exo*-adducts (18) and (19) and no detectable quantity of the *trans*-but-2-ene adduct (20) (90 MHz ^{1}H n.m.r. spectrum). The *trans*-but-2-ene adduct (20) was also formed stereospecifically. The stereospecificity observed here indicates that (8) reacts in a *singlet state* and that it undergoes concerted addition to these olefins.

Observation of Sterically Stabilised 2,3-Naphthoquinodimethanes.—At the time when this study began no simple 2,3-naphthoquinodimethane had been observed.* Since we had prepared some remarkably stable derivatives of *o*-quinodimethane by photodecarbonylation and photode-

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* R. L. Wife, Ph.D. Thesis, Leeds, 1972.

(23)

(24)

(25) $R^1 = R^2 = Me$; $R^3 = H$
(26) $R^1, R^2 = -[CH_2]_4-$; $R^3 = H$
(27) $R^1 = R^2 = Me$; $R^3 = Ph$

(28)

(29)

(30)

(31)

(32)

(33) X = H_2
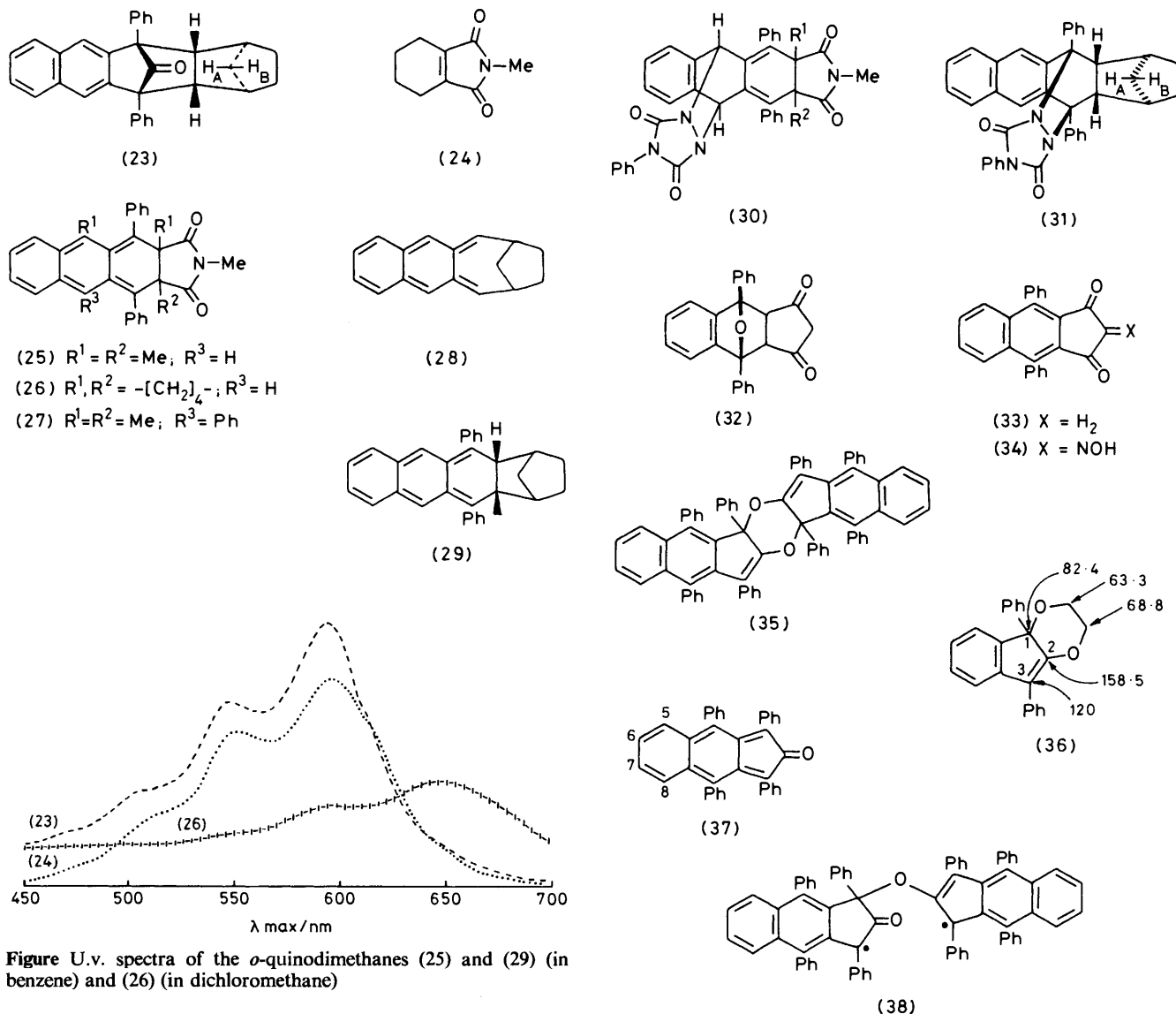(34) X = NOH

(35)

(36)

(37)

(38)

