Condensation between 2-Chloro-3*H*-indol-3-one and Phenols

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2-Chloro-3*H*-indol-3-one condenses with some phenols having only one reactive position to give quinonoid dyes of the type previously described by Friedlaender. Of the two possible tautomeric forms of these dyes, the quinonoid structure is preferred on the basis of u.v. and n.m.r. spectroscopy and the Michael addition reaction with acetone. The *ortho*-quinonoid dyes show intramolecular hydrogen bonding and are decomposed by alkali to give anthranilic acid and a 2-hydroxybenzaldehyde. The aldehyde recovered from this reaction in deuterium oxide has the aldehydic hydrogen atom replaced by deuterium. The *para*-quinonoid dyes are protonated by strong acids on the quinonoid oxygen atom and reaction with alkali causes opening of the heterocyclic system to give a benzil, which rearranges.

FRIEDLAENDER [1,2] prepared some indigoid dyes by condensing 2-chloro-3*H*-indol-3-one (isatin α-chloride) with phenols and naphthols. Dyestuffs of this class are described in the patent literature,[3] but, so far as we are aware, none is currently manufactured. Condensation occurred *ortho* to the phenolic hydroxy-group to give, for example, compounds (1) and (2), or in the *para*-position to yield (3). We originally intended to investigate the reaction between 2-chloro-3*H*-indol-3-one and 3-methoxyphenol, but this proved more complex than was supposed by Friedlaender and will be described in a later paper. Here we have extended the reaction to dimethylphenols having only one *ortho*- or *para*-position available for substitution and have determined the stereochemistry of the products and their characteristic reactions.

2-Chloro-3*H*-indol-3-one and 2,4-dimethylphenol reacted rapidly in benzene to give a red solution which after chromatography over silica gel gave compound (5) as brownish red needles. The related compounds (2) and (4) were prepared similarly. All three dyestuffs have an absorption band at the red end of the visible spectrum (see Table). Each may exist as a tautomeric pair, *e.g.* (5) ⇌ (6). The electronic spectrum of each compound is better in accord with a structure of type (5), containing a chromophore similar to that of indigotin (which is blue), rather than one of type (6), containing a chromophore similar to that of 2-chloro- or 2-phenyl-3*H*-indol-3-one (which are orange).

Long-wavelength bands in the electronic spectra of the indolin-3-one derivatives

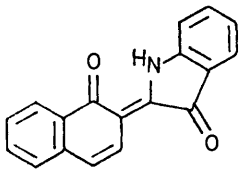
Compound	Solvent	$\lambda_{max.}$/nm	ε
(5)	Benzene	500	4 300
		510	4 300
(2)	Benzene	580	6 200
(2)	Acetonitrile	575	5 000
(4)	Benzene	588	10 000
		628	8 300
(7)	Acetonitrile	534	6 300
2-Phenyl-3*H*-indol-3-one [a]	Dioxan	425	3 000
Indigotin [b]	Xylene	591	

[a] E. Pfeil, G. Geissler, W. Jazquemin, and F. Lomker, *Chem. Ber.*, 1956, **89**, 1210; R. J. Richman and A. Hassner, *J. Org. Chem.*, 1968, **33**, 2548. [b] P. W. Sadler, *J. Org. Chem.*, 1956, **21**, 316.

The ^{1}H n.m.r. spectra of compounds (2) and (5) were

[1] A. Bezdzik and P. Friedlaender, *Monatsh.*, 1908, **29**, 375.
[2] P. Friedlaender and R. Schuloff, *Monatsh.*, 1908, **29**, 387.
[3] For a summary see Colour Index, 3rd edn., 1971, vol. 4, pp. 4613—4615.

obtained in $CDCl_3$ solution but compound (4) was too insoluble for investigation. In these spectra the NH resonance occurs as a sharp singlet at τ *ca.* −3.0 and its



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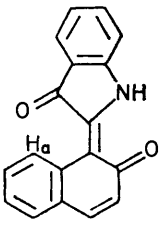

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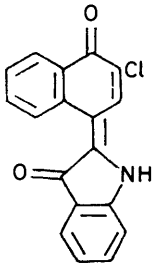

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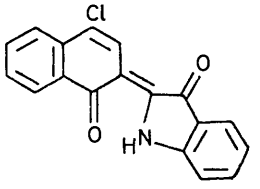
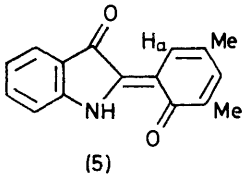


