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THE SYNTHESIS OF QUINODIMETHANES IN THE BENZODIFURANONE AND BENZODIPYRROLIDONE SERIES†

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SUMMARY

The condensation of hydroquinone and 2,5-*substituted hydroquinones with mandelic acids, or of* 1,4-*benzoquinone and* 2,5-*substituted* 1,4-*benzoquinones with mandelic acids or arylacetic acids gives* 3,7-*diaryl*-2,6-*dioxo*-2,6-*dihydrobenzo*[1,2-*b* : 4,5-*b'*]*difuran derivatives. Analogous benzodipyrrolidones have been obtained from* 1,4-*phenylenediamine and N,N'-dimethyl*-1,4-*phenylenediamine. Both series are novel chromogens and have application as dyestuffs. The red compound obtained from* 1,4-*benzoquinone and cyanoacetic acid and reported to be a* lin-*pentacenetriquinone has been shown to be* 3,7-*bis*(4-*hydroxyphenyl*)2,6-*dioxo*-2,6-*dihydrobenzo*[1,2-*b* : 4,5-*b'*]*difuran.*

1. DISCUSSION

The reaction of active methylene compounds with quinones has attracted attention over many years.[1] In its simplest form the reaction with 1,4-benzoquinone involves successive Michael additions and oxidations to give 2,5-disubstituted-1,4-benzoquinones but, depending upon the nature of the methylene activating groups, cyclisation reactions can occur. Thus benzoquinone reacts[2] with ethyl cyanoacetate under basic conditions to give the

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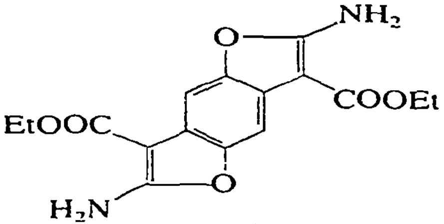
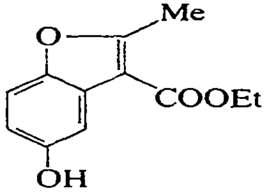
benzodifuran (1). Although basic catalysis is normal for Michael addition reactions, zinc chloride has been used to catalyse the reaction of 1,4-benzoquinone with ethyl acetoacetate when both the mono and dibenzfurans (2) and (3) are obtained.[3–6]



(1)



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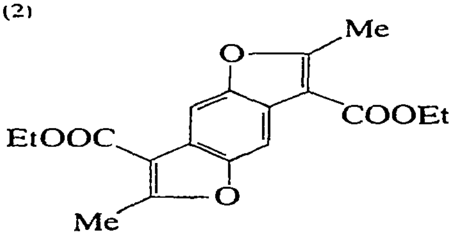
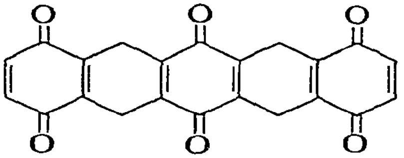


(3)

Junek has reported[7–9] that the reaction of benzoquinone with cyanoacetic acid without added catalyst gives the red *lin*-pentacenequinone (4) in very low yield The structure assignment depended largely on the zinc dust distillation of (4) which gave a compound regarded as being octahydropentacene although a direct comparison with authentic material[10] was not made; however, the u.v. absorption spectra of the zinc dust distillation product showed some similarity to that of 6,13-dihydropentacene [11] The observation that (4) formed diacyl derivatives (5b) was explained on the basis that (4) can exist as the enol (5a) Surprisingly (4) did not react[9] with either cyanoacetic acid or malononitrile by



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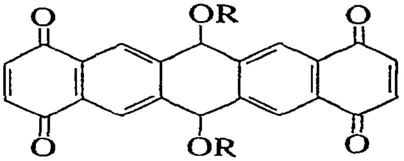


(5a) R = H
(5b) R = acyl

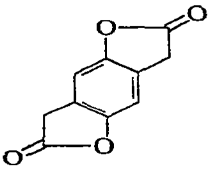
expected Michael addition even under basic conditions, instead (4) and cyanoacetic acid on heating gave a diester with proposed structure (5b) R = COCH$_2$CN. This indicated to us that the benzoquinone/cyanoacetic acid product was not a 1,4-quinone and consequently structures (4) and (5a) were untenable.

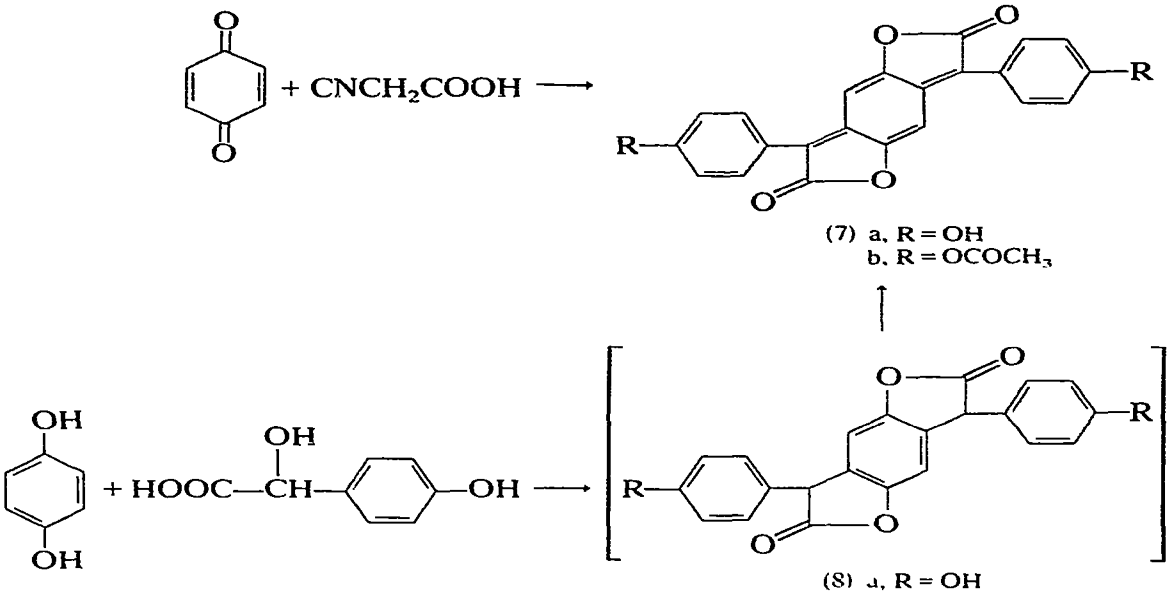
In our studies of this product, mass spectrography (ms) confirmed the empirical formula as $C_{22}H_{12}O_6$. The infrared (i.r.) spectrum showed strong bands at 1725 cm^{-1} typical of an unsaturated lactone carbonyl, and at 3385 cm^{-1} typical of a hydroxyl group together with a weaker band at 3080 cm^{-1} assigned to —CH═CH—. The ready solubility of the product in alkali was consistent with a phenolic group being present and the colour degradation noted on prolonged standing in alkaline solution suggested this was associated with opening of an unsaturated lactone ring. The ^{1}H nuclear magnetic resonance (n.m.r.) spectrum showed a singlet at δ 7·2 (2H, —CH═) and paired doublets at δ 6·95 and 7·78 (8H, aromatic). The ^{13}C n.m.r. spectrum notably had a resonance at 167·3 ppm consistent with an unsaturated lactone carbonyl, since from the data in Table 1 the unsaturated lactone corresponding to (6) would be expected to have a carbonyl resonance at 167·6 ppm (174·1 − 6·5). Quinone carbonyls typically show resonances in the range 183–187 ppm (Table 1). The total data is consistent with the benzoquinone/cyanoacetic acid product being 3,7-bis(4-hydroxyphenyl)2,6-dioxo-2,6-dihydrobenzo-[1,2-b: 4,5-b′]difuran (7a) (Scheme 1).