Figure U.v. spectra of the *o*-quinodimethanes (25) and (29) (in benzene) and (26) (in dichloromethane)

carboxylation [7] it was of interest to attempt the photo-decarbonylation of adducts derived from (8). Dissociation of the dimer (11) in the presence of norbornylene gave a mixture of the *endo*- and *exo*-adducts in which the *endo*-adduct (23) predominated (*endo : exo* ratio 4 : 1); the protons H_A and H_B in the *endo*-adduct appear at high field (δ -0.20 and 0.25 respectively) and clearly distinguish this compound from its *exo*-isomer for which these protons resonate at δ 1.80—2.00. The trimethylmaleimide adduct (21) and the adduct (22) derived from the dienophile (24) were similarly prepared from the dimer (11). Irradiation of solutions of the adducts (21) and (22) through quartz with a medium-pressure mercury lamp gave deep blue solutions of the 2,3-naphthoquino-dimethanes (25) and (26); the long wavelength u.v. bands of these solutions are shown in the Figure. This absorption shows very similar vibrational fine structure to the long wave-length bands subsequently measured for 2,3-naphthoquino-dimethane [8] and the derivative (28),[9] but (25) and (26) have $\lambda_{max.}$ *ca.* 50 nm to longer wavelength. The derivatives (25) and (26) survive for longer than 1 h in fluid solutions at 20 °C. They are therefore much more stable than either 2,3-naph-thoquinodimethane itself or the somewhat more stable derivative (28), neither of which survive above -75 °C in fluid solution. The stability of the 2,3-naphthoquinodi-

methanes (25) and (26) is attributed to protection of the usually reactive ring-c diene system by the phenyl and other ring-c substituents. It is likely that the phenyl groups are prevented from effective conjugation with the naphthoquinonoid system owing to steric clash with the ring-b hydrogens and the other ring-c substituents. The phenyl groups therefore prefer to lie orthogonal to the quinonoid system with their *ortho*-hydrogens projecting above and below the ring-c diene system. This explanation is supported by the u.v. absorption (Figure $\lambda_{max.}$ 648 nm) observed for the 2,3-naphthoquinodimethane (29) formed upon photodecarbonylation of (23) in benzene solution. The reduced number of ring-c substituents in (23) would be expected to permit a greater degree of conjugation of the phenyl groups with the 2,3-naphthoquinonoid system. The stability of the derivatives (25) and (26) does not match that of the corresponding *o*-quinodimethanes [(25) and (26) lacking ring-A] which are isolable and stable in air.[7] This relative instability is associated with the less protected ring-B diene system which is *o*-quinonoid in (25) and (26). Blue solutions of the derivatives (25) and (26) may be titrated to a colourless end-point with 4-phenyltriazoline-3,5-dione (PTD) to give adducts, *e.g.* (30), derived by addition to the ring-B diene system. Prolonged irradiation of (26) gives a ($_\pi 4_s +$

$\pi 4_s$)-dimer in which two monomer units (26) have joined using their ring-B diene systems. In (29) a greater degree of coplanarity of the phenyl groups with the 2,3-naphthoquinonoid system is associated with increased reactivity of the ring-C diene system; titration of (29) with PTD gives the ring-C adduct (31) in which H_A and H_B are strongly shielded by the naphthalene ring (δ −1.10 and 0.20 respectively).

In an effort to protect the vulnerable ring-B diene system in (25) and (26) we sought to prepare the tetraphenyl derivative (27). Reaction of 1,3-diphenylbenzo[c]furan with cyclopent-4-ene-1,3-dione gave the adduct (32) in good yield and acid-catalysed dehydration of (32) gave the desired naphthalene (33). This was converted into the oxime (34) (Bu^{n}ONO–EtOH–HCl) which with phenyl-lithium gave the dihydroxy-oxime (10; X = NOH, Y = OH). Reduction of the latter (HI–HOAc) and bromination of the resulting ketone (10; X = O, Y = H) gave the dibromo-ketone (10; X = O, Y = Br). Reduction of the dibromo-ketone with sodium iodide in boiling acetone gave a dimer of the supposed intermediate 1,3,4,9-tetraphenylbenz[f]inden-2-one. This lacked the high frequency carbonyl absorption characteristic of dimers like (11) and (12). The new dimer type is allocated structure (35) which agrees with the presence of enol-ether absorption (1 640 cm^{-1}) in its i.r. spectrum and the presence in its ^{13}C spectrum of peaks at δ 87.3 (C-1), 121.9 (C-3), and 159.5 p.p.m. (C-2). The ^{13}C spectrum of the known [10] compound (36) was run for comparison; C-1 resonates at δ 82.4 and C-3 and C-2 at δ 120 and 158.5 respectively. On heating with N-phenylmaleimide the dimer (35) gave the adduct (15) of tetraphenylbenz[f]inden-2-one. It is likely that the phenyl substituents at C-4 and C-9 in (37) so reduces the accessibility of these C-1 and C-3 that only the very small oxygen atom of a second molecule of (37) can attack them. This could lead to the biradical intermediate (38) which could readily close to the dimer (35). The same steric inaccessibility of C-1 and C-3 in (37) may account for our inability to prepare its trimethylmaleimide adduct; upon heating (35) and the dienophile together the only product isolated was the ketone (10; X = O, Y = H) which may derive from (37) by hydrogen transfer from the dienophile.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified i.r. spectra refer to Nujol mulls and ^{1}H n.m.r. spectra refer to solutions in deuteriochloroform measured with a Perkin-Elmer R32 spectrometer (90 MHz) or a Perkin-Elmer R 12 spectrometer (60 MHz). ^{13}C Spectra were determined in deuteriochloroform on a JEOL FX 90Q spectrometer. Low-resolution mass spectra were obtained with a Kratos MS 25 instrument and accurate mass measurements were made using a Kratos MS 9/50 instrument. Where accurate mass measurement was used to establish molecular formulae the purity of the sample was checked by t.l.c. in more than one solvent system as well as by n.m.r. measurements and for crystalline material by crystallisation to constant m p. Chromatography on silica refers to short-column chromatography over Kieselgel G (Merck).[11] Ether refers to diethyl ether throughout.

Benz[f]*indan-1,2,3-trione 2-Oxime.*—Benz[f]indan-1,3-dione (7.70 g) was dissolved in dilute sodium hydroxide solution (2M; 332 ml) and the solution cooled to 0 °C. Sodium nitrite (2.62 g) was dissolved in the rapidly stirred solution and hydrochloric acid (2M; 400 ml) added dropwise during 30 min. The filtered product was washed with water, dried *in vacuo*, and recrystallised from ethanol–ethyl acetate to give benz[f]indan-1,2,3-trione 2-oxime (8.80 g, 90%), m.p. 228—231 °C (Found:

C, 69.45; H, 3.15; N, 6.3. $C_{13}H_7NO_3$ requires C, 69.4; H, 3.1; N, 6.2%), $v_{max.}$ 3 400—3 100, 1 745, 1 700, 1 615, 1 600, 1 585, 1 100, and 970 cm^{-1}; m/z 225 (M), 224, 209, 208, and 196 (12, 17, 21, 25, and 100%).

