o-Quinonoid Compounds. Part II.[1] 1,4-Diphenyl-2-benzopyran-3-one and its Iron Carbonyl Complexes †

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1,4-Diphenyl-2-benzopyran-3-one is prepared by dehydration–rearrangement of 1,3-dihydroxy-1,3-diphenylindan-2-one and by dehydration of *o*-benzoylphenyl(phenyl)acetic acid. The reactions of the pyrone and its conversion into related *o*-quinonoid compounds are described. The interconvertible iron carbonyl complexes of the pyrone are prepared by reaction with dodecacarbonyltri-iron. The role of metal–ligand σ-bonding in one of the complexes is discussed.

In 1925 Straus and Ehrenstein[2] described the oxidation of Ziegler's triphenylallene dimer[3] to an oily acid. They did not characterise the acid but noted that with sulphuric acid it gave a yellow solution from which water precipitated a red substance, $C_{21}H_{14}O_2$ or $C_{28}H_{18}O_3$. Assignment of structure (I) to the triphenylallene dimer[4-6] suggested that its acidic oxidation product was the keto-acid (II), and the red substance the benzopyrone (III) which in sulphuric acid existed as the yellow conjugate acid. Repetition of the early work

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† Preliminary communication, J. M. Holland and D. W. Jones, *Chem. Com.*, 1967, 946.

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

[2] F. Straus and M. Ehrenstein, *Annalen*, 1925, **442**, 93.

[3] K. Ziegler, H. Grabbe, and F. Ulrich, *Ber.*, 1924, **57**, 1983; K. Ziegler, K. Richter, and B. Schnell, *Annalen*, 1925, **443**, 161.

[4] D. H. R. Barton and D. W. Jones, *J. Chem. Soc.*, 1965, 3563.

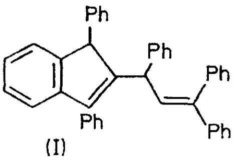
[5] D. Rewicki, *Chem. Ber.*, 1966, **99**, 393.

[6] D. W. Jones, *J. Chem. Soc.* (*C*), 1966, 1026.

confirmed this interpretation. The benzopyrone (III), a stable heterocyclic derivative of *o*-quinodimethane has potential both as a precursor of 1,2-diphenylbenzocyclobutadiene,[7] and as a reactive diene in trapping experiments. We describe a novel and convenient synthesis of (III) together with its properties, reactions, and conversion into related *o*-quinonoid compounds.

Our first objective was a high yield synthesis of the acid (II), which can be converted (78%) into the pyrone (III) by sulphuric acid treatment. Chromic acid oxidation of 1,3-diphenylindene gave mainly *o*-dibenzoylbenzene, the desired acid (II) being formed in only 20% yield. Oxidation of the acyloin (IV) with lead tetraacetate gave (II) in better yield (53%). These preparations confirmed the structure of the acid (II) but did not represent a convenient synthesis of the pyrone (III). Such a synthesis was found in rearrangement of the dihydroxy-ketone (V) to the pyrone (III). Dissolution of (V) in concentrated sulphuric acid followed by addition of water gave (III) (70%). This reaction may proceed through the hydroxy-epoxide (VI; arrows),* or alternatively by valence isomerisation of the keto-keten (VII) produced from (V) by a reaction of the reverse Prins type. The dihydroxy-ketone (V) was prepared from ninhydrin dimethyl acetal (VIII) by reaction with phenylmagnesium bromide, followed by hydrolysis of the dihydroxy-acetal (IX) with hydrochloric acid–acetic acid at room temperature. In addition to (V) this mild hydrolysis gave the acid (II), and when (IX) was boiled with hydrochloric acid–acetic acid the acid (II) was obtained in quantitative yield. Sulphuric acid dehydration of the acid (II) obtained by hydrolysis of the acetal (IX) is a most convenient synthesis of the pyrone (III). The overall yield from the readily available acetal (VIII) is 59%.

The pyrone (III) is a convenient starting material for the synthesis of related *o*-quinonoid heterocyclic compounds. Reaction of (III) with phosphorus pentasulphide gives the thiopyrone (X). In the related thiation of simple α-pyrones the carbonyl oxygen is preferentially replaced by sulphur.[8] The result in the case of the *o*-quinonoid pyrone (III) is not unexpected in view of the susceptibility of this compound to nucleophilic attack at position 1 (see later). The thiopyrone (X) was independently synthesised as follows. The reaction of thiophosgene and 1,2-diphenylbenzocyclobutene gave the chlorosulphide (XI) and not the thiopyrylium salt (XII; X = Cl) expected by analogy with the reaction of 1,4-diphenylbutadiene with thiophosgene.[9] However reaction of (XI) with *N*-bromosuccinimide presumably gives the related salt (XII; X = Br), for subsequent reaction with acetic anhydride gives the thiopyrone (X) in good yield. Surprisingly, (X) undergoes smooth decarbonylation at 290° to give 1,3-diphenylbenzo[*c*]thiophen (71%). This parallels the electron-impact induced decomposition of (X). The mass spectrum shows a strong M — CO peak and subsequent fragmentation identical to that of 1,3-diphenylbenzo[*c*]thiophen. The thiopyrone (XIII) is recovered unchanged after being heated at 290°.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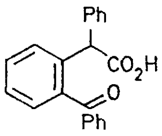
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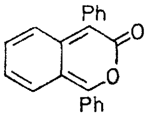
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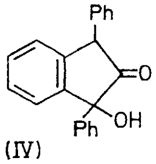
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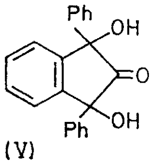
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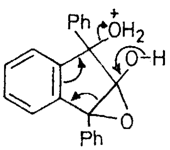
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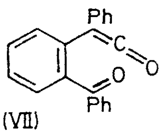
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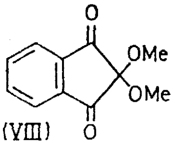
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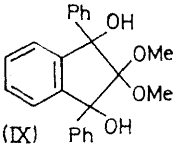
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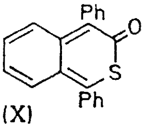
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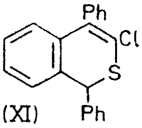
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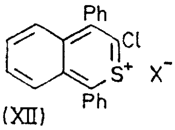
(XII)