(4)

low-field position is attributed to intramolecular hydrogen bonding to the carbonyl oxygen atom of the adjacent six-membered ring. Compounds (2) and (5) must have the *Z*-configuration shown about the olefinic bond joining the two rings so as to allow this hydrogen bonding. A similar stereochemistry can be assumed for (1), (4), and other *ortho*-linked compounds. Consistent with intramolecular hydrogen bonding, all the *ortho*-compounds we have prepared could be sublimed under reduced pressure. The *para*-compounds could not be so sublimed without decomposition and (7) and (9) showed no low-field n.m.r. signal attributable to an intramolecularly hydrogen bonded proton.



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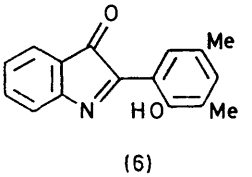

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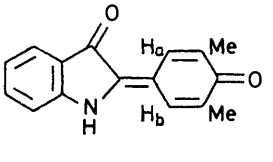

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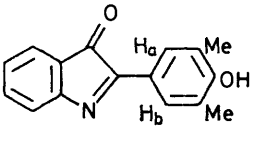

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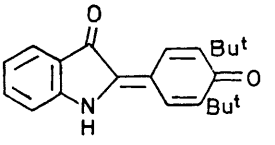
In the n.m.r. spectra of (2) and (5) there is a low-field aromatic resonance which can be attributed to the proton, H_a, in the deshielding cone of the five-membered ring carbonyl oxygen atom. In compound (2) this resonance appears as a multiplet at τ 1.62 which collapses to a singlet on irradiation at the centre of the main aromatic absorption region. The corresponding resonance in (5) is a multiplet at τ 1.82 which collapses to a doublet with J 2 Hz (*meta*-coupling) on irradiation at the methyl frequency.

The reaction between 2-chloro-3*H*-indol-3-one and 2,6-dimethylphenol in benzene to give (7) proceeded readily only after the addition of a little concentrated hydrochloric acid. This was also necessary to catalyse the reaction with 2,6-di-t-butylphenol to give (9). Compound (7) separated as its hydrochloride from the reaction mixture and was conveniently crystallised as the fluoroborate from a mixture of acetic and fluoroboric acids. The neutral compound (7) was obtained by heating the hydrochloride in vacuum.

Compound (7) can exist as a tautomeric pair of structures [(7) and (8)], and such tautomeric pairs can be written for the other *para*-compounds. As discussed previously for the *ortho*-compounds, the electronic absorption spectrum, which shows a band in the red region (see Table), is in accord with the predominance of tautomer (7). Two one-proton singlets are seen in the n.m.r. spectrum of (7) in [$^2H_5$]pyridine–deuterium oxide (τ 1.52 and 2.16) which can be attributed to H_a and H_b, respectively. The fact that these two protons are non-equivalent also shows that the structure must be (7) rather than (8), since in the latter free rotation of the phenol ring is possible. The n.m.r. spectrum of (7) in anhydrous [$^2H_5$]pyridine is considerably more complex, probably owing to intermolecular hydrogen bonding which can be disrupted by addition of deuterium oxide.



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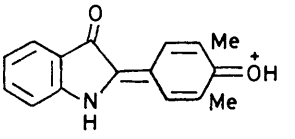


(10)