1,3-Dihydroxy-1,3-diphenylbenz[f]*indan-2-one 2-Oxime* (9; X = NOH, Y = OH).—(a) *Using phenylmagnesium bromide.* Benz[f]indan-1,2,3-trione 2-oxime (9.75 g) was added in portions to phenylmagnesium bromide [from bromobenzene (27.3 g) and magnesium (4.13 g)] in ether (200 ml) and benzene (350 ml) at 20 °C with stirring in a nitrogen atmosphere. The mixture was boiled under reflux (3 h), diluted with benzene (200 ml), cooled to 20 °C, and washed with saturated aqueous ammonium chloride and water, and then dried (Na$_2$SO$_4$), and evaporated to *ca.* 100 ml. When set aside at 20 °C the solution deposited 1,3-*dihydroxy*-1,3-*diphenylbenz*[f]*indan*-2-*one* 2 *oxime* (4.2 g, 25%), m.p. 144—147 °C (from benzene-petroleum) (Found: C, 79.0; H, 5.1; N, 4.1. $C_{25}H_{19}NO_3$ requires C, 78.7; H, 5.0; N, 3.7%), $v_{max.}$ 3 500, 3 600—3 200, 1 600, 1 170, 1 060, 890, 750, and 700 cm^{-1}.

(b) *Using phenyl-lithium.* Benz[f]indan-1,2,3-trione 2-oxime (200 mg) was added in portions to phenyl-lithium [from bromobenzene (2.52 g) and lithium shot (0.12 g)] in ether (20 ml) at 0 °C with stirring in a nitrogen atmosphere. After the final addition the mixture was stirred for a further 5 min, quenched with water, and the organic layer dried (MgSO$_4$), evaporated, and the residue chromatographed on silica in benzene–ether (9 : 1) to give the oxime as a separable mixture of two stereoisomers (93 and 53 mg respectively; 43%). The individual stereoisomers each gave 1,3-diphenyl-benz[f]-indan-2-one on reduction as described below.

1,3-Diphenylbenz[f]*indan-2-one* (9; X = O, Y = H).—1,3-Dihydroxy-1,3-diphenylbenz[f]indan-2-one 2-oxime (0.70 g), hydriodic acid (d 1.7, 6.38 g, freshly distilled from red phosphorus in a nitrogen atmosphere), red phosphorus (*ca.* 150 mg), and acetic acid (21 ml) were stirred vigorously at 100 °C (steam bath) for 3 h under nitrogen. The product was combined with that of an identical experiment. The combined products were diluted with methylene chloride, and the organic layer washed with potassium iodide solution and water, and then dried (Na$_2$SO$_4$). Evaporation of the solvent gave 1,3-*diphenylbenz*[f]*indan-2-one* (1.02 g, 73%), m.p. 155—160 °C (from benzene–ether) (Found: C, 90.15; H, 5.45. $C_{25}H_{18}O$ requires C, 89.9; H, 5.4%), $v_{max.}$ 1 760, 1 600, 750, 720, and 700 cm^{-1}; δ(60 MHz) 7.9—7.1 (16 H, m, aromatic), 4.94br (2 H, s, benzylic); m/z 334 (M), 306, 289, and 228 (54, 84, 13, and 100%).

1,3-Dibromo-1,3-diphenylbenz[f]*indan-2-one* (9; X = O, Y = Br).—1,3-Diphenylbenz[f]indan-2-one (1.75 g) and bromine (1.69 g) and carbon tetrachloride (150 ml) were stirred at 20 °C (17 h). Evaporation of solvent at 30 °C under reduced pressure and crystallisation of the product from benzene-petroleum gave 1,3-*dibromo*-1,3-*diphenylbenz*[f]*indan-2-one* (2.2 g, 83%), m.p. 158—162 °C (Found: C, 61.15; H, 3.3; Br, 32.9. $C_{25}H_{16}Br_2O$ requires C, 61.0; H, 3.3; Br, 32.6%), $v_{max.}$ 1 770, 1 080, 870, and 720 cm^{-1}; δ(60 MHz) 7.7—6.5 (16 H, aromatic).

The Dimer of 1,3-*Diphenylbenz*[f]*indan-2-one* (11).—1,3-Dibromo-1,3-diphenylbenz[f]indan-2-one (1.0 g), sodium iodide (1.78 g), and dry acetone (150 ml) were boiled under reflux in a nitrogen atmosphere (15 h). The mixture was cooled to 20 °C, diluted with methylene chloride (250 ml), and the organic layer washed with sodium thiosulphate solution and water, and then dried (Na$_2$SO$_4$) and evaporated. Trituration of the residue with benzene gave the *dimer* of

1,3-diphenylbenz[f]indan-2-one (650 mg, 96%), m.p. 248—258 °C (from methylene chloride–methanol (Found: C, 90.0; H, 4.8. $C_{50}H_{32}O_2$ requires C, 90.4; H, 4.8%); $\nu_{max.}$ 1 770, 1 600, 1 050, 870, 750, 740, 730, and 700 cm^{-1}; m/z 664 (M), 636 (M − CO), 608 (M − 2CO), 332 (M/2), and 303 (6.6, 4.3, 3.3, 77, and 100%).