Reaction of the pyrone (III) with ammonia affords a mixture of two compounds tentatively identified as the ammonium salt (XIV) and the amide (XV). Both compounds give the tautomeric[1] isoquinolinone (XVI; R = H) when heated. Reaction of (III) with aniline in the presence of boron trifluoride–ether complex gives the isoquinolinone (XVI; R = Ph).

The pyrone (III) is converted into 1,2,3-triphenylisoindole by heating with *N*-sulphinylaniline in the presence of boron trifluoride–ether complex. This reaction can be interpreted as involving Diels–Alder addition of (III) with *N*-sulphinylaniline, followed by decarboxylation and loss of sulphur monoxide. According to Cava and Schlessinger[10] 1,2,3-triphenylisoindole is conveniently prepared from *N*-sulphinylaniline and 1,3-diphenylisobenzofuran. Aniline may conveniently replace *N*-sulphinylaniline in this preparation if the reaction is conducted in boiling xylene.

The pyrone (III) shows considerable reactivity towards nucleophiles. It react rapidly with lithium aluminium hydride and methylmagnesium iodide to give

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* A related intermediate has been implicated in the rearrangement of 2,3-dihydroxy-2,3-diphenylindanone to 5,6-diphenylisocoumarin (C. F. H. Allen and J. W. Gates, *J. Amer. Chem. Soc.*, 1943, **65**, 1230).

[7] *Cf.* M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds,' Academic Press, New York and London, 1967, p. 193, and M. P. Cava and J. McGrady, *Chem. Comm.*, 1968, 1648.

[8] R. Mayer, W. Broy, and R. Zahradnik, in 'Advances in Heterocyclic Chemistry,' ed. A. R. Katritzky, and A. J. Boulton, Academic Press, New York and London, 1967, vol. 8, p. 219.

[9] G. Laban and R. Mayer, *Z. Chem.*, 1967, **7**, 227.

[10] M. P. Cava and R. H. Schlessinger, *J. Org. Chem.*, 1963, **28**, 2464.

the lactones (XVII; R = H) and (XVII; R = Me) respectively. Similarly when boiled with methanol it is converted into the pseudo-ester (XVII; R = OMe). The enhanced stability of the thiopyrone (X) is reflected by its failure to react with boiling methanol. Under mild conditions reaction of (III) with aniline gives the anil of *o*-benzoylphenyl(phenyl)acetic acid, but under more vigorous conditions the anil of *o*-benzylbenzophenone and the anilide (XVIII) are formed.

Like other *o*-quinonoid compounds (III) reacts readily with dienophiles, and in the course of our work on (III) and related compounds[11] several adducts have been prepared. Evidence for the structure of the pyrone (III) was first obtained by its reaction with dimethyl acetylenedicarboxylate to give 2,3-bismethoxycarbonyl-1,4-diphenylnaphthalene. The adducts of (III) with tetracyanoethylene and *N*-phenylmaleimide were prepared for comparison with the products of experiments using these dienophiles as traps for simpler 2-benzopyran-3-ones.[11] The pyrone (III) reacts more slowly than 1,3-diphenylisobenzofuran with *N*-phenylmaleimide. This difference in reactivity may be attributed to the difference in ring sizes and electron demands of the diene components and does not necessarily reflect a lower ground state energy of the pyrone (III). The adduct (XIX) of the pyrone with *trans*-dibenzoylethylene was prepared in the hope of effecting dehydration–decarboxylation to the *o*-quinonoid system (XX).[12] However (XIX) resisted dehydration with boiling acetic anhydride. Decarboxylation of (XIX) at its m.p. was accompanied by loss of benzaldehyde and gave 2-benzoyl-1,4-diphenylnaphthalene. Photolysis of (XIX) affords 1,4-diphenylnaphthalene (13%). Important ions in the mass spectrum of (XIX) appear at *m/e* 105 (base peak), 385 (25%), 384 (10·5%), and 280 (8·5%). The last two peaks correspond to the 2-benzoyl-1,4-diphenylnaphthalene, and 1,4-diphenylnaphthalene ions. The fragmentation of (XIX) under electron impact is therefore similar to both its thermal and its photochemical reactions. Although the pyrone (III) is indefinitely stable to air in the solid state, a solution in benzene absorbs oxygen in the dark at room temperature. The products of the reaction are *o*-dibenzoylbenzene and an unstable compound tentatively identified as the peroxide (XXI), since it shows $\nu_{max.}$ 1764 cm.$^{-1}$ and when heated gives *o*-dibenzoylbenzene. Similar peroxides are formed by other *o*-quinonoid heterocyclic compounds.[13] The pyrone (III) has not proved a suitable precursor for 1,2-diphenylbenzocyclobutadiene. Decarboxylation of (III) requires high temperatures (290°) and a complex mixture of products including 9-phenylanthracene is obtained. Decarboxylation of the valence isomer (XXII) of the pyrone might be a more promising route to 1,2-diphenylbenzocyclobutadiene. However attempts to produce (XXII) by u.v. irradiation of (III) at −70° gave complex mixtures of products.

