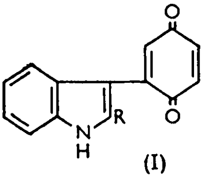
477. *Heterocyclic Compounds of Nitrogen. Part II.*[1] *The Synthesis of Some 3'-Indolylbenzoquinones.*

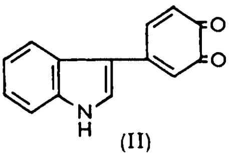
By J. Malcolm Bruce.

2,5- and 3,4-Dimethoxyphenyl-lithium react with *o*-aminoacetophenone to give tertiary alcohols from which 4-(2,5- and 4-(3,4-dimethoxyphenyl)-cinnoline respectively are obtained by dehydration and diazotisation. Demethylation followed by reductive ring contraction then affords 3-(2,5- and 3-(3,4-dihydroxyphenyl)indole which are readily oxidised to the corresponding quinones. These are identical with the condensates obtained in alcoholic solution from indole and 1,4- and 1,2-benzoquinone respectively.

In 1911 Möhlau and Redlich[2] reported that 2-methylindole and 1,4-benzoquinone in alcoholic solution gave a deep violet substance which was readily reduced to a leuco-compound, gave a diacetate on reductive acetylation, and was cleaved by aqueous potassium hydroxide to the parent indole. They assigned to it structure (I; R = Me). A similar compound was formed from 1,2-dimethylindole and 1,4-benzoquinone, but a pure product was not isolated on reaction of indole itself with the quinone. Bu'Lock and Harley-Mason[3] confirmed and extended this work, and isolated pure products, formulated as (I; R = H) and (II), after reaction of indole with 1,4- and 1,2-benzoquinone respectively. These structures were supported by the visible and ultraviolet absorption spectra of the compounds, the failure of 3-substituted indoles to yield coloured products with quinones, and the isolation of the same indolylnaphthaquinone on reaction of indole with either 1,2-naphthaquinone or its sodium 4-sulphonate.



(I)



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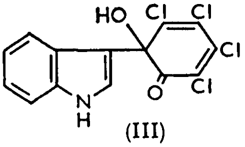

(III)

More recently Horner and Spietschka[4] have shown that indole reacts with tetrachloro-1,2-benzoquinone in tetrahydrofuran to give the yellow cyclohexadienone (III), and in view of this it was necessary to obtain further evidence relating to the structures of the indole–quinone condensates prepared by Möhlau and Redlich[2] and by Bu'Lock and Harley-Mason.[3] The present paper describes the synthesis of the quinones (I; R = H) and (II).

The simplest general synthesis of 3'-indolylbenzoquinones involves oxidation of the corresponding quinols. These were prepared from the appropriate dimethoxyphenyl-lithium, but first the syntheses of 3-phenyl- and 3-*p*-hydroxyphenyl-indole, from phenyl- and *p*-methoxyphenyl-lithium respectively, were examined in order to establish a suitable sequence of reactions.

Phenyl-lithium reacted smoothly with an ethereal suspension of isatin to give 3-phenyldioxindole[5] (IV) from which *o*-aminobenzophenone was obtained by oxidation with alkaline hydrogen peroxide.[6] Reaction of this ketone with methylmagnesium iodide, dehydration of the resulting tertiary alcohol to the amino-olefin (V; R = H), and subsequent diazotisation as described by Stoermer and Fincke[7] afforded 4-phenylcinnoline

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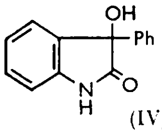
[1] Part I, Bruce and Sutcliffe, *J.*, 1957, 4789.
[2] Möhlau and Redlich, *Ber.*, 1911, **44**, 3605.
[3] Bu'Lock and Harley-Mason, *J.*, 1951, 703.
[4] Horner and Spietschka, *Annalen*, 1955, **591**, 1.
[5] Cf. Kohn, *Monatsh.*, 1910, **31**, 747.
[6] Inagaki, *J. Pharm. Soc. Japan*, 1939, **59**, 5.
[7] Stoermer and Fincke, *Ber.*, 1909, **42**, 3115.

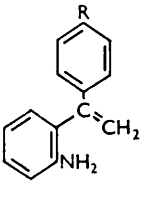
(VI; R = H) from which 3-phenylindole was obtained in good overall yield by reductive ring contraction with amalgamated zinc and aqueous acetic acid.[8] Until the present work was carried out this was the only recorded example of the conversion of a 4-arylcinnoline into a 3-arylindole under acidic conditions; Atkinson and Simpson [9] had prepared 3-*p*-hydroxyphenylindole in poor yield by reduction of 4-*p*-hydroxyphenylcinnoline (VI; R = OH) with sodium in ethanol, but they obtained only a resin from 4-*p*-methoxyphenylcinnoline (VI; R = OMe).