Dissociation of the 1,3-Diphenylbenz[f]inden-2-one Dimer in the Presence of Traps.—(a) N-Phenylmaleimide (21 mg) the dimer of 1,3-diphenylbenz[f]inden-2-one (40 mg) and o-dichlorobenzene (5 ml, distilled from P_2O_5) were heated at 155—160 °C under a nitrogen atmosphere with stirring (2.5 h). The mixture was evaporated to dryness at 100 °C under reduced pressure and the residue chromatographed on silica (20 g) in benzene to give the endo-1,3-*diphenylbenz*[f]*inden-2-one-N-phenylmaleimide adduct* (14) (40 mg, 66%), m.p. 276—279 °C (from CH_2Cl_2–methanol) (Found: C, 83.25; H, 4.4; N, 3.0. $C_{35}H_{23}NO_3$ requires C, 83.1; H, 4.6; N, 2.8%); $\nu_{max.}$ 1 790, 1 775, 1 705, 1 200, 750, 725, and 700 cm^{-1}; δ(60 MHz) 8.0—7.2 (16 H, m, aromatic), 7.15—6.85 (3 H, m, aromatic), 6.2—6.0 (2 H, m, aromatic), 4.35 (2 H, s, methine); m/z 477 (M − CO) and 330 (24 and 100%), m* at 386.

(b) Trimethylmaleimide (400 mg), the dimer of 1,3-diphenylbenz[f]inden-2-one (150 mg), and o-dichlorobenzene (22 ml, distilled from P_2O_5), were heated at 155—160 °C (23.5 h) in a nitrogen atmosphere with stirring. Evaporation of solvent at 100 °C under reduced pressure and trituration of the residue with CH_2Cl_2–MeOH gave the endo-1,3-*diphenylbenz*[f]*inden-2-one–trimethylmaleimide adduct* (21) (119 mg, 56%), m.p. 282—285 °C (from CH_2Cl_2–MeOH) (Found: C, 81.4; H, 5.4; N, 2.8. $C_{32}H_{25}NO_3$ requires C, 81.55; H, 5.3; N, 3.0%), $\nu_{max.}$ 1 755, 1 695, 1 610, 1 310, and 750 cm^{-1}; δ(60 MHz) 8.5—8.25 (4 H, m, aromatic), 7.80—7.20 (12 H, m, aromatic), 2.37 (3 H, s, NMe), and 2.40 (6 H, s); m/z 471 (M), 443 (M − CO), 358 and 332 (1.5, 74, 100, and 81%). The mother liquor obtained by crystallisation of the adduct yielded a further quantity of the adduct (58 mg, 27%) after chromatography on silica in benzene.

(c) N-Methylcyclohex-1-ene-1,2-dicarboximide (70 mg), the 1,3-diphenylbenz[f]inden-2-one dimer (100 mg), and o-dichlorobenzene (15 ml) were heated at 160—170 °C (22 h) in a nitrogen atmosphere. The product was evaporated at 100 °C under reduced pressure and the residue chromatographed on silica in benzene to give the 1,3-*diphenylbenz*[f]-*inden-2-one-N-methylcyclohex-1-ene-1,2-dicarboximide adduct* (22) (65 mg), m.p. 232—235 °C (from CH_2Cl_2–MeOH) (Found: C, 82.0; H, 5.6; N. 3.15. $C_{34}H_{27}NO_3$ requires C, 82.1; H, 5.4; N, 2.8%); $\nu_{max.}$ 1 780, 1 770, and 1 705 cm^{-1}; δ(90 MHz) 8.5—7.0 (16 H, m), 2.6—2.2 (5 H, m, NMe and CH_2), 1.8—1.0 (6 H, m); m/z 497 (M), 469 (M − CO), 384, and 332 (5, 100, 100, and 53%).

(d) 2-Norbornene (500 mg), the 1,3-diphenylbenz[f]inden-2-one dimer (50 mg), and deoxygenated o-dichlorobenzene (5 ml) were heated at 160 °C (22 h) in a bomb in a nitrogen atmosphere. Evaporation of the solvent under reduced pressure at 100 °C and chromatography of the residue on silica in benzene–petroleum (9 : 1) gave the exo-*adduct* (10 mg, 15.6%), m.p. 225—227 °C, from chloroform–ethanol (Found: C, 89.9; H, 6.25. $C_{32}H_{26}O$ requires C, 90.1; H, 6.1%), $\nu_{max.}$ 1 770 cm^{-1}; δ(90 MHz) 8.00—7.00 (16 H, m, aromatic), 2.50 (4 H, m), and 2.00—1.80 (6 H, m); m/z 426 (M), 398 (M − CO), 357, and 330 (39, 100, 30 and 28%). Further elution of the column gave the endo-*adduct* (23) (40 mg, 62.3%), m.p. 305—307 °C, from chloroform–ethanol (Found: C, 89.85; H, 6.15), $\nu_{max.}$ 1 775 cm^{-1}; δ(90 MHz) 7.85—7.55 (2 H, m, aromatic), 7.55—7.00 (14 H, m, aromatic), 2.95 (2 H, s), 2.47 (2 H, s), 1.80—1.30 (4 H, m), 0.25 (1 H, d, J 8

Hz), and −0.20 (1 H, d, J 8 Hz); m/z 398 (M − CO), 357, and 330 (100, 31 and 34%).

(e) trans-But-2-ene (2 ml), the 1,3-diphenylbenz[f]inden-2 one dimer (50 mg), and deoxygenated o-dichlorobenzene (5 ml) were heated at 160 °C (22 h) in a bomb in a nitrogen atmosphere. Evaporation of the solvent under reduced pressure at 100 °C and chromatography of the residue on silica in benzene–petroleum (4 : 1) gave the trans-*adduct* (20) (30 mg, 51%), m.p. 150—154 °C, from methylene chloride–methanol (Found: C, 89.65; H, 6.25. $C_{29}H_{24}O$ requires C, 89.65; H, 6.2%), $\nu_{max.}$ 1 775 cm^{-1}; δ(90 MHz) 7.90—6.60 (16 H, m, aromatic), 2.80—2.50 (1 H, m, methine), 2.10—1.80 (1 H, m, methine), 1.10 (3 H, d, J 7 Hz), and 0.90 (3 H, d, J 7 Hz); m/z 388 (M), 345, 330, 329, 328, and 253 (1, 100, 53, 31, 15, 9, and 21%).