Reaction of the pyrone (III) with dodecacarbonyltri-iron in boiling toluene gave two complexes, in 50% yield. Both give analyses in agreement with the formula $C_{24}H_{14}FeO_5$, show $\nu_{max.}$ (Nujol) *ca.* 2000 and 2060 cm.$^{-1}$, and decompose at 200° to the pyrone (III). Thus both are tricarbonyliron complexes of (III). The first, $\nu_{max.}$ (Nujol) 1693 and 1630 cm.$^{-1}$, is assigned the structure (XXIII). This agrees with the n.m.r. spectrum [τ 2·3—2·8 (phenyl protons), 4 (2H) and 6·2 (2H)]. Two structures may be written for the second complex (m.p. 182°), the π-bonded structure (XXIVa), and structure (XXIVb), involving metal–ligand σ-bonds. Extreme valence-bond structures such as (XXIVa) and (XXIVb) are both implicated in the molecular orbital description of certain diene–metal complexes.[14] The aromaticity of ring A should lead to an increased contribution from structure (XXIVb). The n.m.r. spectrum of the complex agrees with this prediction, for it shows the presence only of 'aromatic' protons (τ 2·0—2·8). In the spectrum of the pyrone (III) the phenyl protons resonate at τ 2·1—2·7, whereas the ring-A protons appear at higher field (τ 2·7—3·3). The i.r. spectrum (Nujol) of the complex shows the lactone carbonyl frequency at 1738 cm.$^{-1}$, whereas the pyrone (III) shows carbonyl absorption at 1693 cm.$^{-1}$ and the lactones (XVII) absorb in the range 1737—1744 cm.$^{-1}$. Since Cais and Maoz[15] have shown that the carbonyl absorptions of a series of $\alpha\beta,\gamma\beta$-unsaturated carbonyl compounds are unchanged in the corresponding iron carbonyl complexes this evidence favours an increased contribution from structure (XXIVb). Doubt is cast on this interpretation by the report[16] that tricarbonyl-α-pyroneiron has $\nu_{max.}$ 1779 cm.$^{-1}$. However further evidence for the aromaticity of ring A in complex (XXIVb) is provided by its failure to react with tetracyanoethylene under conditions successfully used for reaction of the dienophile with tricarbonylcyclo-octatetraeneiron.[17]

Although both complexes are indefinitely stable at room temperature they undergo interconversion when heated briefly in xylene solution. A similar conversion of complex (XXIV) into (XXIII) was induced photochemically. No decarboxylation product was observed in either the thermal or the photochemical reactions of complex (XXIV).

The stability of complex (XXIV), and the fact that the lactone group appeared to play little part in the metal–ligand bonding suggested that *o*-quinodimethane could be stabilised as an iron carbonyl complex. The properties of such a complex might provide further information on the role of metal-ligand σ-bonds. Accordingly *o*-xylylene dibromide was treated with enneacarbonyldi-

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[11] J. M. Holland and D. W. Jones, *Chem. and Ind.*, 1968, 549.

[12] *Cf.* M. P. Cava and J. P. Van Meter, *J. Org. Chem.*, 1969, **34**, 538.

[13] (*a*) W. Theilacker and W. Schmidt, *Annalen*, 1957, **605**, 43; (*b*) C. Dufraisse and S. Ecary, *Compt. rend.*, 1946, 223, 735.

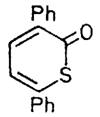
[14] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, **5**, 93.

[15] M. Cais and N. Maoz, *J. Organometallic Chem.*, 1966, **5**, 370.

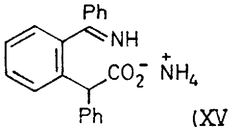
[16] M. Rosenblum and C. Gatsonis, *J. Amer. Chem. Soc.*, 1967, **89**, 5074.

[17] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.

iron in an effort to produce the required complex. The products included 10,11-dihydro-1-methyl-5*H*-dibenzo-[*a,d*]cycloheptene, and the desired complex. At this time the preparation of tricarbonyl-*o*-quinodimethane-iron was reported[18] and our own work was therefore curtailed.



(XIII)



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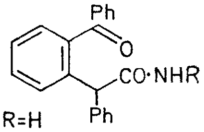
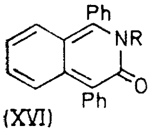


(XV) R=H
(XVIII) R=Ph



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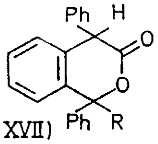

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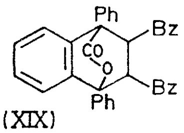

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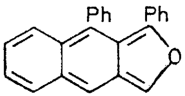

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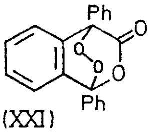
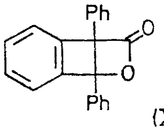


(XXI)



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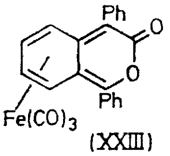

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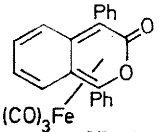
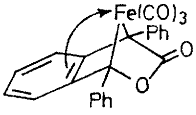


(XXIVa)



(XXIVb)

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 at the University of Hull. Petroleum refers to light petroleum, b.p. 60—80°, and chromatography on silica to short column chromatography over Kieselgel G (Merck).[19]