The amino-olefin (V; R = H) was more conveniently prepared, in excellent yield, by dehydration of the crude tertiary alcohol obtained on reaction of *o*-aminoacetophenone with three equivalents of phenyl-lithium; both hydrogen atoms of the amino-group react with the lithium reagent.[10]

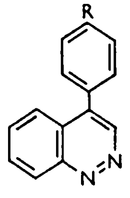
Reaction of *p*-methoxyphenyl-lithium, from *p*-bromoanisole and lithium in ether, with *o*-aminoacetophenone followed by dehydration of the resulting crude alcohol gave 1-*o*-aminophenyl-1-*p*-methoxyphenylethylene (V; R = OMe) together with a small quantity of a substance which is probably 1-*o*-aminophenyl-1-(5-bromo-2-methoxyphenyl)ethylene; Wittig *et al.*,[11] and Müller and Töpel,[12] found that some 5-bromo-2-methoxyphenyl-lithium was formed when *p*-methoxyphenyl-lithium was prepared under the above conditions. Treatment of this bromo-amino-olefin with nitrous acid yielded the corresponding 4-arylcinnoline.



(IV)



(V)



(VI)

Diazotisation of the amino-olefin (V; R = OMe) afforded 4-*p*-methoxyphenylcinnoline [13] (VI; R = OMe) which was smoothly reduced to 3-*p*-methoxyphenylindole by amalgamated zinc and acetic acid. Attempts to demethylate 3-*p*-methoxyphenylindole caused extensive decomposition, but treatment of 4-*p*-methoxyphenylcinnoline with hydrobromic acid readily yielded the corresponding phenol [9,13] (VI; R = OH) from which 3-*p*-hydroxyphenylindole was obtained in good yield by reduction in acidic solution.

Extension of this sequence to 2,5- and 3,4-dimethoxyphenyl-lithium afforded 3-(2,5- and 3-(3,4-dihydroxyphenyl)indole, which were oxidised by sodium iodate to the corresponding quinones (I; R = H) and (II). These were essentially identical (m. p., mixed m. p., infrared and ultraviolet spectrum) with the substances obtained on reaction of indole with ethanolic solutions of 1,4- and 1,2-benzoquinone respectively. The slight differences in properties may be attributed to traces of decomposition products formed during working-up.

For comparison with 3-(3,4-dihydroxyphenyl)indole, the 3-(2,3-dihydroxy)-compound was synthesised in a similar manner from 2,3-dimethoxyphenyl-lithium. It was readily oxidised by sodium iodate to black amorphous material.

The main features of the ultraviolet absorption spectra of the 4-arylcinnolines and 3-arylindoles are shown in Tables 1 and 2. The similarity of the spectra of the individual members of each group establishes the constitutions assigned to them.

Table 2 also lists the yields of purified 3-arylindoles obtained by ring-contraction of the corresponding 4-arylcinnolines with amalgamated zinc and aqueous acetic acid; reduction

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[8] Neber, Knöller, Herbst, and Trissler, *Annalen*, 1929, **471**, 113.

[9] Atkinson and Simpson, *J.*, 1947, 1649.

[10] Jones and Gilman, *Org. Reactions*, 1951, **6**, 339.

[11] Wittig, Pockels, and Dröge, *Ber.*, 1938, **71**, 1903.

[12] Müller and Töpel, *Ber.*, 1939, **72**, 273.

[13] Stoermer and Gaus, *Ber.*, 1912, **45**, 3104.

TABLE 1. *Absorption spectra of substituted* 4-*phenylcinnolines, in dioxan, in the region* 215—350 mμ.

Subst. in 4-phenyl group	$\lambda_{\text{max.}}$		$\lambda_{\text{min.}}$		$\lambda_{\text{max.}}$		$\lambda_{\text{min.}}$		$\lambda_{\text{max.}}$	
	mμ	log ε	mμ *	log ε	mμ •	log ε	mμ	log ε	mμ	log ε
None	227	4·62	260	3·58	298	3·86	311	3·70	327	3·77
4-OMe	226·5	4·60	262·5	3·31	(315)	3·96	—	—	330	4·02
2,5-(OMe)$_2$	225	4·69	(252) 267	3·71 3·49	292	3·77	308	3·58	326	3·71
3,4-(OMe)$_2$	225	4·64	(250) 273	4·04 3·59	286	3·63	295	3·62	335	3·98
2,3-(OMe)$_2$	226	4·67	257	3·67	296	3·73	310	3·59	325	3·67
5-Br-2-OMe	226	4·69	265	3·36	294	3·68	305	3·60	327	3·70
4-OH	225·5	4·60	264	3·50	315	3·97	319	3·97	331	4·04
2,5-(OH)$_2$	225·5	4·64	(255) 269	3·66 3·56	292	3·78	310	3·58	327	3·65
3,4-(OH)$_2$	225	4·60	(251) 275	3·88 3·44	—	—	—	—	335	3·95
2,3-(OH)$_2$	225	4·65	257	3·38	298	3·74	312	3·68	327	3·72

• Figures in parentheses indicate a pronounced inflexion.

TABLE 2. *Yields of substituted* 3-*phenylindoles obtained from the corresponding* 4-*phenylcinnolines; and absorption spectra of the indoles, in dioxan, in the region* 215—350 mμ.