The same compound (7a) was also obtained by independent synthesis from hydroquinone and 4-hydroxymandelic acid, the intermediate dihydro compound (8a) being very readily oxidised to (7a) and not isolated. Acetylation of (7a) gave the orange coloured diacetyl derivative (7b) which on reduction gave a colourless dihydro derivative (8b) and not the tetrahydro derivative of (5b), where R = acetyl, as claimed by Junek.[7] The dihydro compound (8b) was very readily reoxidised even in air to (7b).

TABLE 1

^{13}C N M R. RESONANCES FOR CARBONYL GROUPS

Compound	*ppm*	*Reference*
(7a)	167 3	
methyl acrylate	164·5 $\}$ Δ6 5	12
methyl acetate	171 0	
butyrolactone	178·0	12
 (6)	174 1	13
1,4-benzoquinone	187	14
1,4-naphthaquinone	184 7	15
anthraquinone	183·2	15


(7) a, R = OH
b, R = OCOCH$_3$

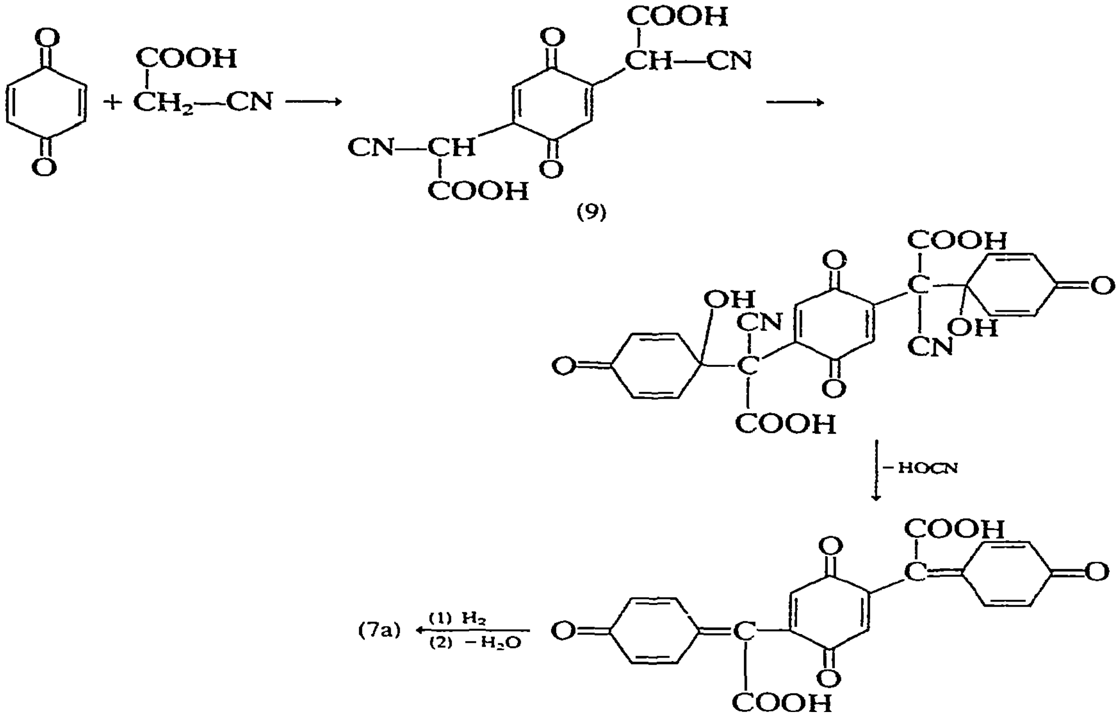
(8) a, R = OH
b, R = OCOCH$_3$

Scheme 1

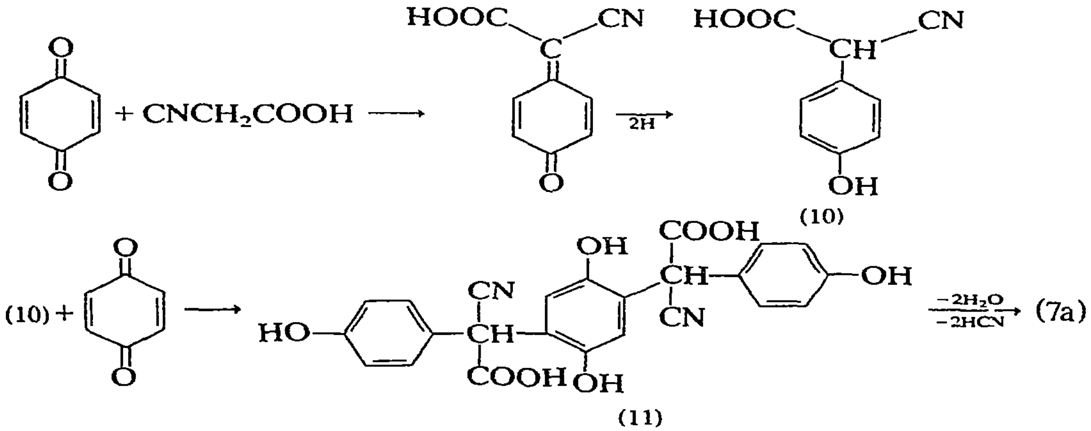
The formation of (7a) from benzoquinone and cyanoacetic acid is remarkable. If the primary reaction is successive Michael additions and oxidations to give (9) then the next steps must involve 1,2-addition of the C_2 and C_5 —CH$<$ groups to benzoquinone with subsequent eliminations of the elements of HO—CN, reduction and lactonisation (Scheme 2).

A preferred mechanism (Scheme 3) involves a Perkin type condensation between benzoquinone and cyanoacetic acid and reaction of the derived α-cyano-4-hydroxyphenylacetic acid (10) with benzoquinone by two successive Michael additions to give the intermediate 2,5-disubstituted hydroquinone (11) which undergoes lactonisation and loss of hydrogen cyanide to give the final product. In support, we find hydrogen cyanide is evolved in this reaction although only to a small extent.