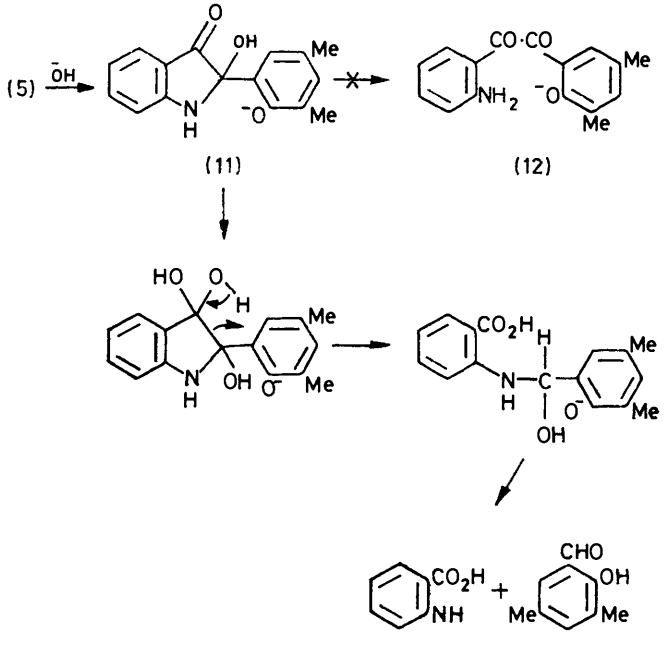
The di-t-butyl derivative (9) does not form a stable salt with hydrochloric or fluoroboric acid and this suggests that protonation of (7) occurs on the carbonyl oxygen atom to give the cation (10). The basicity of the corresponding site in the di-t-butyl analogue (9) will be reduced owing to steric effects which hinder solvation of the protonated form. This situation is analogous to the relative degree of ionisation of 2,6-dimethyl- and 2,6-di-t-butylphenol, which have pK_a 15.27 and 17.08, respectively, in methanol.[4]

Friedlaender characterised the *ortho*-quinonoid compounds by their reaction with aqueous sodium hydroxide solution to give aromatic *ortho*-hydroxy-aldehydes and anthranilic acid. When this reaction was carried out with sodium deuterioxide in deuterium oxide the hydroxy-aldehyde product had the aldehydic proton

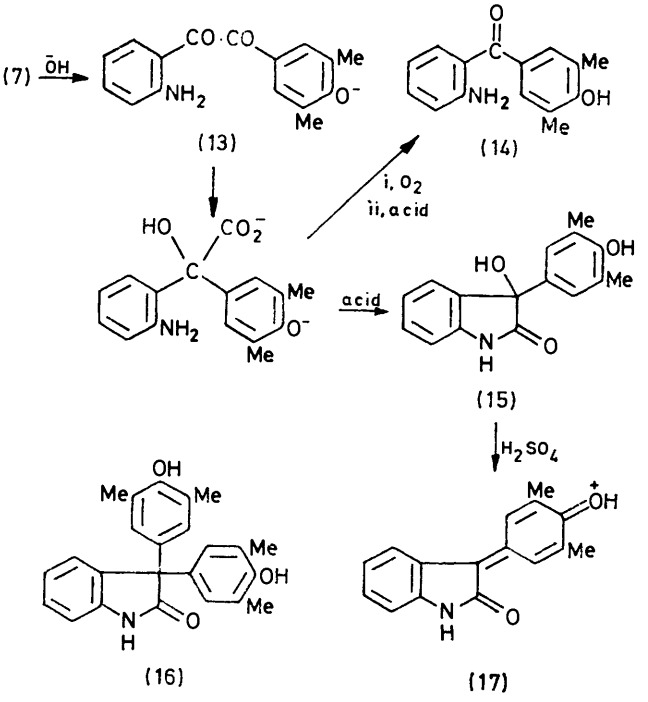
[4] T. N. Pliev, *Doklady Akad. Nauk S.S.S.R.*, 1969, **184**, 1113; C. H. Rochester and B. Rossall, *Trans. Faraday Soc.*, 1969, **65**, 1004.

substituted by deuterium. The process could be a useful synthesis of such specifically labelled *ortho*-hydroxybenzaldehydes. A mechanism for this cleavage is illustrated for compound (5). Hydroxide ion is thought to attack the *ortho*-quinonoid group to generate the phenolate (11). We have not succeeded in isolating the phenol corresponding to (11) but the acetone derivatives (18) and (19), which are the products of a related Michael addition, have been characterised. The cleavage reaction is unlikely to pass through the α-diketone (12). The related α-diketone (13) has not been isolated but it is probably an intermediate in the alkaline decomposition of the *para*-quinonoid compound (7) and under the reaction conditions undergoes a benzilic acid rearrangement. In order to explain the difference in behaviour between the *ortho*- and the *para*-quinonoid compounds, we assume that the Michael addition product from (5) remains in the cyclised form (11) because of hydrogen bonding between the NH and the phenolate group. Cleavage of (11) may then occur by a four-centre mechanism as shown, which would account for the incorporation of deuterium when the reaction is carried out in deuterium oxide.