Subst. in 3-phenyl group	Yield (%)	$\lambda_{\text{min.}}$		$\lambda_{\text{max.}}$		$\lambda_{\text{min.}}$		$\lambda_{\text{max.}}$		$\lambda_{\text{min.}}$		$\lambda_{\text{max.}}$	
		mμ	log ε	mμ	log ε	mμ	log ε	mμ	log ε	mμ *	log ε	mμ *	log ε
None	88	—	—	224·5	4·48	245	3·74	269	4·16	—	—	—	—
4-OMe	76	217·5	4·27	230·5	4·38	245·5	3·97	265	4·21	—	—	—	—
2,5-(OMe)$_2$	58	—	—	225	4·56	251·5	3·79	270·5	4·01	287	3·91	(291) 306	3·93 3·99
3,4-(OMe)$_2$	49	—	—	—	—	249	4·03	266	4·20	(286)	4·05	—	—
2,3-(OMe)$_2$	60	—	—	225·5	4·63	249	3·80	272	4·14	325	1·88	340	1·91
4-OH	75	218	4·28	232	4·38	246·5	4·02	263·5	4·20	—	—	—	—
2,5-(OH)$_2$	55	—	—	224	4·54	249	3·88	267	3·99	286 293	3·85 3·88	291·5 309	3·89 3·96
3,4-(OH)$_2$	65	223·5	4·40	228	4·41	249·5	4·04	262	4·11	286	3·93	293	3·94
2,3-(OH)$_2$	65	—	—	225	4·60	246	3·91	271	4·08	325	1·94	350	1·95

* Figures in parentheses indicate a pronounced inflexion.

of high-melting cinnolines was facilitated by addition of dioxan. The figures indicate the usefulness of the reaction for preparing 3-arylindoles which would otherwise be difficultly accessible.

EXPERIMENTAL

Reactions with organolithium compounds were carried out under oxygen-free nitrogen. Solutions in organic solvents were washed with water unless stated otherwise, and dried (Na_2SO_4). Solvents were removed on the water-bath, where necessary under reduced pressure (water-pump). Light petroleum had b. p. 60—80° unless stated otherwise. Dioxan was purified as described by Vogel.[14] Solids were dried *in vacuo*. 48% Hydrobromic acid was freshly distilled. Amalgamated zinc wool,[15] well washed with water, was freshly prepared for each reaction. Peter Spence grade " H " alumina was used, and " Florisil " was obtained from the Floridin Co. Inc., Warren, Pennsylvania. Sublimation and bulb-to-bulb distillation temperatures are those of the heating-bath. Ultraviolet absorption spectra were measured in purified [14] dioxan in a Perkin-Elmer Model 4000 recording spectrophotometer, and infrared spectra, in Nujol, in a Perkin-Elmer Model 21 double-beam spectrometer. Absorption is strong unless stated otherwise. Figures in parentheses indicate inflexions. M. p.s are corrected.

3-*Phenyldioxindole*.—Phenyl-lithium, from bromobenzene (19·6 g.) and lithium wire (1·8 g.), in ether (80 c.c.) was added during 25 min. to a vigorously stirred suspension of finely powdered

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[14] Vogel, " A Text-Book of Practical Organic Chemistry," Longmans, Green, and Co., London, 1951, p. 175.

[15] *Idem, ibid.*, p. 194, method 2.

isatin (7·4 g.) in ether (75 c.c.) at 0—5°. The light fawn suspension was stirred at 20° for 2 hr., cooled in ice, and decomposed with ice-cold water (75 c.c.). Aqueous 10% sodium hydroxide (120 c.c.) was added, and the aqueous layer was removed, extracted with ether (3 × 20 c.c.), and warmed on the water-bath to expel dissolved ether. The solution was then stirred, and acidified below 10° with 10% hydrochloric acid (210 c.c.). After being left at room temperature for 3 hr. the precipitate was collected, washed with water, and crystallised from aqueous ethanol. Sublimation of the product at 190°/0·01 mm. and crystallisation of the sublimate from aqueous ethanol gave the dioxindole (8·5 g., 75%) as needles, m. p. 212—212·5° (lit.,[5] 213°) (Found: C, 74·5; H, 4·9; N, 6·3. Calc. for $C_{14}H_{11}O_2N$: C, 74·7; H, 4·9; N, 6·2%).

o-*Aminobenzophenone*.—3-Phenyldioxindole (11·3 g.) was added to vigorously stirred aqueous 10% sodium hydroxide (100 c.c.) at 95°, and the suspension was cooled to 80° and treated with 10% hydrogen peroxide (50 c.c.). The mixture was then heated to 90°: a vigorous reaction occurred and the temperature rose to 99°. When the reaction had subsided the mixture was refluxed for 10 min., diluted with water (150 c.c.), and cooled. Crystallisation of the precipitate from ethanol gave the amino-ketone (5·9 g., 60%) as yellow hexagonal plates, m. p. 106—107° (lit.,[6] 107°) (Found: C, 79·4; H, 5·6; N, 7·4. Calc. for $C_{13}H_{11}ON$: C, 79·2; H, 5·6; N, 7·1%).