(f) cis-But-2-ene (2 ml), the 1,3-diphenylbenz[f]inden-2-one dimer (50.5 mg), and deoxygenated o-dichlorobenzene (5 ml) were heated at 160 °C (22 h) in a bomb in a nitrogen atmosphere. Evaporation of the solvent under reduced pressure at 100 °C and chromatography of the residue on silica using benzene gave the cis-exo-*adduct* (19) (20 mg, 34%), m.p. 206—208 °C, from chloroform–methanol (Found: C, 89.3; H, 6.35. $C_{29}H_{24}O$ requires C, 89.65; H, 6.2%), $\nu_{max.}$ 1 770 cm^{-1}; δ(90 MHz) 8.00—7.10 (16 H, m, aromatic), 2.90—2.50 (2 H, m, methine), and 9.04 (6 H, m); m/z 388 (M), 360 (M − CO), 345, 330, 329, 328, and 253 (9, 100, 50, 27, 13, 7, and 18%). Further elution of the column gave the cis-endo-*adduct* (18) (24 mg, 41%), m.p. 230—232 °C, from chloroform–ethanol (Found: C, 89.7; H, 6.45%); $\nu_{max.}$ 1 777 cm^{-1}; δ(90 MHz) 7.90—7.70 (2 H, m, aromatic), 7.60—7.30 (14 H, m, aromatic), 3.60—3.30 (2 H, m, methine), and 0.80 (6 H, m); m/z 388 (M), 360 (M − CO), 345, 330, 329, 328, and 253 (1, 100, 44, 25, 12, 7, and 13%).

(g) Dimethyl fumarate (440 mg), the dimer of 1,3-diphenylbenz[f]inden-2-one (100 mg), and o-dichlorobenzene (20 ml) were heated at 155—160 °C in a nitrogen atmosphere with stirring (20 h). The residue obtained by evaporation at 100 °C under reduced pressure was chromatographed on neutral alumina (Woelm, grade III) in benzene to give the 1,3-diphenylbenz[f]inden-2-one–dimethyl fumarate adduct (16) (38 mg, 27%), m.p. 208—211 °C (from CH_2Cl_2–MeOH) (Found: C, 78.45; H, 5.3. $C_{31}H_{24}O_5$ requires C, 78.15; H, 5.0%); $\nu_{max.}$ 1 785 and 1 725 cm^{-1}; δ(60 MHz) 8.0—7.2 (16 H, m, aromatic), 4.27 (1 H, d, J 4.5 Hz, methine), 3.73 (1 H, d, J 4.5 Hz, methine), and 3.5 (6 H, s); m/z 476, 462, 448, 416, 388, and 357 (3, 11, 10.5, 7.5, 100, and 80%). Further elution of the column gave 2,3-dibenzoylnaphthalene (40 mg) identical with an authentic specimen.

(h) Dimethyl maleate (1.65 g), the dimer of 1,3-diphenylbenz[f]inden-2-one (100 mg), and o-dichlorobenzene (20 ml were heated at 160 °C in a nitrogen atmosphere with stirring (21 h). The residue obtained by evaporation at 100 °C under reduced pressure was chromatographed on silica in benzene to give the endo-1,3-*diphenylbenz*[f]*inden-2-one–dimethyl maleate adduct* (18) (40 mg, 28%), m.p. 214—216 °C (from benzene–petroleum) (Found: C, 78.35; H, 5.15%); $\nu_{max.}$ 1 785, 1 755, 1 740, and 1 725 cm^{-1}; δ(60 MHz) 8.1—7.2 (16 H, m, aromatic), 4.37 (2 H, s, methine), and 3.5 (6 H, s); m/z 476, 448 (M − CO), 416, 388, and 357 (3.9, 58, 3.5, 79, and 100%). The ¹H n.m.r. spectrum of the crude reaction product from this and related dimethyl maleate additions indicated the presence of the dimethyl fumarate adduct. The apparent non-stereospecificity of the dimethyl maleate addition persisted when dimethyl maleate purified by preparative g.l.c. was employed.

(i) Dimethyl maleate (200 mg), dimethyl fumarate (200 mg), the 1,3-diphenylbenz[f]inden-2-one dimer (50 mg), and o-dichlorobenzene (15 ml) were heated at 160—170 °C (22 h)

in a nitrogen atmosphere. The adduct fraction obtained by evaporation and silica chromatography in benzene–ether (9 : 1) was examined by ^{1}H n.m.r. spectroscopy at 300 MHz. This showed the absence of the dimethyl maleate adduct (no 2 H singlet at δ 4.37), and strong peaks for the fumarate adduct (δ 4.27 and 3.73).

Additions to 1,3-Diphenylinden-2-one.—(a) *trans*-But-2-ene (2 ml, condensed at −78 °C), the 1,3-diphenylinden-2-one dimer (100 mg), and xylene (5 ml) were heated in a bomb in an oil-bath at 156 °C (18 h). Chromatography of the evaporated product on silica in benzene gave the 1,3-*diphenylinden-2-one*–*trans-but-2-ene adduct* (75 mg), m.p. 137—138 °C (from CHCl$_3$–EtOH) (Found: C, 88.75; H, 6.6. C$_{25}$H$_{20}$O requires C, 88.7; H, 6.5%); ν$_{max.}$ 1 780 cm^{-1}; δ(90 MHz) 7.8—6.8 (14 H, m), 3.10 (1 H, m), 2.85 (1 H, m), 1,05 (3 H, d, *J* 7 Hz), and 0.85 (3 H, d, *J* 7 Hz).