Oxidation of 1,3-*Diphenylindene*.—Sodium dichromate monohydrate (2·33 g., 8·3 mmoles), sodium benzenesulphonate (137 mg.), sulphuric acid (6·6 ml.), and water (31 ml.) were stirred at 65°, and 1,3-diphenylindene[2] (2 g., 7·5 mmoles) was added in portions. Stirring and heating were then continued for 20 hr. Extraction of the product into ether and isolation of the acid fraction in the usual way gave o-*benzoylphenyl*(*phenyl*)*acetic acid* (260 mg., 10%) as an oil, τ 0·5 (1H, s, CO_2H), 2·1—2·9 (14H, s, aromatic), and 4·53 (1H, s, PhC*H*). The *methyl ester* was obtained as an oil by reaction with diazomethane, and purified by chromatography on silica with benzene–ether (19 : 1) as eluant (Found: C, 79·75; H, 5·4. $C_{22}H_{18}O_3$ requires C, 80·0; H, 5·5%), $\nu_{max.}$ ($CHCl_3$) 1660 and 1732 cm.$^{-1}$, τ (CCl_4) 2·2—3·1 (14H, m, aromatic), 4·6 (1H, s, PhC*H*), and 6·48 (3H, s, OMe). An improved yield of the acid was obtained by oxidation of the indene (0·5 g., 1·87 mmoles) in acetic acid (40 ml.), and sulphuric acid (0·7N; 29 ml.), with chromium trioxide (373 mg., 3·73 mmoles) at 20° for 20 hr. Separation into acidic and neutral fractions in the usual way gave *o*-benzoylphenyl(phenyl)acetic acid (115 mg., 23%), and neutral material (525 mg.) which was chromatographed on silica. Elution with benzene–ether (19 : 1) gave *o*-dibenzoylbenzene (250 mg., 47%) identical with an authentic sample[20] (mixed m.p. and i.r. spectrum).

Oxidation of 1-*Hydroxy*-1,3-*diphenylindan*-2-*one*.—The acyloin[21] (100 mg., 0·67 mmole), lead tetra-acetate (165 mg., 0·68 mmole), and glacial acetic acid (40 ml.) were heated at 55° for 3 hr., then set aside overnight. The product was diluted with sulphuric acid (2N) and filtered. The filtrate was evaporated to small bulk and digested with warm sodium hydroxide solution (2N; 20 ml.), and the extract was washed with ether, acidified with hydrochloric acid (2N), and extracted into ether to give *o*-benzoylphenyl-(phenyl)acetic acid (56 mg., 53%), identical with material already prepared (i.r. spectrum).

1,3-*Dihydroxy*-2,2-*dimethoxy*-1,3-*diphenylindane*.— Ninhydrin dimethyl acetal[22] (17 g., 0·083 mole) in ether (100 ml.) was added dropwise to phenylmagnesium bromide [from bromobenzene (52·3 g., 0·33 mole) and magnesium (8·11 g., 0·33 g. atom)] in ether (400 ml.). The mixture was boiled under reflux (45 min.), cooled, washed with sulphuric acid (2N) then water, dried ($MgSO_4$), and evaporated to give 1,3-*dihydroxy*-2,2-*dimethoxy*-1,3-*diphenylindane* (22·5 g., 75%), m.p. 116—118° (from petroleum) (Found: C, 76·25; H, 6·05. $C_{23}H_{22}O_4$ requires C, 76·2; H, 6·1%), $\nu_{max.}$ 3050 cm.$^{-1}$, τ 2·3—3·1 (14H, m, aromatic), 6·0 (2H, s, OH), and 7·2 (6H, s, OMe).

1,3-*Dihydroxy*-1,3-*diphenylindan*-2-*one*.—The foregoing dihydroxy-acetal (200 mg.), acetic acid (25 ml.), concentrated hydrochloric acid (12·5 ml.) and water (12·5 ml.) were set aside at 20° (5 days). The solid which separated was filtered off to give 1,3-*dihydroxy*-1,3-*diphenylindan*-2-*one* (112 mg., 64%), m.p. 225—240° (decomp.) (from ethyl acetate) (Found: C, 79·7; H, 5·1. $C_{21}H_{16}O_3$ requires C, 79·2; H, 4·9%), $\nu_{max.}$ 1736 and 3500 cm.$^{-1}$. The filtrate was diluted with water (30 ml.) and extracted with ether. Separation into acidic and neutral fractions in the usual way gave *o*-benzoylphenyl(phenyl)acetic acid (35 mg., 20%), and non-acidic products (30 mg.) which were subjected to thick-layer chromatography on silica. Developing with benzene–ether (7 : 3) gave starting material (20 mg., 10% recovery) and more (7 mg., 4%) of the dihydroxy-ketone, m.p. 225—240° (decomp.).

Reaction of 1,3-*Dihydroxy*-2,2-*dimethoxy*-1,3-*diphenylindane with Hydriodic Acid*.—The dihydroxy-acetal (390 mg.), hydriodic acid (*d* 1·7; 1·6 ml.; freshly distilled from phosphorus under nitrogen), red phosphorus (100 mg.), and acetic acid (3·2 ml.) were heated on a water-bath for 2 hr. under nitrogen. The mixture was cooled in ice and the product was filtered off and washed with potassium iodide solution and then water. It was dissolved in dichloromethane; the solution was then filtered, dried ($MgSO_4$), and evaporated to give 1,3-diphenylindan-2-one (268 mg., 88%), m.p. 155° (decomp.), identical with authentic material.[23]

[18] W. R. Roth and J. D. Meier, *Tetrahedron Letters*, 1967, 2053.
[19] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.
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Conversion of 1,3-*Dihydroxy*-2,2-*dimethoxy*-1,3-*diphenylindane into* o-*Benzoylphenyl*(*phenyl*)*acetic Acid*.—The dihydroxy-acetal (10 g.), glacial acetic acid (1000 ml.), conc. hydrochloric acid (500 ml.), and water (500 ml.) were boiled under reflux (4 hr.). Evaporation to small bulk under reduced pressure on a water-bath, extraction into ether, and isolation of acids in the usual way gave *o*-benzoylphenyl(phenyl)acetic acid (8·7 g., 100%), identical with material prepared before (i.r. spectrum).