o-*Aminoacetophenone*.—This was prepared as described by Kiang *et al.*,[16] but (*a*) only 1% excess of phosphorus pentachloride was used in the preparation of *o*-nitrobenzoyl chloride, (*b*) ether (200 c.c.) was added to facilitate stirring during the condensation with diethyl malonate, and (*c*) reduction was effected by adding hydrochloric acid to a mixture of the nitro-compound and tin at a rate sufficient to maintain gentle reflux, and then heating at 100° for 1 hr. The amine (85% overall) was obtained as a light greenish-yellow oil, b. p. 60°/0·01 mm. (Found: C, 70·8; H, 6·9; N, 10·4. Calc. for C_8H_9ON: C, 71·1; H, 6·7; N, 10·4%).

1-o-*Aminophenyl*-1-*phenylethylene*.—*o*-Aminoacetophenone (6·75 g.) in ether (50 c.c.) was added during 10 min. to a stirred solution of phenyl-lithium, from bromobenzene (27 g.) and lithium wire (2·5 g.), in ether (100 c.c.), stirring was continued at room temperature for 1 hr., and the mixture was then cooled in ice and decomposed with water (50 c.c.). The ethereal phase was separated and washed, and the solvent was removed. The residue was shaken with a mixture of concentrated sulphuric acid (25 c.c.) and water (85 c.c.), a little insoluble material was removed by extraction with light petroleum (b. p. 40—60°), and the solution was then refluxed for 1 hr., cooled, and diluted with water (250 c.c.). An excess of concentrated aqueous ammonia was added, the suspension was stirred at 10—15° until the oil solidified, and the solid was collected, washed with water, and distilled. Crystallisation of the fraction with b. p. 110—112°/0·02 mm. from light petroleum (b. p. 40—60°) gave the olefin (8·9 g., 91%) as rods, m. p. 77—77·5°, undepressed on admixture with authentic [7] material (Found: C, 86·3; H, 6·7; N, 7·2. Calc. for $C_{14}H_{13}N$: C, 86·2; H, 6·7; N, 7·2%).

4-*Phenylcinnoline*.—The foregoing olefin (3·9 g.) was dissolved in 10% hydrochloric acid (40 c.c.), and the solution, cooled in ice, was treated with a slight excess of aqueous 7% sodium nitrite. Water (20 c.c.) was added, stirring at 0° was continued for 30 min., and the suspension was then basified below 10° with concentrated aqueous ammonia. The precipitate was collected, triturated with dilute ammonia and then with water, and distilled, the fraction with b. p. 138—140°/0·02 mm. (a yellow viscous oil) being crystallised from light petroleum to give the cinnoline (3·6 g., 88%) as yellow needles, m. p. 65·5—66° (lit.,[7] 67—67·5°) (Found: C, 81·5; H, 5·0; N, 13·7. Calc. for $C_{14}H_{10}N_2$: C, 81·6; H, 4·9; N, 13·6%).

3-*Phenylindole*.—A mixture of 4-phenylcinnoline (2·1 g.), amalgamated zinc wool (4 g.), acetic acid (3·5 c.c.), and water (7·5 c.c.) was refluxed for 2 hr., cooled, and diluted with water (25 c.c.). The precipitate was isolated by extraction with ether, and crystallised from light petroleum to give the indole (1·7 g., 88%) as plates, m. p. 87—88° undepressed on admixture with authentic [17] material (Found: C, 87·2; H, 6·0; N, 7·5. Calc. for $C_{14}H_{11}N$: C, 87·0; H, 5·7; N, 7·3%).

1-o-*Aminophenyl*-1-p-*methoxyphenylethylene and* 1-o-*Aminophenyl*-1-(5-*bromo*-2-*methoxyphenyl*)*ethylene*.—*o*-Aminoacetophenone (6·75 g.) in ether (50 c.c.) was added during 10 min. to a stirred and ice-cooled solution of *p*-methoxyphenyl-lithium,[18] from *p*-bromoanisole (37·4 g.)

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[16] Kiang, Mann, Prior, and Topham, *J.*, 1956, 1319.

[17] Fischer and Schmidt, *Ber.*, 1888, **21**, 1811.

[18] Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1932, **54**, 1957; Gilman and Benkeser, *ibid.*, 1947, **69**, 123.