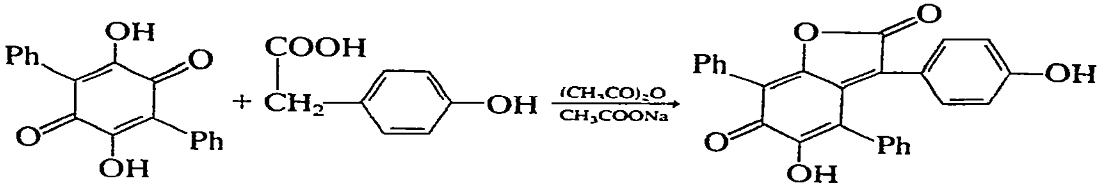
The benzodifuranone (7a) shows some relationship to the fungal pigment xylerythrin (12)[16] which has been synthesised[17] by the Perkin type condensation of 2,5-dihydroxy-3,6-diphenyl-1,4-benzoquinone with 4-hydroxyphenylacetic acid (Scheme 4) The application of this approach to the synthesis of (7a) by the reaction of 2,5-dihydroxy-1,4-benzoquinone with 4-hydroxyphenylacetic acid failed, the reaction mixture was complex, by thin layer chromatography (t l.c.) (7a) was absent but the presence of an orange coloured component suggested that only one unsaturated lactone ring had been formed as in (12).



Scheme 2



Scheme 3

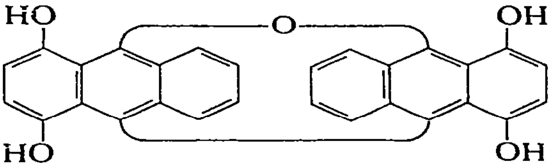


(12)

Scheme 4

Our synthesis of (7a) is of general applicability and has been applied to the synthesis of benzodifuranones (7) with substituents in the 4 and 8 positions and in the pendant aryl rings by the reaction of hydroquinones optionally substituted in the 2,5-positions with optionally substituted mandelic acids. 1,4-Benzoquinones can be substituted for the quinol in this reaction and in these cases an intermediate oxidation step is not required. In a further variant, chloranil was reacted with an arylacetic acid or mandelic acid. These synthetic routes (Scheme 5) give only modest yields (up to 35%) of benzodifuranones and the underlying reasons are being studied: one factor is the reported thermal instability of mandelic acid(s) [18]

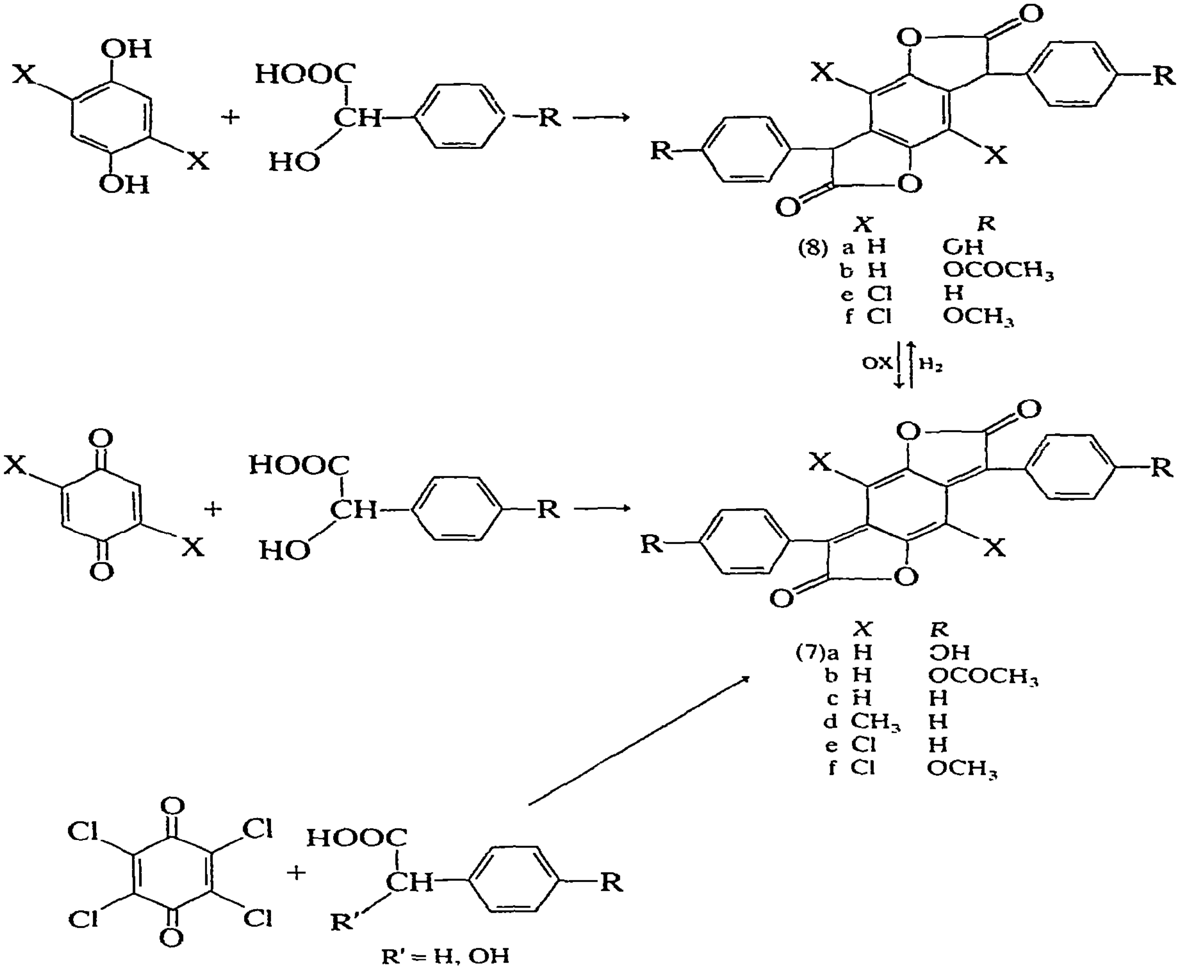
The reaction of 2,5-dichlorohydroquinone with mandelic acid gave (7e) together with significant amounts of (7c) and (7) where X = Cl and H. The reaction of hydroquinone with mandelic acid has been reported[19] previously to give the dianthracene derivative (13) but from the melting point, colour and analytical data given it is clearly the benzodifuranone (7c).



(13)

The ^{1}H n m.r. spectra at ambient temperature of the leuco compounds (8a), (8e) and (8f) each showed two singlet resonances corresponding to the C_3 and C_7 protons suggesting the presence of *syn* and *anti* forms At higher temperatures these resonances merged, probably due to rapid interconversion occurring via the enol forms.