The reaction between a *para*-quinonoid compound in this series and alkali has not been recorded previously. Compound (7) dissolved in hot aqueous sodium hydroxide and the solution rapidly became bright yellow. Precautions were not taken to exclude air and acidification with carbon dioxide precipitated an amine $C_{15}H_{15}NO_2$. I.r. and mass spectral data indicated this to be the



benzophenone (14), and this was confirmed by comparison with an authentic sample prepared by the same route as used [5] in the preparation of 2-amino-4'-hydroxybenzophenone. Isatin was condensed with 2,6-dimethylphenol in the presence of polyphosphoric acid, which proved a more satisfactory reagent than the sulphuric acid employed previously.[6] The product (16) afforded the benzophenone (14) on oxidation with alkaline hydrogen peroxide.

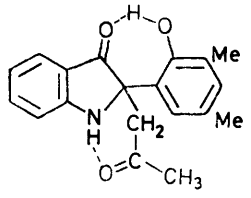


When precautions were taken to exclude oxygen during the reaction of (7) with aqueous sodium hydroxide, acidification of the reaction mixture precipitated a compound, $C_{10}H_{15}NO_3$. This showed a carbonyl absorption in the i.r. at 1 710 cm^{-1} which is probably due to a γ-lactam system. It was assigned structure (15) on the basis of the molecular formula, the i.r. spectral evidence, and the method of preparation. This lactam gave a violet solution in concentrated sulphuric acid containing the ion (17). The α-diketone (13) is probably formed during the reaction of the *para*-quinonoid dye (7) with alkali and then undergoes the benzilic acid rearrangement to give a product which in the free acid form rapidly cyclises to a γ-lactone. In alkaline solution the benzilic acid must be oxidised by air to give the benzophenone (14).

The *ortho*- and *para*-quinonoid dyes reacted with acidified acetone to give pale yellow 1 : 1 adducts formed by a Michael addition. The product from the *ortho*-quinonoid dye (5) showed an n.m.r. spectrum which is consistent with structure (18). In particular a methyl singlet occurs at τ 8.33 and the methylene group adjacent to a chiral centre gives rise to the expected AB system with τ_A 7.54, τ_B 7.90, and J_{AB} 13 Hz. The product obtained from the dye (2) is assigned the analogous structure (19). Compound (19) decomposed in $CDCl_3$ solution to regenerate acetone and compound (2). Acetone derivatives of the *ortho*-quinonoid compounds showed unusually low wavenumber carbonyl

[5] S. Inogaki, *J. Pharm. Soc. Japan*, 1933, **53**, 686.
[6] A. Baeyer and M. J. Lazarus, *Ber.*, 1885, **18**, 2637.

absorption in the i.r. at 1 670 and 1 620 cm^{-1}, and this suggests that both carbonyl groups in each molecule must be hydrogen-bonded. The most likely arrangement of hydrogen bonds is illustrated.



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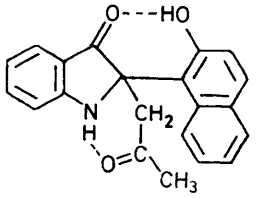

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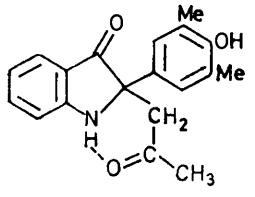

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The acetone adduct from the *para*-quinonoid dye (7) showed an n.m.r. spectrum consistent with structure (20); in particular the methylene group is adjacent to a chiral centre and so gives rise to an AB quartet. Carbonyl i.r. absorption bands occur at 1 720 and 1 680 cm^{-1}. The higher wavenumber band is attributable to the five-membered ring carbonyl group and the lower to the intramolecularly hydrogen bonded side chain carbonyl.

EXPERIMENTAL

2-Chloro-3H-indol-3-one (Isatin α-Chloride).—Isatin (5 g) and phosphorus(v) chloride (8.5 g) were refluxed for 1 h with anhydrous benzene (15 ml) under nitrogen. Hydrogen chloride was evolved and on cooling the solution deposited orange needles of isatin α-chloride (3.5 g, 62%), m.p. 180° (decomp.) (lit.,[7] 180°), which were collected and washed with light petroleum (b.p. 60—80°). The product is sensitive to moisture.