Preparation of 1,4-*Diphenyl*-2-*benzopyran*-3-*one*.—(*a*) *o*-Benzoylphenyl(phenyl)acetic acid (1·0 g.) was dissolved in conc. sulphuric acid (2·5 ml.) by brief and gentle warming on a water-bath. The yellow solution was diluted with water (350 ml.) and rapidly extracted with ethyl acetate (350 ml.). The extract was washed with water (2 × 200 ml.) dried ($MgSO_4$), and evaporated to give the *benzopyranone* (783 mg., 78%) as scarlet needles, m.p. 182—183° (from benzene–petroleum) [Found: C, 84·2; H, 4·75%; *M* (mass spectrum), 298·0998. $C_{21}H_{14}O_2$ requires C, 84·5; H, 4·7%; *M*, 298·0990], $\lambda_{max.}$ (C_6H_{12}) 479, 270, and 233 nm. (ε 9480, 20,600, and 23,400), identical with material prepared from the triphenylallene dimer[1] (m.p. and i.r. spectrum).

(*b*) 1,3-Dihydroxy-1,3-diphenylindan-2-one (70 mg.) was dissolved in conc. sulphuric acid (0·4 ml.) with gentle warming on a water-bath. Water (50 ml.) was added and the product was extracted into ether. The washed extract was dried ($MgSO_4$) and evaporated to give the benzopyranone (45 mg., 68%), m.p. 179—181° (from benzene–petroleum), identical with the product of (*a*) (mixed m.p. and i.r. spectrum).

Diels–Alder Reactions of 1,4-*Diphenyl*-2-*benzopyran*-3-*one*.—(*a*) Dimethyl acetylenedicarboxylate (248 mg., 2·0 mmoles), the title compound (179 mg., 0·6 mmole), and xylene (3 ml.) were boiled under reflux under nitrogen. Addition of petroleum (25 ml.) and cooling in ice gave a crystalline precipitate which yielded 2,3-bismethoxycarbonyl-1,4-diphenylnaphthalene (183 mg., 77%), m.p. 225·5—228° (from methanol–chloroform), identical with an authentic sample[24] (mixed m.p. and i.r. spectrum).

(*b*) Tetracyanoethylene (192 mg., 1·5 mmole), the title compound (298 mg., 1·0 mmole), and ether (75 ml.) were set aside at 20° under nitrogen (48 hr.). Ethyl acetate was added to dissolve the solid which had separated, and the solution was washed with saturated sodium hydrogen carbonate solution. The dried ($MgSO_4$) organic layer was evaporated under reduced pressure at 20° to give the *adduct* (379 mg., 89%), m.p. 163—174° (decomp.) (from cold ethyl acetate by precipitation with cold petroleum) (Found: C, 76·05; H, 3·4; N, 13·45. $C_{27}H_{14}N_4O_2$ requires C, 76·05; H, 3·3; N, 13·1%), $\nu_{max.}$ 1792 cm.$^{-1}$.

(*c*) *N*-Phenylmaleimide (86·5 mg., 0·5 mmole), the title compound (149 mg., 0·5 mmole), and benzene (10 ml.) were set aside at 20° under nitrogen (11 days). Evaporation of solvent then gave the *adduct* (contaminated with only a trace of starting material), which yielded needles, m.p. 242° (from dichloromethane–petroleum) (Found: C, 79·2; H, 4·5; N, 3·05. $C_{31}H_{21}NO_4$ requires C, 79·0; H, 4·5; N, 3·0%), $\nu_{max.}$ 1717 and 1762s cm.$^{-1}$, τ ($CF_3{\cdot}CO_2H$) 1·8—2·8 (17H, m, aromatic), 3·4—3·7 (2H, m, aromatic), and 4·95 (2H, apparent s). When 1,3-diphenylisobenzofuran (135 mg., 0·5 mmole) was treated in the same way reaction was complete in 45 min.; evaporation of solvent gave the *adduct* (199 mg., 90%), m.p. 206—207° (from ether–petroleum) (Found: C, 81·15; H, 4·8; N, 3·2. $C_{30}H_{21}NO_3$ requires C, 81·2; H, 4·8; N, 3·2%), $\nu_{max.}$ 1710 and 1772w cm.$^{-1}$, τ 1·8—2·15 (4H, m, aromatic), 2·3—3·1 (13H, m, aromatic), 3·35—3·7 (2H, m, aromatic), and 5·8 (2H, s).

(*d*) *trans*-Dibenzoylethylene (236 mg., 1·0 mmole), the title compound (298 mg., 1·0 mmole), and xylene (15 ml.) were boiled under reflux under nitrogen (14 hr.). The *adduct* (422 mg., 79%) separated on cooling, and after being washed with ether had m.p. 249—252° (Found: M^+, 534·1831. $C_{37}H_{26}O_4$ requires *M*, 534·1831), $\nu_{max.}$ 1764 and 1675 cm.$^{-1}$, τ 2·1—3·1 (24H, m, aromatic), 5·13 (1H, d, *J* 7 Hz), and 5·33 (1H, d, *J* 7 Hz). The adduct was unchanged after being heated in boiling acetic anhydride.

(*e*) The title compound (100 mg.) in benzene (8 ml.) was set aside in the dark in an open flask (38 days); benzene was added periodically to maintain the volume. The supposed peroxide (XXI) (57 mg.) was filtered off; m.p. 150—160° (with gas evolution), $\nu_{max.}$ 1763 cm.$^{-1}$. The instability and insolubility of this compound prevented its preparation in pure form. When heated at the m.p. it was cleanly converted into *o*-dibenzoylbenzene. Evaporation of the mother liquor obtained after removal of peroxide (XXI) gave *o*-dibenzoylbenzene (57 mg.).