The benzodifuranones are highly coloured and have application as dyestuffs particularly for synthetic fibres.[20] A detailed study of the effect on colour of substitutents in the aryl rings and in the 4 and 8 positions is in hand and will be reported later. Table 2 records some representative examples. Electron donating substitutents in the aryl groups effect large bathochromic shifts whereas the



	X	R
(8) a	H	OH
b	H	$OCOCH_3$
e	Cl	H
f	Cl	OCH_3

	X	R
(7)a	H	OH
b	H	$OCOCH_3$
c	H	H
d	CH_3	H
e	Cl	H
f	Cl	OCH_3

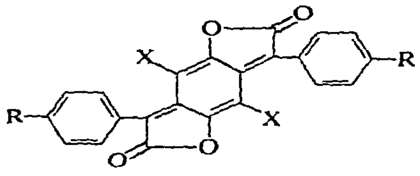
Scheme 5

electron donating methyl substituent in the 4 and 8 positions gives a hypsochromic shift and reduction in the extinction coefficient consistent with increased steric strain. The electron withdrawing chloro substituent in the 4 and 8 positions effects a bathochromic shift with only a small reduction in extinction coefficient.

Synthesis of the related benzodipyrrolidones was based on 1,4-phenylenediamine (14) (Scheme 6). Thus (14) reacted with mandelic acid gave the diamide (15) which was cyclised in sulphuric acid to the dipyrrole (16). The

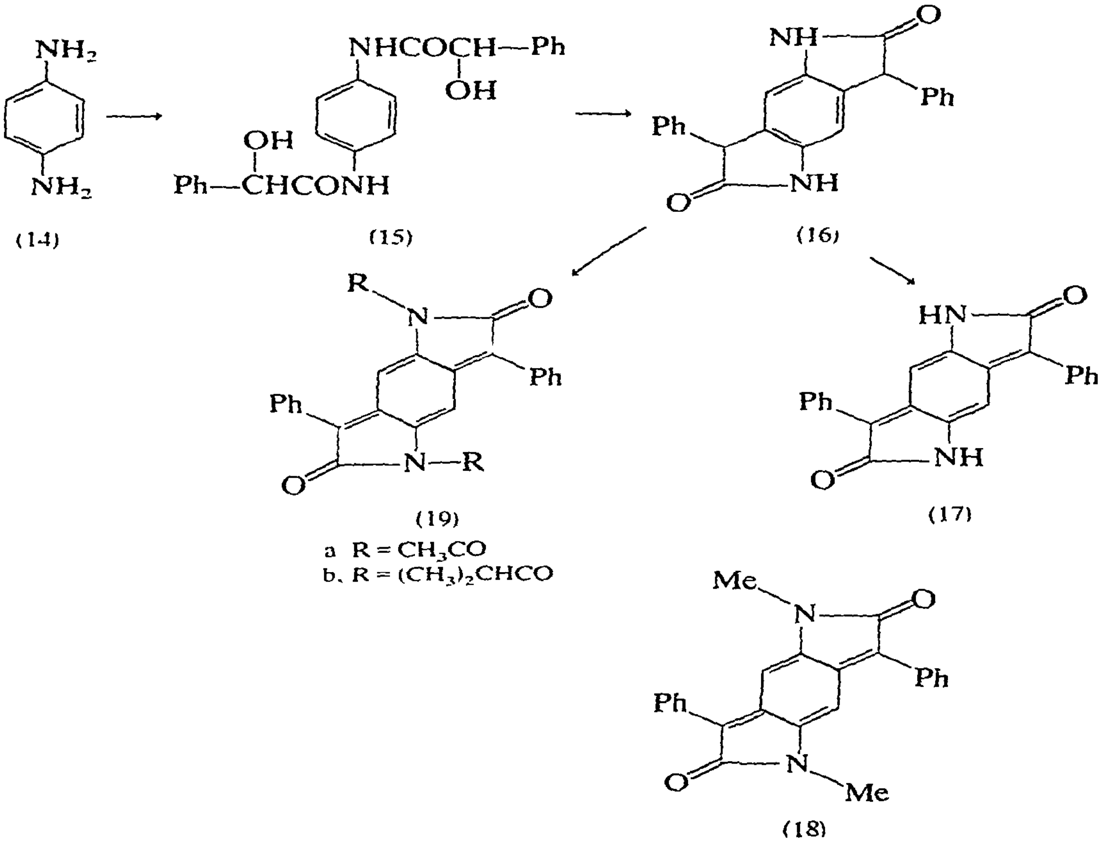
TABLE 2

VISIBLE SPECTRA OF BENZODIFURANONES



(7)

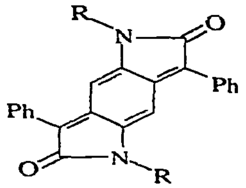
(7)	*X*	*R*	λ_{max}	ε_{max}	*Solvent*
a	H	OH	523	49 200	Acetone
b	H	$OCOCH_3$	475	48 600	Dimethyl formamide
c	H	H	466	51 000	Chloroform
d	CH_3	H	428	37 300	Toluene
e	Cl	H	457	46 000	Chloroform
f	Cl	OCH_3	536	42 300	Chloroform



Scheme 6

TABLE 3

VISIBLE SPECTRA OF BENZODIPYRROLIDONES



Compound	*R*	λ_{max}	ε_{max}	*Solvent*
(17)	H	452	36 000	Dimethyl formamide
(18)	CH_3	455	31 500	Chloroform
(19a)	CH_3CO	470	42 800	Toluene
(19b)	$(CH_3)_2CHCO$	474	35 900	Toluene

dipyrrole (16) was very readily oxidised in alkaline solution to the highly coloured dipyrrolidone (17). An analogous synthesis based on N,N′-dimethyl-1,4-phenylenediamine gave the N,N′-dimethyl dipyrrolidone (18) having similar colourimetric properties. Acylation of (16) was invariably accompanied by oxidation to give N,N′-diacyldipyrrolidones (19a, 19b) which show bathochromic shifts over the non-acylated compounds. Table 3 shows the visible absorption data in this series. The compounds, like the benzodifuranones, are useful as dyestuffs particularly for synthetic fibres.[20] Natural colouring matters related to the benzodipyrrolidone chromophore are not known.

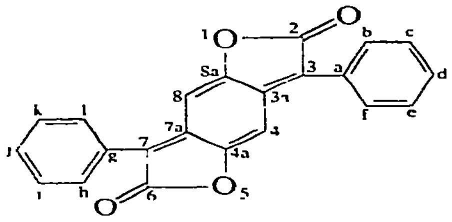
Work on the benzodifuranone and benzodipyrrolidone series is continuing and will be reported later.

2. EXPERIMENTAL

Infrared spectra were recorded with a Perkin Elmer 177 spectrophotometer (Nujol mulls). Nuclear magnetic resonance spectra were taken with a Varian HA-100, a Perkin Elmer R32 90 MHz, a Bruker WH 90 or a GEOL FX 100Q spectrophotometer. Mass spectra were taken with an AEI MS9 or Finnegan 4000 mass spectrometer. Visible spectra were determined on a Perkin Elmer 554 spectrophotometer. Thin-layer chromatography was carried out on Eastman Chromatogram sheet, 13181 silica gel with fluorescent indicator (6060) using a mixture of toluene (90), pyridine (5) and acetic acid (5) as eluant.