and lithium (3·8 g.), in ether (100 c.c.), and stirring was then continued at room temperature for 2 hr. The mixture was decomposed at 0° with water (75 c.c.), and the ethereal phase was separated, combined with an ether extract of the aqueous phase, and then washed and dried. Removal of the solvent and distillation of the residue afforded a yellow very viscous oil, b. p. 148—150°/0·03 mm., which largely solidified. This was shaken with a mixture of concentrated sulphuric acid (10 c.c.) and water (120 c.c.), a little undissolved solid was removed by filtration, and the filtrate was extracted with ether, then with light petroleum, and heated on the boiling-water bath for 2 hr. The solution was cooled, diluted with water (130 c.c.), and basified with concentrated ammonia solution. The precipitate was isolated by extraction with ether and distilled, giving an orange oil, b. p. 130—135°/0·03 mm., which was stirred with 10% hydrochloric acid (100 c.c.) on the water-bath for 15 min. A colourless solid (A) separated and, after being cooled, was collected. The filtrate was basified with ammonia, and the precipitate, isolated by ether-extraction, was distilled to give an orange viscous oil, b. p. 132—134°/0·07 mm., from which pale fawn prisms, m. p. 49—50°, were obtained by fractional crystallisation from light petroleum. This product, in benzene, was chromatographed on alumina (50 × 12 mm.), and the column was eluted with benzene. Removal of the solvent from the eluate left a colourless oil (4·75 g., 42%) which solidified, m. p. 49·5—50°, and, on being crystallised from light petroleum (b. p. 40—60°), gave 1-o-*aminophenyl*-1-p-*methoxyphenylethylene* as needles, m. p. 50·5° (lit.,[13] 49°) (Found: N, 6·4. Calc. for $C_{15}H_{15}ON$: N, 6·2%). The solid (A) was washed with water, dried, and sublimed at 115°/0·01 mm. Crystallisation of the sublimate from light petroleum gave 1-o-*aminophenyl*-1-(5-*bromo*-2-*methoxyphenyl*)*ethylene* (1·15 g., 8%) as prisms, m. p. 111° (Found: C, 59·4; H, 4·7; N, 4·5; Br, 26·1. $C_{15}H_{14}ONBr$ requires C, 59·2; H, 4·6; N, 4·6; Br, 26·3%).

4-(5-*Bromo*-2-*methoxyphenyl*)*cinnoline*.—Sodium nitrite (75 mg.) in water (2 c.c.) was added during 5 min. to a stirred, ice-cooled suspension of the foregoing amino-bromo-olefin (0·30 g., finely powdered) in a mixture of water (13·5 c.c.) and concentrated hydrochloric acid (1·5 c.c.), and the orange suspension was then stirred at room temperature for 2 hr. An excess of concentrated ammonia solution was added, and the precipitate, isolated by extraction with benzene, was distilled (bulb-to-bulb, 195°/0·04 mm.) to give a viscous oil which solidified and, on being crystallised from light petroleum (b. p. 100—120°), afforded the *cinnoline* as pale yellow needles, m. p. 138—138·5° (Found: C, 57·3; H, 3·6; N, 8·9; Br, 25·2. $C_{15}H_{11}ON_2Br$ requires C, 57·2; H, 3·5; N, 8·9; Br, 25·4%).

4-p-*Methoxyphenylcinnoline*.—1-*o*-Aminophenyl-1-*p*-methoxyphenylethylene (4·25 g.) was treated as described for 4-phenylcinnoline, but benzene was used to isolate the crude product. Distillation of this, and crystallisation of the fraction with b. p. 176—178°/0·06 mm. from light petroleum, gave the cinnoline as yellow stout needles (3·6 g., 81%), m. p. 85° (lit.,[13] 85°) (Found: N, 11·7. Calc. for $C_{15}H_{12}ON_2$: N, 11·9%).

3-p-*Methoxyphenylindole*.—4-*p*-Methoxyphenylcinnoline (2·4 g.) was reduced as described for 3-phenylindole, but the material obtained by extraction with ether was distilled to give a pale yellow oil, b. p. 160°/0·04 mm., which solidified and, after being crystallised several times from light petroleum (b. p. 80—100°), afforded 3-p-*methoxyphenylindole* (1·7 g., 76%) as needles, m. p. 134° (Found: C, 80·7; H, 5·9; N, 6·5. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8; N, 6·3%).

4-p-*Hydroxyphenylcinnoline*.—A mixture of 4-*p*-methoxyphenylcinnoline (4·72 g.) and 48% hydrobromic acid (35 c.c.) was stirred and refluxed for 75 min., cooled, and filtered, and the yellow solid was then boiled for 5 min. with water (100 c.c.). A slight excess of ammonia was added, boiling was continued for 5 min., the mixture was cooled and filtered, and the solid was washed with water and dried. Sublimation of the product at 225°/0·02 mm., trituration of the sublimate with light petroleum (15 c.c.), and crystallisation of the insoluble material from butan-1-ol gave the cinnoline (3·75 g., 84%) as orange-yellow irregular crystals, m. p. 237—238° (lit.,[9, 13] 234—235°, 230°) (Found: N, 12·6. Calc. for $C_{14}H_{10}ON_2$: N, 12·6%).

3-p-*Hydroxyphenylindole*.—A mixture of 4-*p*-hydroxyphenylcinnoline (1·11 g.), amalgamated zinc wool (2 g.), glacial acetic acid (2·5 c.c.), dioxan (2·5 c.c.), and water (5 c.c.) was refluxed for 2½ hr., cooled, and diluted with water (12 c.c.). The precipitate was isolated by extraction with ethyl acetate, and sublimed, in a vertical tube, at 145°/0·01 mm. to give an upper diffuse band (65 mg.) which was discarded, and a lower band of almost colourless needles from which, by crystallisation from benzene, the indole (0·78 g., 75%) was obtained as colourless needles, m. p. 150·5—151° raised to 151·5—152° by resublimation and recrystallisation (lit.,[9] golden, m. p. 152—154°) (Found: N, 7·0. Calc. for $C_{14}H_{11}ON$: N, 6·7%).