Pyrolysis of the Adduct (XIX).—The adduct (200 mg.) in a nitrogen-flushed sealed tube was heated with a free flame until just molten (gas evolution). The product was chromatographed on silica; elution with benzene–petroleum (1 : 1) gave 2-*benzoyl*-1,4-*diphenylnaphthalene* (54 mg.), m.p. 124—127° (from benzene–petroleum) (Found: M^+, 384·1515. $C_{29}H_{20}O$ requires *M*, 384·1514), $\nu_{max.}$ ($CHCl_3$) 1665 cm.$^{-1}$, τ 1·8—2·9 (m, aromatic).

Photolysis of the Adduct (XIX).—The adduct (150 mg.) in purified dioxan (1 l.) was irradiated with a 100 w medium-pressure mercury lamp in a Hanovia photochemical reactor (19 hr.). After removal of solvent under reduced pressure on a water-bath, chromatography on silica, and elution with benzene–petroleum (3 : 7) gave 1,4-diphenylnaphthalene (10 mg., 13%), m.p. 130—133° (from ethanol), identical with an authentic sample[25] (mixed m.p. and i.r. spectrum).

Reaction of 1,4-*Diphenyl*-2-*benzopyran*-3-*one with Nucleophilic Reagents*.—(*a*) The title compound (100 mg.) in methanol (50 ml.) was heated under reflux under nitrogen (3·5 hr.). Evaporation of solvent left an oil which was chromatographed on silica. Elution with benzene–ether (19 : 1) gave an oil (98 mg.) from which the *pseudo-ester* (XVII; R = OMe) was obtained, m.p. 154—157° (from benzene–petroleum) (38 mg., 34%) (Found: C, 80·05; H, 5·55. $C_{22}H_{18}O_3$ requires C, 80·0; H, 5·5%), $\nu_{max.}$ 1738 cm.$^{-1}$, τ 2·3—3·3 (14H, m, aromatic), 5·25 (1H, s, benzylic), 6·66 (3H, s, OMe). The mother liquor gave an oil (60 mg.) which showed in addition to the proton resonances just cited, peaks at τ 7·7 (1H, s) and 6·56 (3H, s), attributed to a second isomer of the pseudo-ester.

(*b*) To the title compound (100 mg., 0·34 mmole) in benzene (10 ml.) was added methylmagnesium iodide [from methyl iodide (510 mg., 3·6 mmoles) and magnesium (88 mg., 3·6 mg. atom)] in ether (10 ml.) and the mixture was heated under reflux (30 min.). The product was worked up with saturated ammonium chloride solution in the usual way to give the *lactone* (XVII; R = Me) (40 mg., 38%),

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m.p. 190—191° (from ethanol) (Found: C, 83·95; H, 5·85. $C_{22}H_{18}O_2$ requires C, 84·05; H, 5·8%), $\nu_{max.}$ 1744 cm.$^{-1}$, τ 2·1—3·5 (14H, m, aromatic), 5·78 (1H, s, PhC*H*), and 7·88 (3H, s, Me).

(*c*) The title compound (100 mg., 0·34 mmole) and lithium aluminium hydride (13 mg., 0·34 mmole) in ether (20 ml.) were heated under reflux (10 min.). Work-up in the usual way gave an oil which was chromatographed on silica. Elution with benzene–ether (19 : 1) gave a mixture of the *cis*- and *trans*-forms of the *lactone* (XVII; R = H) (44 mg., 44%), m.p. 155—168° (from benzene–petroleum) (Found: C, 84·0; H, 5·2. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·4%), $\nu_{max.}$ 1737 cm.$^{-1}$, τ 2·5—3·3 (14H, m, aromatic), 3·55 and 3·76 (1H, two singlets, HC·O·CO), and 4·95 and 5·04 (1H, two singlets, HC·CO).

(*d*) The title compound (94 mg.) and ether (50 ml.) were heated under reflux while a slow stream of ammonia was bubbled through the solution (1 hr.). The white precipitate was filtered off and heated in boiling benzene. Ammonia was evolved to give 1,4-diphenylisoquinolin-3-ol (42 mg., 45%), m.p. 226—227° (from benzene), and identical with an authentic specimen [1] (mixed m.p. and i.r. spectrum). The filtrate gave a solid (21 mg.), which on sublimation (180°/0·05 mm.) gave more (20 mg., total yield 66%) of the isoquinolinol.

(*e*) The title compound (250 mg., 0·84 mmole), aniline (1·0 ml., 1·02 g., 11·0 mmoles), and benzene (30 ml.) were heated under reflux under nitrogen (35 min.). The product was diluted with ether, washed with water, dried ($MgSO_4$), and evaporated under reduced pressure at 20°. The product (278 mg., 85%), o-*benzoylphenyl(phenyl)acetic acid anil*, had m.p. 171—173° (precipitated from cold ethyl acetate with petroleum) (Found: C, 82·6; H, 5·6; N, 3·65, $C_{27}H_{21}NO_2$ requires C, 82·8; H, 5·4; N, 3·6%), $\nu_{max.}$ 1594, 1617, and 1706 cm.$^{-1}$, $\lambda_{max.}$ 253 and 326 nm. (ε 14,350 and 1980).