(b) *cis*-But-2-ene (2 ml), the 1,3-diphenylinden-2-one dimer (50 mg), and xylene (5 ml) were heated in a bomb in an oil-bath at 156 °C (18 h). Evaporation of solvent at 100 °C under reduced pressure and chromatography of the residue on silica in benzene gave the exo-1,3-*diphenylinden-2-one*–*cis-but-2-ene adduct* (35 mg, 29%), m.p. 189—191 °C (from CHCl$_3$–EtOH) (Found: C, 88.7; H, 6.8. C$_{25}$H$_{22}$O requires C, 88.7; H, 6.5%); ν$_{max.}$ 1 760 cm^{-1}; δ(90 MHz) 7.90—7.65 (4 H, m, aromatic), 7.65—7.30 (6 H, m, aromatic), 7.30—6.80 (4 H, m, aromatic), 2.70—2.40 (2 H, m), and 0.92 (6 H, d); *m/z* 310 (*M* − CO), 295, 282, 280, 267, 205, and 105 (100, 69, 22, 20, 41, 64, and 51%). Further elution of the column gave the endo-1,3-*diphenylinden-2-one*–*cis-but-2-ene adduct* (43 mg, 36%), m.p. 210—213 °C (from CHCl$_3$–EtOH) (Found: C, 88.45; H, 6.5%), ν$_{max.}$ 1 785 cm^{-1}; δ(90 MHz) 7.60—7.00 (14 H, m, aromatic), 3.55—3.20 (2 H, m), 0.74 (6 H, m); *m/z* 310 (*M* − CO), 295, 282, 280, 267, 205, and 105 (100, 64, 6, 23, 39, 62, and 33%). The ^{1}H n.m.r. spectrum (90 MHz) of the crude reaction product showed the absence of signals at 2.85 and 1.05 δ due to the *trans*-but-2-ene adduct.

(c) *trans*-But-2-ene (2 ml) and *cis*-but-2-ene (2 ml) were condensed at −80 °C, mixed with xylene (5 ml) and the 1,3-diphenylinden-2-one dimer (100 mg), and the mixture heated in a bomb placed in an oil-bath at 156 °C (18 h). Chromatography of the evaporated product on silica in benzene gave the *exo-cis*-but-2-ene adduct (16.5 mg), the *trans*-but-2-ene adduct (41.3 mg), and the *endo-cis*-but-2-ene–1,3-diphenylinden-2-one adduct (22.1 mg) which were eluted in that order and identical with the authentic adducts previously prepared (comparison of i.r. spectra and mixed m.p. determinations).

Photodecarbonylation of the 1,3-Diphenylbenz[f]inden-2-one–Trimethylmaleimide Adduct (21).—The adduct (250 mg) in oxygen-free benzene (500 ml) was irradiated (Hanovia 100-W medium-pressure lamp) at 20 °C in a nitrogen atmosphere. After 20 min a deep blue colour had developed which was immediately discharged by titration with a solution of PTD in benzene. The photolysis-titration procedure was repeated until the blue colour failed to appear on photolysis. After evaporation under reduced pressure at 60 °C the residue was chromatographed on silica in benzene–ether (9 : 1) to give the *adduct* (30; R^1 = R^2 = Me) (168 mg, 50%), m.p. 263—264 °C (from CH$_2$Cl$_2$–MeOH) (Found: C, 75.8; H, 5.0; N, 9.25. C$_{39}$H$_{30}$N$_4$O$_4$ requires C, 75.7; H, 4.9; N, 9.1%); ν$_{max.}$ 1 775, 1 720, 1 710, 1 605, 775, and 705 cm^{-1}; δ(60 MHz) 7.60—7.00 (19 H, m, aromatic), 5.42 (2 H, s), 2.86 (3 H, s, NMe), and 1.28 (6 H, s); *m/z* 618 (*M*), 443 (*M* − dienophile), and 358 (2, 77, and 100%).

Photodecarbonylation of the 1,3-Diphenylbenz[f]inden-2-one–N-Methylcyclohex-1-ene-1,2-dicarboximide Adduct (22).—

(a) The adduct (34 mg) in deoxygenated benzene (5 ml) was irradiated in a quartz flask placed close to a water-cooled 1-kW medium-pressure mercury lamp (2 min) and the strong blue colour that had developed discharged by addition of PTD in benzene. The photolysis-titration sequence was repeated until no further colour developed on further photolysis (total irradiation time 80 min). Evaporation of solvent and crystallisation of the residue from benzene–petroleum gave the *adduct* [30; R^1, R^2 = (CH$_2$)$_4$] (30 mg), m.p. 168—170 °C (Found: C, 76.65; H, 5.25; N, 8.3. C$_{41}$H$_{32}$N$_4$O$_4$ requires C, 76.4; H, 4.9; N, 8.7%), ν$_{max.}$ 1 715, 1 760, and 1 780 cm^{-1}; δ(90 MHz) 7.7—7.0 (19 H, m, aromatic), 5.67 (2 H, s), 2.9 (3 H, s), 2.0—1.8 (8 H, m).

(b) The adduct (22) (30 mg) in deoxygenated benzene (20 ml) was irradiated in a nitrogen atmosphere in a quartz flask placed close to the window of a water-cooled 1-kW medium-pressure mercury lamp (1.75 h). The deep blue colour of the solution was discharged on admitting air into the apparatus. Evaporation of solvent and chromatography on silica in benzene–ether (9 : 1) gave first a fraction (12 mg) that was not further examined followed by the dimer of (26) (15 mg), m.p. >325 °C (from CH$_2$Cl$_2$–MeOH) [Found: C, 84.35; H, 5.75; N, 2.95; *M* (osmometer), 853. C$_{66}$H$_{54}$N$_2$O$_4$ requires C, 84.4; H, 5.75; N, 3.0%; *M*, 938], ν$_{max.}$ 1 715 and 1 780 cm^{-1}; δ(90 MHz) 7.4—6.7 (28 H, m), 3.55 (4 H, s), 2.75 (6 H, s), and 1.6—0.8 (16 H, m). Irradiation of the dimer in the manner described above gave the deep-blue colour characteristic of the monomer.