1-o-*Aminophenyl*-1-(2,5-*dimethoxyphenyl*)*ethylene*.—1,4-Dimethoxybenzene (34·5 g.) in ether (75 c.c.) was added during 15 min. to a stirred solution of *n*-butyl-lithium, from *n*-butyl bromide (41 g.) and lithium (4·5 g.), in ether (150 c.c.) cooled in an ice-bath, and stirring was then continued for 5 hr. at 18°. The solution was cooled in ice, *o*-aminoacetophenone (10·1 g.) in ether (75 c.c.) was added during 20 min., and the brown mixture was stirred at room temperature for 5 hr. and then decomposed at 0° with water (80 c.c.). The ethereal phase, combined with an ether extract of the aqueous phase, was washed with water, and dried. Removal of the solvent and distillation of the residue gave, as the last fraction, a pale yellowish-green oil (11·1 g.), b. p. 165—168°/0·01 mm. This was shaken with a mixture of concentrated sulphuric acid (10 c.c.) and water (120 c.c.) until no further material dissolved, a small quantity of oil was removed by extraction with ether, and the orange aqueous phase was heated on the boiling-water bath for 2 hr. The solution was cooled (the base sulphate separated as short blades) and basified with concentrated aqueous ammonia, and the precipitate, isolated by extraction with ether, was distilled to give a pale yellowish-green oil (9·5 g., 50%), b. p. 142—143°/0·02 mm., which solidified, m. p. 55·5—56·5°. Crystallisation of this from light petroleum (b. p. 40—60°) gave the *ethylene* as rhombic prisms, m. p. 57—57·5° (Found: C, 75·5; H, 6·7; N, 5·3. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%).

4-(2,5-*Dimethoxyphenyl*)*cinnoline*.—The foregoing amino-olefin (9 g.) was refluxed for 5 min. with 8% hydrochloric acid (105 c.c.), and the mixture, vigorously stirred, was cooled to 0° and treated with sodium nitrite (2·8 g.) in water (40 c.c.). The cinnoline hydrochloride separated as a deep orange-red sludge which, soon after addition of the nitrite had been completed, rapidly became chocolate-brown. After 1 hour's stirring at room temperature the suspension was cooled in ice and basified with concentrated ammonia solution. The precipitate, isolated by extraction with benzene, was triturated with ether (25 c.c.) to give a yellow powder (A), m. p. 126·5—127·5°. Distillation (bulb-to-bulb, 205°/0·01 mm.) of the ether-soluble fraction afforded unchanged amino-olefin (1·6 g.) which was treated as above, and the ether-insoluble product was combined with (A) and crystallised (charcoal) from light petroleum (b. p. 100—120°) to give sulphur-yellow needles (7·95 g., 85%), m. p. 129°. Sublimation at 128°/0·01 mm. and crystallisation of the sublimate from light petroleum (b. p. 100—120°) afforded the *cinnoline* as bright greenish-yellow needles, m. p. 130° (Found: C, 72·2; H, 5·3; N, 10·6. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3; N, 10·5%).

3-(2,5-*Dimethoxyphenyl*)*indole*.—A mixture of the foregoing cinnoline (0·27 g.), amalgamated zinc wool (0·4 g.), glacial acetic acid (0·5 c.c.), dioxan (0·5 c.c.), and water (1 c.c.) was refluxed for 2½ hr., cooled, and diluted with water (2 c.c.). The precipitate was isolated by extraction with ether, triturated with boiling light petroleum (4 c.c.), and the insoluble material was distilled (bulb-to-bulb, 170°/5 × 10^{-3} mm.) to give a colourless oil from which, by crystallisation from benzene–light petroleum, the *indole* (0·15 g., 58%) was obtained as hexagonal plates, m. p. 114·5° (Found: C, 75·6; H, 5·9; N, 5·8. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%).

4-(2,5-*Dihydroxyphenyl*)*cinnoline*.—A mixture of 4-(2,5-dimethoxyphenyl)cinnoline (5·32 g.) and 48% hydrobromic acid (55 c.c.) was stirred and refluxed for 3 hr., then cooled, and the deep maroon needles which separated were collected, suspended in water (100 c.c.), and decomposed by the addition of a slight excess of aqueous 10% ammonia. The suspension was boiled for 10 min., then cooled, and the yellow solid was collected, washed with water, and dried. Sublimation at 230°/5 × 10^{-3} mm. gave yellow needles (4·35 g., 91%), m. p. 281—284° (decomp.). Two further sublimations of this product afforded the *cinnoline* as bright yellow needles, m. p. 285—287° after becoming brown at 277° (Found: C, 70·6; H, 4·5; N, 12·1. $C_{14}H_{10}O_2N_2$ requires C, 70·6; H, 4·2; N, 11·8%). The solution in aqueous 5% sodium hydroxide was deep wine-red, slowly changing to brown when exposed to air.