Melting points were determined on an instrument developed by ICI Ltd using differential thermal analysis.

The numbering system used in the nomenclature for the ^{13}C n.m.r. spectra of benzodifuranones and related compounds is as follows:



2 1 3,7-*Bis(4-hydroxyphenyl)2,6-dioxo-2,6-dihydrobenzo[1,2-b:4,5-b']difuran*. (*7a*)

(a) *From 1,4-benzoquinone and cyanoacetic acid:* This follows Junek's conditions[7] with modified isolation A mixture of 1,4-benzoquinone (4·3 g, 0·04 mol), cyanoacetic acid (6·8 g, 0·08 mol), acetone (20 ml) and water (30 ml) was stirred and heated under reflux for 5 min. After cooling to 20°C the crystalline product was isolated, washed successively with aqueous acetone (1 . 1), acetonitrile and diethyl ether and dried to give 3,7-bis(4-hydroxyphenyl)-2,6-dioxo-2,6-dihydrobenzo[1,2-b:4,5-b']difuran (7a) as needle crystals with a black reflex (0·3 g, 2%) (further material of lower purity (1·0 g) was isolated from the mother liquors by dilution with water), m p. >400°C, λ_{max} (acetone) 523 nm, ε_{max} 49 200, ν_{max} 3385 (OH), 3080 (—CH=CH—) and 1725 (unsaturated lactone C=O): ^{1}H n.m.r. (d_6 DMSO) δ 6·95 (4H, d, aromatic), 7·78 (4H, d, aromatic), 7·2 (2H, s, =CH—). ^{13}C n m r. (d_6 DMSO) ppm 97·8 (4, 8), 115·9 (c, e, k, i), 120·3 (a, g), 123·6 (3a, 7a), 130·5 (b, f, l, h), 134·9 (3, 7), 152·9 (4a, 8a), 159·5 (d, j), 167·3 (2, 6).

Found C, 70·6, H, 3·3%, M$^+$ 372. $C_{22}H_{12}O_6$ requires C, 70·95, H, 3·25%; M 372

The above reaction was repeated on a ×2 scale in water (140 ml) as solvent and the mixture stirred and heated at 75°C for 0·5 h while purging the atmosphere over the reaction with nitrogen and passing the off gases through N/1 sodium hydroxide solution. After cooling, the precipitated product was collected, washed with water and dried (3·25 g, ε_{max} 12 900 ≡ 0·84 g, 8·5% yield at 100% strength). By t.l.c. the filtrates contained no product Analysis of the sodium hydroxide solution for cyanide showed 61·3 mg HCN had been evolved equivalent to 8·35% on product isolated at 100%.

(b) *From hydroquinone and 4-hydroxymandelic acid:* A mixture of hydroquinone (2·2 g, 0·02 mol), 4-hydroxymandelic acid (10·1 g, 0·06 mol) and *o*-dichlorobenzene (200 ml) was heated under reflux for 1·5 h in a slow stream of nitrogen and allowing formed water to distil. Nitrobenzene (10 ml) was then added and heating continued for a further 0·5 h. After cooling, the precipitate was collected, washed with toluene then water and dried (10·2 g, ε_{max} 9700 ≡ 27% yield at 100% strength). Trituration ×2 with cold acetonitrile gave pure material (1·12 g, 15%) identical (t.l.c , i.r., m.s. and ^{1}H n.m.r.) to that prepared as in (a).

2.2. *Condensation of* 2,5-*dihydroxy*-1,4-*benzoquinone and* 4-*hydroxyphenylacetic acid*

A mixture of 2,5-dihydroxy-1,4-benzoquinone (1·4 g, 0·01 mol), 4-hydroxyphenylacetic acid (4·56 g, 0·03 mol), sodium acetate (0·6 g, 0·006 mol) and acetic anhydride (50 ml) was stirred and heated under reflux for 5 h. After cooling, the reaction mixture was poured into water and the oily product examined by t.l.c. This showed mainly base-line material and weak yellow/brown bands. A red band corresponding to (7a) was absent.

2.3. 3,7-*Bis*(4-*acetoxyphenyl*)2,6-*dioxo*-2,6-*dihydrobenzo*[1,2-*b* : 4,5-*b*′]*difuran*, (7*b*)

The dihydroxy compound (7a) (0·5 g), acetic anhydride (20 ml) and sulphuric acid (0·4 ml) were stirred and heated under reflux for 1h during which time the product crystallised out (0·5 g) m.p. 316°C. Recrystallisation from nitrobenzene gave fine needle crystals (0·4 g, 81% with a violet reflex of 3,7-bis(4-acetoxyphenyl)2,6-dioxo-2,6-dihydrobenzo[1,2-b : 4,5-b′]difuran (7b) m.p. 324°C (ref. 7: 324°C), λ_{max} (DMF) 475 nm, ε_{max} 48 600; ν_{max} 1780 (unsaturated lactone C═O), 1740 (ester C═O); ^{1}H n.m.r. (d_6, CF_3COOH) δ 2·5 (6H, s, CH_3), 7·1 (2H, s, ═CH—), 7·3 (4H, d, aromatic), 7·8 (4H, d, aromatic); ^{13}C n.m.r. (d_6, CF_3COOH), ppm 21·6 (CH_3) 101·7 (4, 8), 124·3 (c, e, i, k), 128·6 (a, g or 3a, 7a) 129·0 (3a, 7a or a, g), 132·6 (b, f, h, l), 141·1 (3, 7), 154·0 (4a, 8a or d, j), 156·4 (d, j or 4a, 8a), 173·2 (2, 6), 177·0 ($COCH_3$).

2.4. 3,7-*Bis*(4-*acetoxyphenyl*)2,6-*dioxo*-2,6,3,7-*tetrahydrobenzo*[1,2-*b* : 4,5-*b*′]-*difuran*, (8*b*)

The diacetoxy derivative (7b) (0·5 g), acetic acid (10 ml) and zinc dust (2·0 g) were stirred and heated under reflux until the solution became virtually colourless (0·5 h). After cooling and screening, the product was precipitated with water, collected, washed with water and dried to give 3,7-bis(4-acetoxyphenyl)2,6-dioxo-2,6,3,7-tetrahydrobenzo[1,2-b : 4,5-b′] difuran (8b) (0·3 g, 60%) m.p. 275°C (ref: 7: 280°C *ex dioxan*) which tended to oxidise to (6b) on attempted recrystallisation; ν_{max} 1750 (ester C═O), 1810 (lactone C═O); ^{1}H n.m.r. (d_6 DMSO), δ 2·25 (6H, s, CH_3), 5·48 and 5·52 (2H, s, >CH—CO—, these resonances merge at higher temperatures suggesting *syn* and *anti* forms involving the aryl groups which are interconverting rapidly via the enol at the higher temperature) 7·1–7·45 (10 H, aromatic); ^{13}C n.m.r.