Photodecarbonylation of the 1,3-Diphenylbenz[f]inden-2-one–2-Norbornene Adduct (23).—The adduct (42 mg) in deoxygenated benzene (2 ml) was irradiated as described in (a) above for 2 min. The resulting deep blue solution (λ$_{max.}$ 648 nm) was titrated with a solution of PTD in benzene to a colourless end-point. The above process was repeated for a total irradiation time of 39 min. Evaporation of the solvent and chromatography of the residue on silica in benzene–ether (9 : 1) gave the *adduct* (31) (27 mg, 48%), m.p. 320—322 °C (from benzene–petroleum) (Found: C, 81.75; H, 5.5; N, 7.4. C$_{39}$H$_{31}$N$_3$O$_2$ requires C, 81.65; H, 5.45; N, 7.3%), ν$_{max.}$ 1 770 and 1 716 cm^{-1}; δ(90 MHz) 8.00—7.00 (21 H, m, aromatic), 3.20 (2 H, s), 2.42br (2 H, s), 1.55br (4 H, s), 0.20 (1 H, d, *J* 8 Hz), −1.10 (1 H, d, *J* 8 Hz); *m/z* 573 (*M*), 398, 357, and 330 (4, 100, 28, and 17%).

Diels-Alder Addition of 1,3-Diphenylbenzo[c]furan to Cyclopent-4-ene-1,3-dione.—1,3-Diphenylbenzo[*c*]furan (18 g) and cyclopent-4-ene-1,3-dione (6.4 g) were dissolved in benzene (100 ml) at 25 °C. The mixture was stirred for 45 min after which the heavy white precipitate was filtered off to give the 1,3-diphenylbenzo[*c*]furan–cyclopent-4-ene-1,3-dione adduct (32) (19.5 g, 80%), m.p. 224—225 °C (Found: *M*, 366.129. C$_{23}$H$_{18}$O$_3$ requires *M*, 366.125), ν$_{max.}$ 1 640 and 1 590 cm^{-1}; δ(90 MHz, [^{2}H$_5$]pyridine) 8.40 (4 H, m), 7.73—7.30 (8 H, m), and 7.10—6.90 (4 H, m), and 4.16 (2 H, s).

Dehydration of the 1,3-Diphenylbenzo[c]furan–Cyclopent-4-ene-1,3-dione Adduct (32).—The furan adduct (18 g) was added portionwise to a hot solution (oil bath temp. 110 °C) of acetic acid (180 ml) and concentrated hydrochloric acid (30 ml) (5 min). The mixture was stirred for 40 min, poured into ice and neutralised with sodium hydrogen carbonate solution. The aqueous layer was extracted several times with ether. The combined ether layers were washed with water and dried (MgSO$_4$). Evaporation of the ether and slow crystallisation from benzene–petroleum gave 4,9-*diphenylbenz[f]indan-1,3-dione* (33) (4.2 g, 25%), m.p. 240—254 °C (decomp.) (Found: C, 86.4; H, 4.9. C$_{25}$H$_{16}$O$_2$ requires C, 86.2; H, 4.6%), ν$_{max.}$

1 740 and 1 710 cm^{-1}; δ(90 MHz) 8.20—7.2 (14 H, m, aromatic), and 3.25 (2 H, s, methylene); m/z 348 (M), 276, and 138 (100, 17, and 10%).

4,9-*Diphenylbenz*[f]*indan*-1,2,3-*trione* 2-*Oxime* (34).—A mixture of 4,9-diphenylbenz[f]indan-1,3-dione (33) (1.1 g) n-butyl nitrite (7 g), 95% ethanol (10 ml), and concentrated hydrochloric acid (3 ml) were stirred at 80 °C (oil bath temp.) for 1 h. The mixture was cooled to 25 °C, n-butyl nitrite (7 g) was added and the mixture stirred (18 h). The deep yellow precipitate was filtered off to give 4,9-*diphenylbenz*[f]*indan*-1,2,3-*trione* 2-*oxime* (34) (796 mg, 67%), m.p. 226—238 °C (decomp.) (from methylene chloride–methanol) (Found: C, 79.35; H, 3.9; N, 4.0. C$_{25}$H$_{15}$NO$_3$ requires C, 79.6; H, 4.0; N, 3.7%), $\nu_{max.}$ 3 420, 1 740, and 1 707 cm^{-1}; m/z 377 (M), 360, 356, 305, and 276 (61, 89, 84, 39, and 100%).

1,3,4,9-*Tetraphenyl*-1,3-*dihydroxybenz*[f]*indan*-2-*one* 2-*Oxime* (10; X = NOH, Y = OH).—The foregoing oxime (500 mg) in ether (500 ml) was added to phenyl-lithium [from lithium shot (190 mg), bromobenzene (2.1 g), and ether (20 ml)] during 5 min. After being stirred (30 min) the reaction was quenched with water and the organic layer was washed with water, dried (MgSO$_4$), and evaporated. Chromatography of the residue on silica in benzene–ether (7 : 3) gave *one stereoisomer of* 1,3,4,9-*tetraphenyl*-1,3-*dihydroxybenz*[f]*indan*-2-*one* 2-*oxime* (170 mg), m.p. 148—162 °C (from CHCl$_3$–MeOH) (Found: M, 533.199. C$_{37}$H$_{27}$NO$_3$ requires M, 533.199), $\nu_{max.}$ 3 360 cm^{-1}; δ(90 MHz) 7.80—6.0 (25 H) and 3.40 (2 H, s, 2 × OH). Continued elution of the column gave a *second stereoisomer* of 1,3,4,9-*tetraphenyl*-1,3-*dihydroxybenz*[f]*indan*-2-*one* 2-*oxime* (72 mg), m.p. 221—226 °C (from benzene–dichloromethane) (Found: C, 82.8; H, 5.0; N, 2.6. C$_{37}$H$_{27}$NO$_3$ requires C, 83.3; H, 5.1; N, 2.6%); $\nu_{max.}$ 3 400 cm^{-1}; δ(90 MHz) 9.56 (1 H, s, exch. D$_2$O), 7.50—6.10 (24 H, m), 5.70 (1 H, s, exch. D$_2$O), and 4.50 (1 H, s, exch. D$_2$O).