3-(2,5-*Dihydroxyphenyl*)*indole*.—The foregoing cinnoline (1·2 g.) was reduced as described for 3-*p*-hydroxyphenylindole, and the glass which remained after removal of the ethyl acetate was refluxed with benzene (20 c.c.) until crystallisation (initiated by scratching) was complete (3 hr.). The suspension was cooled and filtered, and the solid (0·80 g.) was combined with further crystalline material (0·09 g.) obtained by concentration of the mother liquor. The product was refluxed with benzene (5 c.c.) for 30 min., the hot suspension was filtered, and the pale pink solid was distilled (bulb-to-bulb, 200—205°/4 × 10^{-3} mm.). The orange distillate was dissolved in boiling ethyl acetate (12 c.c.), light petroleum (30 c.c.; b. p. 100—120°) was added, and the solution, under nitrogen, was concentrated on the steam-bath until it became just turbid. Crystallisation was induced by scratching, and the solution was then left overnight at room temperature. Rectangular prisms (0·60 g., 55%), m. p. 163·5—165°, slightly contaminated on the surface by olive-green material, separated and, on being sublimed at 150°/3 × 10^{-3} mm., afforded the *indole* as very pale yellow prisms, m. p. 164·5—165° (Found: C, 75·0; H, 5·0; N, 6·5. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The solution in aqueous 5% sodium hydroxide was deep green, changing in air to brown and eventually depositing a brown flocculent precipitate.

3'-*Indolyl*-1,4-*benzoquinone*.—(*a*) Sodium iodate hydrate (0·25 g.) in ethanol-water (3 c.c., 15 c.c.) was added to 3-(2,5-dihydroxyphenyl)indole (0·25 g.) in ethanol–water (7 c.c., 25 c.c.), the mixture was left at room temperature for 6 hr., and the precipitate was collected, washed with aqueous 15% ethanol and then with water, and dried. The product (0·15 g.), m. p. 134·5—135·5°, was extracted with ethanol (25 c.c.) at 50° for 15 min., the insoluble material was removed, and the filtrate, cooled to 0°, was diluted with water (75 c.c.) at 5°. After 30 min. at room temperature the precipitate was collected, washed as above, and dried (P_2O_5) to give the quinone (90 mg., 36%) as deep violet needles, m. p. 135·5—136·5° (Found: C, 74·5; H, 4·1; N, 5·9. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·0; N, 6·3%), $\lambda_{max.}$ 221, 258, 502 mμ (log ε 4·52, 4·32, 3·65), $\lambda_{min.}$ 241, 348 mμ (log ε 4·19, 2·94), $\nu_{max.}$ 3196, 1670, 1644, 1604, (1568) (m), 1558 cm.$^{-1}$.

(*b*) The preparation described by Bu'Lock and Harley-Mason [3] could not be repeated, and the following modification was used. Concentrated hydrochloric acid (5 drops) was added to a stirred solution of indole (1 g.) and 1,4-benzoquinone (2 g.) in ethanol (100 c.c.) at 8°, stirring at 7—8° was continued for 15 min., and water (300 c.c.) was then added. After 8 hr. at room temperature the precipitate was collected, washed with aqueous 30% ethanol and then with water, and dried (yield 0·32 g.). The solid was heated at 50° with ethanol (20 c.c.) for 10 min., the insoluble fraction [(A), 90 mg.] was collected, and the mother-liquor was cooled in solid carbon dioxide for 5 hr., and then filtered [solid (B), 77 mg.]. The filtrate was concentrated at *ca.* 40°/50 mm. to 6 c.c., solid (A) was added, and the suspension was shaken at 45—50° for 10 min., and filtered [solid (C)], the filtrate being cooled overnight in solid carbon dioxide to yield further product [(D), 37 mg.]. Substance (C) was refluxed with ethanol (5 c.c.) for 5 min., the insoluble material (60 mg.), m. p. $\nless$ 200°, was removed, and the mother-liquor was diluted at 0° with water (10 c.c.) to yield solid [(E), 12 mg.]. Products (B), (D), and (E) were combined and extracted with ethanol (20 c.c.) at 50° for 10 min., and the extract, after being filtered, was cooled to 0° and diluted with water (50 c.c.) at 5°. After 10 min. the precipitate was collected, washed with aqueous 25% ethanol and then with water, and dried (P_2O_5) to give the quinone (100 mg., 5%) as deep violet small needles, m. p. 137·5—138·5° undepressed on admixture with material prepared by method (*a*) (lit.,[3] violet-black, decomp. without melting at *ca.* 140°) (Found: C, 74·8; H, 4·1; N, 6·2%), $\lambda_{max.}$ 221, 258, 503 mμ (log ε 4·52, 4·32, 3·66), $\lambda_{min.}$ 241, 346 mμ (log ε 4·18, 2·66), $\nu_{max.}$ 3183, 1671, 1645, 1607, 1569, 1559 cm.$^{-1}$. Addition of water to an ethanolic solution of either of these products precipitated the quinone as a mixture of pink, blue, and intensely violet needles, but after several hours the suspension contained only the violet form.