(Z)-2-[2-Oxo-1(2H)-naphthylidene]indolin-3-one (2).—A solution of isatin α-chloride (6.16 g) in benzene (90 ml) was refluxed under nitrogen during dropwise addition of 2-naphthol (6.44 g) in benzene (110 ml) over 2 h with stirring. The solution was then cooled and the precipitated dyestuff (2) collected and recrystallized from benzene; m.p. 165—167° (lit.,[1] no m.p. given) (Found: C, 79.0; H, 4.3; N, 5.3. Calc. for $C_{18}H_{11}NO_2$: C, 79.1; H, 4.0; N, 5.1%), ν_{CO} 1 710 and 1 630 cm^{-1}; *m/e* 273 (100%, M^+), 245 (82), 244 (45), and 217 (41); τ ($CDCl_3$) −2.98 (1 H, s, NH), 1.62 (1 H, m, H_a), 2.38 (1 H, d, *J* 9 Hz), 2.48—3.0 (m, aromatic), and 3.24 (1 H, d, *J* 9 Hz).

Alkaline decomposition. A solution of the dyestuff (2) (1.0 g) in 10% sodium hydroxide (15 ml) was refluxed for 1.5 h, cooled, and saturated with carbon dioxide. 2-Hydroxy-1-naphthaldehyde (0.25 g, 78%) precipitated and was purified by sublimation at 60° and 1 mmHg; m.p. 81—82° (lit.,[8] 82°); τ ($C_6D_5{\cdot}NO_2$) −3.30 (1 H, s, OH) and −0.68 (1 H, s, CHO). The aldehyde (70 mg), acetic anhydride (84 mg), and fused sodium acetate (100 mg) were heated at 190 °C in a sealed tube for 4 h. The mixture was shaken with water and extracted with ether and the extract washed with sodium carbonate, dried ($MgSO_4$), and evaporated. The residue crystallised from aqueous ethanol as needles of naphtho[2,1-*b*]pyran-3-one (70 mg, 88%), m.p. 116—118° (lit.,[9] 118°).

Reaction between the dyestuff (2) and 10% NaOD in deuterium oxide gave, after washing with water, 2-hydroxy-[α-^{2}H]-1-naphthaldehyde, τ ($C_5D_5{\cdot}NO_2$) −3.30 (1 H) (peak at −0.68 absent); *m/e* 173 (M^+); ν_{CO} 1 620, ν_{CD} 2 130 cm^{-1}.

Reaction with acetone. The dyestuff (2) (0.20 g) was stirred for 0.5 h with acetone (10 ml) containing a few drops of concentrated hydrochloric acid. The resulting precipitate of *2-acetonyl-2-(2-hydroxy-1-naphthyl)indolin-3-one hydrochloride* (0.16 g, 60%), m.p. 150—160° (decomp.), was collected (Found: C, 68.6; H, 5.1; Cl, 9.4; N, 3.7. $C_{21}H_{17}NO_3$,HCl requires C, 68.6; H, 4.9; Cl, 9.6; N, 3.8%); *m/e* 331 (100%, M^+ for free base), 302 (53), 275 (51), and 218 (67). It rapidly decomposed in all solvents tried, to regenerate (2).

(Z)-2-[4-Chloro-1-oxo-2(1H)-naphthylidene]indolin-3-one (4).—A solution of isatin α-chloride (5.5 g) in benzene (90 ml) was stirred and refluxed under nitrogen during dropwise addition of 4-chloro-1-naphthol (7.1 g) in benzene (120 ml) over 3 h. The solution was cooled and the *precipitate* (4) (5.7 g, 56%) was collected and crystallised from xylene as fine violet-blue needles, m.p. 293—295°, sublimed at 165° and 0.01 mmHg (Found: C, 70.5; H, 3.2; Cl, 11.7; N, 4.3. $C_{18}H_{10}ClNO_2$ requires C, 70.3; H, 3.3; Cl, 11.5; N, 4.5%); ν_{CO} 1 690 cm^{-1}; *m/e* 309 (32%, M^+), 307 (100%, M^+), and 279 (64); too insoluble in all solvents for an n.m.r. spectrum to be obtained.

Alkaline decomposition. Reaction with 10% sodium hydroxide as described for compound (2) afforded *4-chloro-1-hydroxy-2-naphthaldehyde* (52%), m.p. 102—105° (Found: C, 64.1; H, 3.3; Cl, 17.2. $C_{11}H_7ClO_2$ requires C, 63.9; H, 3.4; Cl, 17.2%), τ ($CDCl_3$) −2.60 (1 H, s, OH) and 0.10 (1 H, s, CHO). A sample was treated with acetic anhydride and sodium acetate at 190 °C to give *6-chloronaphtho[1,2-b]pyran-2-one*, cream-coloured needles (from aqueous ethanol), m.p. 167—168° (Found: C, 67.4; H, 3.1; Cl, 15.5. $C_{13}H_7ClO_2$ requires C, 67.7; H, 3.1; Cl, 15.4%).