1,3,4,9-*Tetraphenylbenz*[f]*indan*-2-*one* (10; X = O, Y = H).—A mixture of the foregoing dihydroxy-oximes (160 mg), glacial acetic acid (6 ml), hydriodic acid (1 g), and red phosphorus (100 mg) were heated on a steam-bath with vigorous stirring in an argon atmosphere (3 h). The cooled product was diluted with dichloromethane and the organic layer washed with sodium metabisulphite solution and with water, dried (MgSO$_4$), and evaporated. Chromatography of the residue on silica in benzene gave a mixture of the *cis*- and *trans*-isomers of 1,3,4,9-*tetraphenylbenz*[f]*indan*-2-*one* (80 mg), m.p. 192—207 °C (from benzene–petroleum) (Found: M, 486.198. C$_{37}$H$_{26}$O requires M, 486.198); $\nu_{max.}$ 1 760 cm^{-1}; δ(90 MHz) 8.40—6.80 (24 H, m) and 5.10 (2 H, s).

1,3-*Dibromo*-1,3,4,9-*tetraphenylbenz*[f]*indan*-2-*one* (10; X = O, Y = Br).—1,3,4,9-Tetraphenylbenz[f]indan-2-one (50 mg), bromine (36 mg), and dry carbon tetrachloride (3 ml) were stirred at 20 °C (18 h). The solvent was evaporated under reduced pressure at 30 °C and the residue triturated with petroleum to give 1,3-*dibromo*-1,3,4,9-*tetraphenylbenz*[f]*indan*-2-*one* (60 mg), m.p. 230—247 °C (decomp.) (from benzene–petroleum) (Found: M, 644.016. C$_{37}$H$_{24}$^{79}Br^{81}BrO requires M, 644.017); $\nu_{max.}$ 1 768 cm^{-1}; δ 8.20—6.80 (24 H, m).

The Dimer (35) *of* 1,3,4,9-*Tetraphenylbenz*[f]*inden*-2-*one*.—The foregoing dibromo-compound (58.7 mg), sodium iodide (78 mg), and acetone (6 ml) were boiled under reflux (30 min) in an argon atmosphere. The product was diluted with dichloromethane and washed with sodium metabisulphite solution and with water, and then dried (MgSO$_4$) and evaporated. Crystallisation of the residue from CH$_2$Cl$_2$–petroleum gave the *dimer of* 1,3,4,9-*tetraphenylbenz*[f]*inden*-2-*one* (32 mg), m.p. 304—306 °C [Found: C, 91.6; H, 5.1; M (osmometer), 910. C$_{74}$H$_{48}$O$_2$ requires C, 91.7; H, 5.4%; M, 968]; $\nu_{max.}$ 1 640 and 1 600 cm^{-1}; δ(90 MHz) 7.70—5.90 (48 H, m); δ(^{13}C) 87.3, 121.9, 124.5, 124.8, 125.4, 125.8, 126.0, 126.3, 126.7, 127.0, 127.5, 129.7, 130.1, 130.5, 131.3, 131.5, 131.9, 132.8, 134.0, 135.6, 135.9, 136.7 137.8, 139.6, and 159.5. The ^{13}C spectrum of compound (36) was measured for comparison purposes: δ 63.28 (CH$_2$), 68.75 (CH$_2$), 82.35 (C-1), 119.5, 120.04 (C-3), 124.0—129.6 (9 lines including one degeneracy), 132.1, 141.2, 144.75, 158.46 p.p.m. (C-2). In 1,3-diphenylindene C-1 appeared at δ 55.3 and the lowest field carbon resonated at 149.1 p.p.m.

The 1,3,4,9-*Tetraphenylbenz*[f]*inden*-2-*one-N-Phenyl-maleimide Adduct* (15).—The foregoing dimer (20 mg), N-phenylmaleimide (15 mg), and degassed diphenyl ether (3 ml) were boiled under reflux in an argon atmosphere (3 h). After partial removal of diphenyl ether at 100 °C under reduced pressure the residue was chromatographed on silica in benzene to give the 1,3,4,9-*tetraphenylbenz*[f]*inden*-2-*one-N-phenylmaleimide adduct* (15) (10.2 mg), m.p. >318 °C (from CHCl$_3$–MeOH) (Found: C, 85.45; H, 4.7; N, 2.1. C$_{47}$H$_{31}$NO$_3$ requires C, 85.8; H, 4.7; N, 2.1%); $\nu_{max.}$ 1 787 and 1 720 cm^{-1}; δ(90 MHz) 7.80—6.20 (29 H, m) and 4.20 (2 H, s). Boiling the dimer (20 mg), trimethylmaleimide (35 mg), and diphenyl ether (3 ml) during 18 h (argon atmosphere) and silica chromatography of the product in benzene–petroleum (4 : 1) gave 1,3,4,9-tetraphenylbenz[f]indan-2-one (17 mg) identical (i.r. spectrum) with a sample previously prepared.

References

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