(*f*) The title compound (200 mg., 0·67 mmole), aniline (4·7 ml., 4·8 g., 51·6 mmoles), and xylene (15 ml.) were heated under reflux under nitrogen (2 hr.). Work-up as described in (*e*) gave an oil (192 mg.) which was chromatographed on silica. Elution with benzene–petroleum (9 : 1) gave o-*benzylbenzophenone anil* (117 mg., 50%) as a yellow oil (Found: C, 89·75; H, 6·2; N, 4·05. $C_{26}H_{21}N$ requires C, 89·9; H, 6·1; N, 4·0%), $\nu_{max.}$ ($CHCl_3$) 1620 and 1598 cm.$^{-1}$, $\lambda_{max.}$ 253 and 324sh (ε 15,890 and 3090), τ 2·1—3·4 (19H, m, aromatic) and 6·3 (2H, s, CH_2). Elution with benzene–ether (19 : 1) gave o-*benzoylphenyl(phenyl)acetanilide* (51 mg., 19%) as needles, m.p. 165—166° (from ethanol–water) (Found: C, 82·65; H, 5·55; N, 3·7. $C_{27}H_{21}NO_2$ requires C, 82·8; H, 5·4; N, 3·4%), τ 2·0—3·0 (20H, m, aromatic protons and NH), 4·54 (1H, s, PhC*H*), and (on addition of trifluoroacetic acid) 1·8br (s, NH).

(*g*) The title compound (150 mg., 0·5 mmole), aniline (200 mg., 2·2 mmoles), boron trifluoride–ether complex (100 mg., 0·7 mmole), and benzene (4 ml.) were heated under reflux under nitrogen (18 hr.). The product was diluted with ether and washed with water. After addition of chloroform to dissolve solid material which had separated the solution was dried ($MgSO_4$) and evaporated to give 1,2,4-*triphenylisoquinolin*-3-*one* (122 mg., 65%) as orange prisms, m.p. 274—275° (from chloroform–methanol) (Found: C, 87·0; H, 5·15; N, 3·85. $C_{27}H_{19}NO$ requires C, 86·8; H, 5·1; N, 3·85%), $\nu_{max.}$ 1635 cm.$^{-1}$, $\lambda_{max.}$ 445 nm. (ε 9360).

Conversion of the Pyrone (III) *into* 1,2,3-*Triphenylisoindole*.—The pyrone (100 mg., 0·34 mmole), *N*-sulphinylaniline (150 mg., 1·09 mmoles), boron trifluoride–ether complex (50 mg., 0·35 mmole), and benzene (110 ml.) were heated under reflux under nitrogen (48 hr.). The yellow product was chromatographed on silica. Elution with benzene–ether (4 : 1) gave 1,2,3-triphenylisoindole (73 mg., 63%), m.p. 230—233° (from choroform–ethanol), identical with an authentic sample [13a] (m.p. and i.r. spectrum). Continued elution with benzene–ether (4 : 1) gave 1,2,4-triphenylisoquinolin-3-one (22 mg., 18%), m.p. 274—275° (from chloroform–ethanol), identical with material already prepared (mixed m.p. and i.r. spectrum).

Reaction of 1,3-*Diphenylisobenzofuran with Aniline*.—The furan (250 mg.), aniline (750 mg., 3·23 mmoles), xylene (15 ml.), and boron trifluoride–ether complex (120 mg.) were heated under reflux under nitrogen (3 hr.). The product was diluted with chloroform, washed with water, dried ($MgSO_4$), and evaporated to give 1,2,3-triphenylisoindole (186 mg., 60%), m.p. 234—235° (from chloroform–ethanol), identical with the sample aready prepared (mixed m.p. and i.r. spectrum).

Reaction of the Pyrone (III) *with Phosphorus Pentasulphide*.—The pyrone (400 mg., 1·34 mmoles), carbon disulphide (40 ml.), and phosphorus pentasulphide (1·2 g., 5·4 mmoles) were set aside at room temperature (18 hr.). After addition of petroleum (60 ml.) and decantation the precipitate was extracted with chloroform and filtered through a short column of silica. Elution with chloroform–ether (1 : 1) gave 1,4-*diphenyl*-2-*benzothiopyran*-3-*one* (193 mg., 46%) as red needles, m.p. 198—199° (from benzene–petroleum) [Found: C, 80·2; H, 4·6; S, 10·5%; *M* (mass spectrum), 314·07680. $C_{21}H_{14}OS$ requires C, 80·2; H, 4·5; S, 10·2%); *M*, 314·07653], $\lambda_{max.}$ (C_6H_{12}) 530sh, 402, 278, and 256 nm. (ε 5070, 5490, 15,500, and 2,700).

Synthesis of 1,4-*Diphenyl*-2-*benzothiopyran*-3-*one*.—1,2-Diphenylbenzocyclobutene [23] (0·55 g., 2·15 mmoles), thiophosgene (1·5 ml., 2·26 g., 19·7 mmoles), and benzene (8 ml.) were heated under reflux (18 hr.). The total product was chromatographed on silica and eluted with benzene–petroleum (1 : 9) to give 3-*chloro*-1,4-*diphenyl*-2-*benzothiopyran* (330 mg., 46%) as colourless prisms, m.p. 117—118° (from petroleum) (Found: M^+, 334·05895. $C_{21}H_{15}ClS$ requires *M*, 334·05842), τ 2·5—3·3 (14H, m, aromatic) and 4·7 (1H, s, PhC*H*).

This thiopyran (40 mg., 0·12 mmole), *N*-bromosuccinimide (22 mg., 0·12 mmole), and carbon tetrachloride (5 ml.) were heated under reflux. A yellow colour formed rapidly and a yellow crystalline solid separated during 2 hr. After addition of acetic anhydride (2·5 ml.) heating was continued for a further 18 hr. The product was evaporated under reduced pressure on a water-bath and subjected to layer chromatography on silica. Development with ether–benzene (1 : 6) gave a red band from which the thiopyrone was isolated as red crystals (23 mg., 61%), m.p. 198—199° (from benzene–petroleum), identical with material obtained before (mixed m.p. and i.r. spectrum).