Decomposition in deuterium oxide gave 4-chloro-1-hydroxy-[α-^{2}H]-2-naphthaldehyde (n.m.r. and mass spectral evidence), ν_{CD} 2 180 cm^{-1}.

(Z)-2-(3,5-Dimethyl-6-oxocyclohexa-2,4-dienylidene)indolin-3-one (5).—A solution of 2,4-dimethylphenol (3.31 g) in benzene (10 ml) was added dropwise during 15 min to a refluxing solution of isatin α-chloride (3.74 g) in benzene (35 ml) under nitrogen. After a further 15 min, reaction (followed by t.l.c. on silica gel eluted with dichloromethane) was complete. The solution was cooled and chromatographed on a short column of silica gel. Elution with dichloromethane and evaporation of the eluate afforded the *product* (5), which crystallised from ethanol as brownish red hair-like needles (1.0 g, 18%), m.p. 216—218° (Found: C, 76.3; H, 5.2; N, 5.4. $C_{16}H_{13}NO_2$ requires C, 76.5; H, 5.2; N, 5.6%), ν_{CO} 1 725 cm^{-1}; τ ($CDCl_3$) −2.87 (1 H, s, NH), 1.82 (1 H, m, H_a), 2.40—2.80 (m, aromatic), 2.93

[7] A. Baeyer, *Ber.*, 1879, **12**, 456.

[8] A. Russell and L. B. Lockhart, *Org. Synth.*, Coll. Vol. III, p. 463.

[9] B. B. Day, R. H. R. Rau, and Y. Sankaranarayanan, *J. Indian Chem. Soc.*, 1932, **9**, 71.

(1 H, m, H_b), 7.72 (3 H, s, CH_3), and 7.74 (3 H, s, CH_3) (decoupling at τ 7.72—7.74 results in the multiplets at τ 1.82 and 2.93 collapsing to an AB quartet with J 2 Hz); *m/e* 251 (86%, M^+), 224 (18), 223 (100, $M^+ - 28$), and 194 (22).

Alkaline decomposition. Compound (5) (2.7 g) was stirred with 10% sodium hydroxide (100 ml) at 70—80 °C for 2 h; it slowly passed into solution and the colour changed from green to bright yellow. The solution was acidified and steam distilled. 3,5-Dimethyl-2-hydroxybenzaldehyde (1.24 g, 77%) crystallised from the distillate and was collected in ether and purified by sublimation at 30° and 0.05 mmHg (solid CO_2 condenser); m.p. 23—24° (lit.,[10] 15°) (Found: C, 71.2; H, 6.6. Calc. for $C_9H_{10}O_2$: C, 71.5; H, 6.7%). The oxime crystallised from aqueous ethanol as needles, m.p. 138° (lit.,[10] 138.5—139.5°).

Decomposition in deuterium oxide gave 3,5-dimethyl-2-hydroxy[α-^{2}H]benzaldehyde τ ($CDCl_3$) −1.13 (1 H, s, OH) [peak at 0.20 (CHO) absent]; ν_{CO} 2 210 cm^{-1}.

Reaction with acetone. Compound (5) (0.1 g) was dissolved in acetone (5 ml) containing a few drops of concentrated hydrochloric acid. After 1 h the solution was evaporated and the yellow residue chromatographed in ether on a column of neutral alumina. The first small fraction was discarded and the second recrystallised from light petroleum (b.p. 80—100°) to give 2-*acetonyl*-2-(2-*hydroxy*-3,5-*dimethylphenyl*)*indolin*-3-*one* (18) as yellow prisms (0.040 g, 33%), m.p. 183—190° (decomp.) (Found: C, 73.9; H, 6.3; N, 4.5. $C_{19}H_{19}NO_3$ requires C, 73.8; H, 6.2; N, 4.5%), ν_{CO} (KBr) 1 670 (ring CO) and 1 620 cm^{-1} (acetonyl CO), *m/e* 309 (53%, M^+), 280 (94), 267 (26), 252 (100), and 238 (37), τ ($CDCl_3$) 2.20—3.70 (m, aromatic), 3.80 (1 H, s), 7.02 (1 H, s), 7.54 (1 H, d, H_A), 7.90 (1 H, d, H_B) (J_{AB} 13 Hz), 7.86 (3 H, s, aryl CH_3), 7.91 (3 H, s, aryl CH_3), and 8.32 (3 H, s, MeCO).