(d_6 DMSO), ppm 20·56 (q, CH_3), 48·6 (d, 3, 7), 107·4 (d, 4, 8), 121·6 (d, b, h or c, i), 128·4 (d, c, i or b, h), 131·96 (s, a, g or 3a, 7a), 149·0 (s, 4a, 8a or d, j), 148·4 (s, d, j or 4a, 8a), 168·2 (s, —$COCH_3$), 174·1 (s, 2, 6).

Found: C, 67·9; H, 3·9%; M^+ 458. $C_{26}H_{18}O_8$ requires C, 68·1, H, 3·95%; M 458

2 5. 2,6-*Dioxo*-2,6,3,7-*tetrahydrobenzo*[1,2-*b*:4,5-*b'*]*difuran*, (6)

The literature procedure[13] gave colourless needles m.p. 288°C (ref. 13 288°C), ν_{max} 1780 (C=O), ^1H n.m.r. (d_6 DMSO) δ 3·9 (4H, s, CH_2), 7·15 (2H, s, aromatic), ^{13}C n.m.r. (d_6 DMSO), ppm 33·2 (t, 3, 7), 107·3 (d, 4, 8), 123·9 (s, 3a, 7a), 150·0 (s, 4a, 8a), 174·1 (s, 2, 6).

2 6 3,7-*Diphenyl*-2,6-*dioxo*-2,6-*dihydrobenzo*[1,2-*b*:4,5-*b'*]*difuran*, (7c)

(a) *From hydroquinone and mandelic acid* A mixture of hydroquinone (2·2 g, 0 02 mol), mandelic acid (9 12 g, 0·06 mol) and *o*-dichlorobenzene (50 ml) was heated under reflux for 18 h in a slow stream of air and formed water allowed to distil off. Nitrobenzene (5 ml) was then added and the mixture heated under reflux for 2 h to ensure that oxidation of the leuco compound was complete After cooling to 20°C the precipitate was collected, washed successively with *o*-dichlorobenzene, ethanol and petroleum ether (b p 80–100°C) and dried to give 3,7-diphenyl-2,6-dioxo-2,6-dihydrobenzo[1,2-b:4,5-b']difuran (7c) as plate crystals with a bronze reflex (2 38 g, 35%), m.p. 298°C; λ_{max} ($CHCl_3$) 466 nm, ε_{max} 51 000, ν_{max} 1760 (unsaturated lactone C=O); ^1H n.m.r. ($CDCl_3$) δ 6·7 (2H, s, =CH—), 7·3 (6H, d, aromatic), 7·6 (4H, d, aromatic), ^{13}C n m r ($CDCl_3$), ppm 98 0 (4, 8), 125 9 (3a, 7a), 129 1 (b, c, d, e, f, h, i, j, k, l), 130·4 (a, g), 138·4 (3, 7), 154·3 (4a, 8a) Because of low solubility the spectrum was too weak to allocate a resonance corresponding to C_2 and C_6

Found C, 77 6, H, 3 4%, M^+ 340 $C_{22}H_{12}O_4$ requires C, 77·65, H, 3·55%, M 340

(b) *From benzoquinone and mandelic acid* A mixture of 1,4-benzoquinone (4·32 g, 0 04 mol) mandelic acid (18 24 g, 0·12 mol) and trichlorobenzene (30 ml) was heated at 180°C for 7 h while allowing formed water to distil off After cooling, the product was collected, washed with toluene and petroleum ether (b.p. 80–100°C) and dried (3·4 g, 25%), identical by t l.c. and i.r. to material prepared as in (a)

2 7 4,8-*Dimethyl*-3,7-*diphenyl*-2,6-*dioxo*-2,6-*dihydrobenzo*[1,2-*b*:4,5-*b'*]*difuran* (7d)

2,5-Dimethylhydroquinone (2·76 g, 0 02 mol) and mandelic acid (7·6 g, 0·05 mol) were added to sulphuric acid (98 g, 85%) with stirring at <10°C. The reaction mixture was stirred at 20°C for 18 h, poured into iced water (500 ml) and the product isolated via extraction with ethyl acetate. The crude product was stirred with water (100 ml) containing sodium carbonate (50 ml, 2N) and potassium persulphate (3·0 g) at 70°C for 15 min. and after acidification with dilute hydrochloric acid the product was collected (7 g) and crystallised from toluene (extraction) to give 4,8-dimethyl-3,7-diphenyl-2,6-dioxo-2,6-dihydrobenzo[1,2-b:4,5-b']difuran (7d) as orange crystals (1·1 g, 15%) m.p. 270°C, λ_{max} (toluene) 428 nm, ε_{max} 37 300; ν_{max} 1760 (unsaturated lactone C═O); ^{1}H n.m.r. ($CDCl_3$) δ 1·98 (6H, s, CH_3), 7·2 (10 H, unresolved, aromatic).

Found: C, 78·1; H, 4·2%; M^+ 368. $C_{24}H_{16}O_4$ requires C, 78·25; H, 4·35%; M 368.

The product was also obtained from the reaction of 2,5-dibromo-3,6-dimethyl-1,4-benzoquinone (2·94 g, 0·01 mol) with phenylacetic acid (4·08 g, 0·03 mol) in boiling trichlorobenzene (50 ml) for 3 h.

2.8. 4,8-*Dichloro*-3,7-*diphenyl*-2,6-*dioxo*-2,6-*dihydrobenzo*[1,2-*b* : 4,5-*b'*]*difuran*. (7*e*)

(a) *From chloranil and phenylacetic acid:* A mixture of chloranil (7·38 g, 0·03 mol), phenylacetic acid (12·24 g, 0·09 mol), zinc chloride (3·0 g) and trichlorobenzene (50 ml) was stirred and heated at 180–190°C for 4 h while allowing formed water to distil off. After cooling, the crude product was collected, crystallised from toluene (extraction) and the product (2 g) extracted into chloroform, screened from insoluble material and the solution washed successively with water, dilute sodium carbonate solution and water, dried, evaporated to dryness and the residue triturated with ethanol to give 4,8-dichloro-3,7-diphenyl-2,6-dioxo-2,6-dihydrobenzo[1,2-b 4,5-b']difuran (7e) as orange crystals (2·0 g, 16%) m.p. 318°C; λ_{max} ($CHCl_3$) 457 nm, ε_{max} 46 000; ν_{max} 1780 (unsaturated lactone C═O).

Found: C, 64·2, H, 2·2, Cl, 17·8%; M^+ 408. $C_{22}H_{10}Cl_2O_4$ requires C, 64·55; H, 2·45; Cl, 17·35%; M 408. ^{1}H and ^{13}C n.m.r. spectra could not be obtained because of low solubility.

(b) *From chloranil and mandelic acid:* A mixture of chloranil (4·9 g, 0·02 mol), mandelic acid (12·1 g, 0·08 mol) and trichlorobenzene (25 ml) was stirred and heated at 180–190°C for 18 h. Isolation and purification was as in (a) to give the product (0·6 g, 7%) m.p. 318°C.