Pyrolysis of 1,4-*Diphenyl*-2-*benzothiopyran*-3-*one*.—The thiopyrone (40 mg.) in a nitrogen-flushed sealed tube was heated at 295—290° (30 min.). Chromatography on silica and elution with benzene–petroleum (3 : 7) gave 1,3-diphenylbenzo[*c*]thiophen (26 mg., 71%) as yellow needles, m.p. 118—120° (from petroleum), identical with an authentic sample [24] (mixed m.p. and i.r. spectrum).

Pyrolysis of 1,4-*Diphenyl*-2-*benzopyran*-3-*one*.—The title compound (90 mg.) in a nitrogen-flushed sealed tube was heated at 285—290° (2 hr.), and the product was chromatographed on silica. Elution with petroleum gave 9-phenylanthracene (22 mg., 29%), m.p. 150—153° (from ethanol), identical with an authentic sample[26] (mixed m.p. and i.r. spectrum). Elution with benzene–petroleum (1 : 19) gave a crystalline fraction (23 mg.) which was further purified by preparative layer chromatography on silica with benzene–petroleum (1 : 9) as developer (×5). The product, m.p. 263—264° (from ethanol) was not further examined.

The Iron Carbonyl Complexes of 1,4-*Diphenyl*-2-*benzopyran*-3-*one*.—The title compound (500 mg., 1·68 mmole), dodecacarbonyltri-iron (2·7 g., 5·4 mmoles), and toluene (100 ml.) were heated under reflux under nitrogen (90 min.). More dodecacarbonyltri-iron (1·0 g., 2·0 mmoles) was added and heating was continued (2·5 hr.). The precipitate was filtered off and washed with ether, and the combined filtrate and washing were evaporated under reduced pressure at 30°. Chromatography on silica, and elution with benzene–ether (19 : 1) gave the *complex* (XXIV) (81 mg., 11%) as yellow prisms, m.p. 182° (decomp.) (from benzene–petroleum) [Found: C, 65·85; H, 3·55; O, 18·20%; *M* (osmometer), 447. $C_{24}H_{14}FeO_5$ requires C, 65·8; H, 3·2; O, 18·3%; *M*, 438], $\nu_{max.}$ ($CHCl_3$) 1727, 1998, 2010, and 2070 cm.$^{-1}$, $\nu_{max.}$ 1738, 2000, and 2060 cm.$^{-1}$, τ 2·0—2·8 (m, aromatic and ring A protons). Continued elution with the same solvent gave *complex* (XXIII) (161 mg., 22%) as orange plates, m.p. 191—193° (decomp.) (from benzene–petroleum) [Found: C, 65·75; H, 8·1; O, 18·0%; *M* (osmometer), 397], $\nu_{max.}$ ($CHCl_3$) 1693, 1990, 2000, and 2060 cm.$^{-1}$, $\nu_{max.}$ 1630, 1693, 2000, and 2060 cm.$^{-1}$, τ 2·3—2·8 (10H, m, aromatic), 4·0 (2H, m, central diene protons), and 6·2 (2H, m, diene protons). Further elution with the same solvent gave starting material (147 mg., 29%).

Thermal Interconversion of the Complexes (XIII) *and* (XXIV).—Complex (XXIII) (50 mg.) and toluene (2·5 ml.) were heated under reflux under nitrogen (30 min.). After evaporation of solvent under reduced pressure at 30°, chromatography as just described gave complex (XXIII) (36 mg., 72%), complex (XXIV) (7 mg., 14%), and 1,4-diphenyl-2-benzopyran-3-one (1 mg., 3%). Similarly, complex (XXIV) was converted into a mixture of the two complexes.

Photochemical Interconversion of Complexes (XXIV) *and* (XXIII).—Complex (XXIV) (26 mg.) in ether (20 ml.) was irradiated in a silica flask with a medium-pressure (150 w) mercury lamp while a slow stream of nitrogen was bubbled through the solution. After 5 hr. conversion into complex (XXIII) was complete [t.l.c. on silica, with benzene–ether (19 : 1) as developer]. Chromatography as already described gave complex (XXIII) (13 mg., 50%) and a trace of the pyrone (III). Similarly irradiated, complex (XXIII) was unchanged. However irradiation of complex (XXIII) (50 mg.) in benzene (8 ml.) for 120 hr. followed by chromatography gave complex (XXIV) (8 mg., 16%), starting material (37 mg., 74%), and a trace of the pyrone (III).

Reaction of o-*Xylylene Dibromide with Enneacarbonyldiiron*.—The dibromide (5 g., 19 mmoles), enneacarbonyldiiron (15 g., 41 mmoles), and benzene (75 ml.) were stirred at 20° under nitrogen (48 hr.). The solution was filtered and evaporated, and the crude product (1·55 g.) was chromatographed over silica. Elution with benzene–petroleum (19 : 1) gave tricarbonyl-*o*-quinodimetheneiron (30 mg.) as a yellow oil, identical (n.m.r. spectrum) with authentic material.[18] Continued elution with the same solvent gave first *o*-benzyltoluene (120 mg.), τ 2·9 (9H, m, aromatic), 6·03 (2H, s, CH_2), and 7·78 (3H, s, Me), and then 10,11-dihydro-1-methyl-5*H*-dibenzo[*a*,*d*]cycloheptene (370 mg.) identical with authentic material[27] (m.p. and n.m.r. spectrum).

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