2-(3,5-*Dimethyl*-4-*oxocyclohexa*-2,5-*dienylidene*)*indolin*-3-*one* (7).—A solution of 2,6-dimethylphenol (7.12 g) in benzene (40 ml) was added dropwise over 1 h to a refluxing solution of isatin α-chloride (8.04 g) in benzene (100 ml) containing a few drops of concentrated hydrochloric acid under nitrogen. Reaction was complete (t.l.c. evidence) after a further 1 h under reflux. The solution was cooled and the precipitate collected and extracted with benzene (Soxhlet) until the washings were colourless. The black residue consisting of (7) as its hydrochloride (4.0 g, 29%) was crystallised from a mixture of acetic acid (9 vol.) and aqueous 42% fluoroboric acid (1 vol.) as brownish red needles of 2-(3,5-*dimethyl*-4-*oxocyclohexa*-2,5-*dienylidene*)-*indolin*-3-*one* (7) *hydrofluoroborate*, which decomposed above 213° (Found: C, 56.4; H, 4.2; N, 4.2; F, 22.7. $C_{16}H_{14}BF_4NO_2$ requires C, 56.7; H, 4.2; N, 4.1; F, 22.4%); $\nu_{max.}$ (KBr) 1 725 (ring carbonyl), 1 630, 1 610, and 1 570 cm^{-1}. The hydrochloride was heated at 50—60° and 0.01 mmHg for 48 h, leaving a residue of the *indolin*-3-*one* (7), m.p. 246—249° (decomp.) (Found: C, 76.2; H, 5.3; N, 5.3. $C_{16}H_{13}NO_2$ requires C, 76.5; H, 5.2; N, 5.6%); $\nu_{max.}$ (KBr) 1 690 and 1 625 cm^{-1}; *m/e* 252 (13%, M^+), 251 (67), 224 (17), and 223 (100); τ (C_5D_5N–D_2O) 1.52 (1 H, s, H_a), 2.16 (1 H, s, H_b), 2.0—3.0 (m, aromatic), and 7.64 (6 H, s, 2 × CH_3).

Alkaline decomposition. (i) Compound (7) hydrochloride (0.50 g) was stirred and heated to 70 °C with 1% sodium hydroxide (30 ml) for 1 h. The solution was cooled and adjusted to pH 8.3 with carbon dioxide. The cream-coloured precipitate was collected, dried, and adsorbed on silica gel in ethanol, which was then evaporated off. Chromatography over silica gel and elution with ether afforded 2-*amino*-4′-*hydroxy*-3′,5′-*dimethylbenzophenone* (14), which crystallised from aqueous ethanol as pale yellow needles (0.04 g, 10%), m.p. 145—146°, undepressed on admixture with the sample described below (Found: C, 74.7; H, 6.3; N, 5.8. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); ν_{CO} (KBr) 1 620 cm^{-1}, *m/e* 241 (96%, M^+), 240 (100), 226 (85), 149 (25), and 120 (26).

(ii) Compound (7) hydrochloride (0.80 g) was stirred with oxygen-free 12% sodium hydroxide (30 ml) under nitrogen for 2 h at 70 °C. The solution was cooled and adjusted to pH 8.3 with carbon dioxide, and the resulting precipitate was discarded. The filtrate was acidified with 2N-hydrochloric acid to precipitate 3-*hydroxy*-3-(4-*hydroxy*-3,5-*dimethylphenyl*)*indolin*-2-*one* (15), which crystallised from aqueous ethanol as prisms (0.50 g, 67%), m.p. 235—255° (decomp.) (Found: C, 71.0; H, 5.5; N, 5.1. $C_{16}H_{15}NO_3$ requires C, 71.4; H, 5.6; N, 5.2%); $\lambda_{max.}$ (H_2SO_4) 517 nm (ε 21 600); ν_{CO} (KBr) 1 710 cm^{-1}; *m/e* 269 (69%, M^+), 253 (28), 241 (40), 240 (100), 226 (87), 149 (44), 120 (27), and 77 (36).