(c) *From 2,5-dichlorohydroquinone and mandelic acid:* 2,5-Dichlorohydroquinone (3·6 g, 0·02 mol) and mandelic acid (6·08 g, 0·04 mol) were heated together at 230°C for 2 h. After cooling to 125°C toluene (25 ml) was added and the mixture screened, evaporated to dryness and the residue triturated with cold methanol. The crude product (0·9 g) was crystallised from methanol to give the product (0·4 g) m.p. 195°C, having M^+ 408 (major), 374 and 340 corresponding to the dichloro compound (7e), the mono chloro compound (7), where one X is Cl and the other H, and the 4,8-unsubstituted compound (7c).

2.9. 4,8-*Dichloro-3,7-diphenyl-2,6-dioxo-2,6,3,7-tetrahydrobenzo-[1,2-b:4,5-b′]difuran,* (8*e*)

4,8-Dichloro-3,7-diphenyl-2,6-dioxo-2,6-dihydrobenzo[1,2-b:4,5-b′]difuran (7e) (0·3 g) was hydrogenated in ethyl acetate (500 ml) using a palladium/charcoal catalyst. After removal of this catalyst the solution was evaporated *in vacuo* to give 4,8-dichloro-3,7-diphenyl-2,6-dioxo-2,6,3,7-tetrahydrobenzo[1,2-b:4,5-b′]difuran (8e) as a pale cream solid (0·2 g, 67%): m.p 294°C; ν_{max} 1830 (lactone C═O); ^{1}H n.m.r. (d_6 DMSO) δ 5·63 and 5·69 (2H, s, C*H*—CO—), 7·4 (10 H, unresolved, aromatic).

Found: C, 64·2; H, 2·7; Cl, 17·0%, M^+ 410 $C_{22}H_{12}Cl_2O_4$ requires C, 64·25, H, 2·9, Cl, 17·25%, M 410.

2.10. 4,8-*Dichloro-3,7-bis*(4-*methoxyphenyl*)2,6-*dioxo-2,6-dihydrobenzo-[1,2-b:4,5-b′]difuran,* (7*f*)

A mixture of chloranil (24·6 g, 0·1 mol), 4-methoxyphenylacetic acid (53·2 g, 0·2 mol) and trichlorobenzene (80 ml) was stirred and heated at 180–190°C for 3·5 h. After allowing to cool and stand for 24 h the product was collected, washed successively with chlorobenzene, ethanol and acetone to give 4,8-dichloro-3,7-bis (4-methoxyphenyl) 2,6-dioxo-2,6-dihydrobenzo[1,2-b:4,5-b′]difuran (7f) (13·1 g, 28%) m.p. 303°C, λ_{max} ($CHCl_3$) 536 nm, ε_{max} 42 300; ν_{max} 1775 (unsaturated lactone C═O); ^{1}H n.m.r. (d_6 DMSO) δ 3·7 (6H, s, OC*H*$_3$), 6·9 (4H, broad d, aromatic), 7·3 (4H, broad d, aromatic); ^{13}C n m.r (d_6 DMSO), ppm 55·1 (OCH_3), 78·6 (4, 8), 113·1 (c, e, i, k), 119·5 (a, g), 128 0 (3a, 7a), 132·2 (b, f, h, l) 134·2 (3, 7), 148·9 (4a, 8a), 160·8 (d, j), 165·3 (2, 6).

Found· C, 61·1; H, 3·0; Cl, 15·3%; M^+ 468. $C_{24}H_{14}Cl_2O_6$ requires C, 61·4, H, 3·0, Cl, 15·15%, M 468

2.11. 4,8-*Dichloro-3,7-bis*(4-*methoxyphenyl*)2,6-*dioxo-2,6,3,7-tetrahydro-benzo*[1,2-*b*:4,5-*b′*]*difuran,* (8*f*)

A mixture of 4,8-dichloro-3,7-bis(4-methoxyphenyl)2,6-dioxo-2,6-dihydrobenzo[1,2-b·4,5-b′]difuran (7f) (0·5 g), zinc dust (2·0 g) and acetic acid (200 ml) was heated under reflux for 2 h during which time the solution became straw coloured. After cooling and screening, the filtrate was diluted with water and the precipitate collected, washed with water and dried *in vacuo* to give 4,8-dichloro-3,7-bis(4-methoxyphenyl)2,6-dioxo-2,6,3,7-tetrahydrobenzo[1,2-b.4,5-b′]difuran (8f) as a pale pink solid (0·25 g, 50%) m.p. 272°C; ν_{max} 1830 (lactone C=O); ^{1}H n.m.r. (d_6 DMSO) δ 5·55 and 5·59 (2H, s, C*H*—CO—), 6·9 (4H, d, aromatic), 7·2 and 7·3 (4H, d, aromatic). When the spectrum is run at 70°C the resonances at δ 5·55 and 5·59 merge as do those at δ 7·2 and 7·3 suggesting that *syn* and *anti* forms present at ambient temperatures are interconverting at the higher temperature.

Found: C, 61·2; H, 3·5; Cl, 15·0%: M^+ 470. $C_{24}H_{16}O_6Cl_2$ requires C, 61·15; H, 3·4 and Cl, 15·05%; M 470.

2.12. 1,4-*Bis*(*α-hydroxyphenylacetylamino*)*benzene*, (15)

A mixture of 1,4-phenylenediamine (5·4 g, 0·05 mol) and mandelic acid (22·8 g, 0·15 mol) in chlorobenzene (100 ml) was stirred and heated at 120–125°C for 18 h in a slow stream of nitrogen while allowing the formed water to distil off. After cooling, the precipitate was filtered off, washed with methanol, dried and recrystallised from nitrobenzene to give 1,4-bis(α-hydroxyphenylacetylamino)benzene (15) as colourless crystals (15·2 g, 81%), m.p. 264–267°C; ν_{max} 3440 (OH), 3260 (amide NH) and 1630 (amide C=O).

Found: C, 70·2; H, 5·3, N, 7·5%; M^+, 376. $C_{22}H_{20}N_2O_4$ requires C, 70·2; H, 5·3; N, 7·45%; M, 376.

2.13. 3,7-*Diphenyl*-2,6-*dioxo*-1,2,3,5,6,7-*hexahydrobenzo*[1,2-*b* : 4,5-*b′*]*di-pyrrole*, (16)

1,4-Bis(α-hydroxyphenylacetylamino)benzene (15) (5 g, 0·013 mol) was added to sulphuric acid (50 ml, 98%), with stirring, and the solution obtained stirred at 20°C for 18 h. The reaction mixture was poured into iced water (500 ml) and the precipitate filtered off, washed with water and dried to give 3,7-diphenyl-2,6-dioxo-1,2,3,5,6,7-hexahydrobenzo[1,2-b . 4,5-b′]di-pyrrole (16) as a cream solid (4·1 g, 91%) m.p. gradual decomposition >150°C, ν_{max} 3200 (amide NH) and 1690 (amide C=O).