Reaction with acetone. Compound (7) hydrofluoroborate (0.10 g) was stirred with acetone (3 ml) for 15 min and the solution was diluted with water. 2-*Acetonyl*-2-(4-*hydroxy*-3,5-*dimethylphenyl*)*indolin*-3-*one* (20) separated and crystallised from aqueous acetone as yellow plates (0.08 g, 90%), m.p. 191—194° (Found: C, 73.6; H, 6.2; N, 4.7. $C_{19}H_{19}NO_3$ requires C, 73.8; H, 6.2; N, 4.5%); τ ($CDCl_3$) 2.4—3.5 (m, aromatic), 4.0 (1 H, s), 4.97 (1 H, s), 6.38 (1 H, d, J 17 Hz), 7.37 (1 H, d, J 17 Hz), 7.90 (6 H, s, 2 × CH_3), and 7.94 (3 H, s, acetonyl CH_3); ν_{CO} (KBr) 1 720 and 1 680 cm^{-1}; *m/e* 309 (53%, M^+), 280 (94), 267 (26), 252 (100), 238 (37), 224 (31), and 223 (26).

2-(4-*Oxo*-3,5-*di*-t-*butylcyclohexa*-2,5-*dienylidene*)*indolin*-3-*one* (9).—A solution of 2,6-di-t-butylphenol (6.25 g) and isatin α-chloride (5.0 g, 1 equiv.) in benzene (20 ml) and trifluoroacetic acid (4 ml) was stirred for 1 h at room temperature, then chromatographed in benzene on silica gel. The first dark red eluate was evaporated to give a low yield of the *indolin*-3-*one* (9), which crystallised from benzene as brownish red needles showing a phase change at *ca.* 125° and m.p. 244—250° (decomp.) (Found: C, 78.3; H, 7.8; N, 3.9. $C_{22}H_{25}NO_2$ requires C, 78.8; H, 7.5; N, 4.2%), ν_{CO} (KBr) 1 670 cm^{-1}; *m/e* 335 (100%, M^+), 320 (70), and 279 (35).

The major fraction was collected to give 2,2-*bis*-(4-*hydroxy*-3,5-*di*-t-*butylphenyl*)*indolin*-3-*one* (21), which crystallised from light petroleum (b.p. 80—100°) as plates, m.p. 240—250° (decomp.) (Found: C, 79.8; H, 8.6; N, 2.4. $C_{36}H_{47}NO_3$ requires C, 79.8; H, 8.7; N, 2.6%). A sample crystallised from aqueous acetic acid to give the *hydrate*, m.p. 240—250° (decomp.) (Found: C, 77.4; H, 8.9; N, 2.3. $C_{36}H_{47}NO_3,H_2O$ requires C, 77.2; H, 8.8; N, 2.5%).

3,3-*Bis*-(4-*hydroxy*-3,5-*dimethylphenyl*)*indolin*-2-*one* (16).—Isatin (10.0 g) and 2,6-dimethylphenol (20.7 g) were heated with polyphosphoric acid (300 ml) at 140 °C with stirring for 1 h, after which the mixture was cooled and poured into iced water. The yellow precipitate was collected and dissolved in 4% sodium hydroxide (150 ml); the solution was filtered and the filtrate acidified with dilute sulphuric acid to precipitate the *product* (16) (9.0 g, 36%), m.p. >300° (Found: C, 77.0; H, 6.4; N, 3.9. $C_{24}H_{23}NO_3$

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requires C, 77.2; H, 6.2; N, 3.8%); ν_{CO} 1 690 cm^{-1}; *m/e* 373 (82%, M^+), 344 (40), and 330 (100).

2-*Amino*-4′-*hydroxy*-3′,5′-*dimethylbenzophenone* (14).—Compound (16) (2.0 g) was dissolved in 12% sodium hydroxide (20 ml) and heated under reflux during dropwise addition of 15% hydrogen peroxide (40 ml). The solution was cooled and saturated with carbon dioxide to precipitate the benzophenone (14) (0.3 g, 23%), which was collected and sublimed at 100° and 0.01 mmHg; m.p. 141—144°, undepressed on admixture with the sample previously described (Found: C, 74.5; H, 6.5; N, 5.7. Calc. for $C_{15}H_{15}NO_2$: C, 74.7; H, 6.3; N, 5.8%), ν_{CO} (KBr) 1 620 cm^{-1}; *m/e* 241 (96%, M^+).

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