Found: C, 77·3; H, 4·5; N, 7·9%; M^+ 340, 338, the latter probably being formed in the spectrometer. $C_{22}H_{16}H_2O_2$ requires C, 77·65; H, 4·7; N, 8·25%; M 340.

2.14. 3,7-*Diphenyl*-2,6-*dioxo*-1,2,5,6-*tetrahydrobenzo*[1,2-*b* : 4,5-*b′*]*dipyrrole*, (17)

Sodium hydroxide solution (4 ml, 2N) was added dropwise to a stirred suspension of (16) (1 g) in ethanol (25 ml) at 20°C and a solution obtained. Hydrogen peroxide (5 ml, 100 vol) was then added and the mixture stirred at 20°C for 1 h during which time the product separated out. The product was collected, washed with ethanol and recrystallised from nitrobenzene to give 3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-b : 4,5-b′] dipyrrole (0·35 g, 35%) as brown crystals m.p. 365°C; λ_{max} (DMF) 452 nm, ε_{max} 36 000; ν_{max} 3130 (amide NH) and 1680 (amide C=O), ^{1}H n.m.r. (d_6 DMSO) δ 6·4

(2H, s, =CH—), 7·5 (10 H, m, unresolved aromatic), M^+ 338 (major), 340. $C_{22}H_{14}N_2O_2$ requires M 338.

2.15 *N,N'-Diacetyl-3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo-[1,2-b:4,5-b']dipyrrole* (19*a*)

A mixture of 3,7-diphenyl-2,6-dioxo-1,2,3,5,6,7-hexahydrobenzo[1,2-b 4,5-b']dipyrrole (16) (4·0 g, 0·012 mol), acetic anhydride (50 ml) and sulphuric acid (1·0 ml, 98%) was stirred and heated under reflux for 2 h during which time the product separated out. After cooling, the product was collected, washed successively with acetic acid and diethyl ether and dried to give N,N'-diacetyl-3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-b·4,5-b']dipyrrole (19a) as orange–brown crystals (2·8 g, 56%), m p. 303°C, λ_{max} (toluene) 470 nm, ε_{max} 42 800; ν_{max} 1740, 1715 (amide C=O); ^{1}H *n* m.r. ($CDCl_3$) δ 2·7 (6H, s, CH_3), 7·5 (6H, aromatic), 7·7 (4H, aromatic), 8·1 (2H, s, —CH=)

Found: C, 74·2, H, 4·3, N, 6·4%; M^+ 422. $C_{26}H_{18}N_2O_4$ requires C, 73·95, H, 4 25, N, 6 65%, M 422

2 16 *N,N'-Di-iso-butyryl-3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo-[1,2-b.4,5-b']dipyrrole* (19*b*)

iso-Butyryl chloride (8 g, 0·075 mol) was added slowly to a solution of 3,7-diphenyl-2,6-dioxo-1,2,3,5,6,7-hexahydrobenzo[1,2-b 4,5-b']dipyrrole (5·0 g, 0·0148 mol) in pyridine (50 ml) keeping the temperature <20°C. The solution was heated under reflux for 2 h, cooled and poured into iced dilute hydrochloric acid, the product collected, washed with ethanol and dried (4·3 g). Recrystallisation from acetic acid gave N,N'-di-*iso*-butyryl-3,7-diphenyl-2,6-dioxo[1,2,5,6-tetrahydrobenzo[1,2-b:4,5-b']dipyrrole (19b) as orange–brown crystals (1·5 g, 21%) m.p 270–271°C, λ_{max} (toluene) 474 nm, ε_{max} 35 900, ν_{max} 1740 (amide C=O).

Found. C, 75·5, H, 5·2, N, 5·4%, M^+478 $C_{30}H_{26}N_2O_4$ requires C, 75·30, N, 5·45%, M 478

2 17 1,4-*Bis*(*α-acetoxy-N-methylphenylacetylamino*)*benzene*

A mixture of N,N'-dimethyl-*p*-phenylene diamine (2·72 g, 0·02 mol), acetylmandelyl chloride (12·7 g, 0 06 mol), anhydrous sodium acetate (4·9 g, 0·06 mol) and chlorobenzene (100 ml) was stirred and heated under reflux for 4 h. After cooling and screening, the solution was evaporated *in vacuo* and the residual oil triturated with diethyl ether when it solidified and was filtered off, washed with diethyl ether and dried to give 1,4-bis(α-acetoxy-N-methylphenylacetylamino)benzene as colourless crystals (3·5 g, 36%), m.p. 183–185°C.

Found. C, 68·7, H, 5·9; N, 5·6%, M^+ 488. $C_{28}H_{28}N_2O_6$ requires C, 48·85, H, 5·75; N, 5·75%; M 488

2.18. *N,N′-Dimethyl-3,7-diphenyl-2,6-dioxo-1,2,3,5,6,7-hexahydrobenzo [1,2-b:4,5-b′]dipyrrole*

A mixture of 1,4-bis(α-acetoxy-N-methylphenylacetylamino)benzene (1·8 g, 0·0037 mol) and polyphosphoric acid (10 g) was stirred and heated at 140°C for 8 h giving a weak red solution. The reaction mixture was poured into water and the precipitated N,N′-dimethyl-3,7-diphenyl-2,6-dioxo-1,2,3,5,6,7-hexahydrobenzo[1,2-b:4,5-b′]dipyrrole filtered off, washed with water and dried to give a fawn powder (1·4 g, 100%) m.p. 180–183°C. The product was used in the next step without further purification.

2.19. *N,N′-dimethyl-3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-b:4,5-b′]dipyrrole*, (18)

A solution of potassium persulphate (3·0 g) in water (10 ml) was added to a stirred suspension of N,N′-dimethyl-3,7-diphenyl-2,6-dioxo-1,2,3,5,6,7-hexahydrobenzo[1,2-b:4,5-b′]dipyrrole (1·4 g, 0·0037 mol) in ethanol (10 ml) containing sodium hydroxide (1·5 ml, 5N) and the mixture stirred and heated under reflux for 2 h. After cooling the reaction mixture was isolated via dilute hydrochloric acid and the crude product crystallised from ethanol (extraction) to give N,N′-dimethyl-3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-b:4,5-b′]dipyrrole (18) as orange–brown crystals (0·15 g, 11%) m p 295°C; λ_{max} ($CHCl_3$) 455 nm, ε_{max} 31 500, ν_{max} 1685 (amide C=O) ^1H n.m.r. ($CDCl_3$) δ 3·17 (6 H, s, CH_3), 6·34 (2 H, s, —CH=) and 7·2–7·7 (10 H, aromatic)

Found C, 78·4, H, 4·8; N, 7·4%, M^+ 366. $C_{24}H_{18}N_2O_2$ requires C, 78·70; H, 4·90, N, 7·65%, M 366

Material (0·7 g) isolated from the mother liquor triturated with acetonitrile gave further product (0·5 g, total yield 48%)

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