4-*Bromoveratrole*.—Bromine (80 g.) in glacial acetic acid (300 c.c.) was added during 2 hr. to veratrole (69 g.) in acetic acid (200 c.c.) stirred at 5—10°, stirring was continued for 30 min. at 10—15°, and the solvent was removed at *ca.* 40°/20 mm. The residual oil, in light petroleum (250 c.c.), was washed with aqueous 5% sodium hydroxide, then with water, and dried. Distillation through a short Dufton column afforded 4-bromoveratrole (82 g., 76%), b. p. 69—70°/0·04 mm.

1-o-*Aminophenyl*-1-(3,4-*dimethoxyphenyl*)*ethylene*.—4-Bromoveratrole (36 g.) in ether (100 c.c.) was added during 50 min. to a vigorously stirred solution of *n*-butyl-lithium, from *n*-butyl bromide (27·5 g.) and lithium (3 g.), in ether (220 c.c.) at −70° to −65°, and the pale grey thick suspension was then allowed to warm [19] during 1½ hr. to −45°. The mixture was diluted with ether (50 c.c.) and then, at −40°, *o*-aminoacetophenone (7·4 g.) in ether (50 c.c.) was added during 30 min. The bright yellow suspension was stirred at room temperature for 2½ hr. (it became brown), left overnight, and then decomposed at 0° with water (80 c.c.). The ethereal phase, combined with an ether extract of the aqueous phase, was washed and dried, the solvent was removed, and the residue was distilled. The fraction with b. p. 158—160°/0·01 mm. was shaken with a mixture of concentrated sulphuric acid (10 c.c.) and water (120 c.c.) until no further material dissolved, a little insoluble oil was removed by extraction with ether, and the

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[19] Cf. Howell and Taylor, *J.*, 1956, 4252.

orange aqueous solution was then heated on the boiling-water bath for 2 hr. Water (120 c.c.) was added, the solution was basified with concentrated aqueous ammonia, and the precipitate was collected, washed with water, dried, and triturated with ether (50 c.c.). Distillation of the insoluble material gave an oil (4·8 g., 34%), b. p. 158—160°/0·01 mm., which solidified, m. p. 141—142°, and, after two crystallisations from light petroleum (b. p. 100—120°), afforded the *ethylene* as rhombic plates, m. p. 142·5° (Found: C, 75·5; H, 6·8; N, 5·3. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%).

4-(3,4-*Dimethoxyphenyl*)*cinnoline*.—A stirred solution of the foregoing olefin (4·1 g.) in hot 9% hydrochloric acid (55 c.c.) was cooled to 0°, then treated with sodium nitrite (1·3 g.) in water (20 c.c.), and the resulting yellow suspension was stirred at room temperature for 1 hr., cooled in ice, and basified with concentrated aqueous ammonia. Ether (40 c.c.) was added, vigorous stirring was continued until the precipitate had become finely divided, and the suspension was filtered, the solid being triturated with water and then, after drying, with a little ether. The insoluble material (m. p. 111—113°, resolidifying at *ca.* 116°, and remelting at 147—150°) was subjected to short-path distillation at 155—160°/0·01 mm., and the distillate was crystallised from light petroleum (b. p. 100—120°) to give the *cinnoline* (3·3 g., 77%) as pale yellow blades, m. p. 152° raised to 152·5° by redistillation and recrystallisation (Found: C, 72·4; H, 5·4; N, 10·4. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3; N, 10·5%).

3-(3,4-*Dimethoxyphenyl*)*indole*.—A mixture of the foregoing cinnoline (0·13 g.), amalgamated zinc wool (0·2 g.), glacial acetic acid (0·25 c.c.), dioxan (0·25 c.c.), and water (0·5 c.c.) was refluxed for 2½ hr., cooled, and diluted with water (1 c.c.). The precipitate, isolated by extraction with 3 : 1 ether–ethyl acetate, was triturated with boiling light petroleum (3 c.c.), and the insoluble material was sublimed at 140°/5 × 10^{-3} mm. Crystallisation of the sublimate from benzene–light petroleum (3 : 7) gave the *indole* (60 mg., 49%) as rhombic prisms, m. p. 144—145° raised by resublimation and recrystallisation to 148° (Found: C, 75·7; H, 6·1; N, 5·5. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%).

4-(3,4-*Dihydroxyphenyl*)*cinnoline*.—A solution of 4-(3,4-dimethoxyphenyl)cinnoline (2·65 g.) in 48% hydrobromic acid (100 c.c.) was stirred and refluxed for 3 hr., then cooled, and the orange platelets which separated were collected and suspended in water (100 c.c.). A slight excess of concentrated aqueous ammonia was added, the yellow suspension was boiled for 10 min., and the solid was collected, washed with water, and dried. Sublimation at 230°/5 × 10^{-3} mm. gave the *cinnoline* (2·2 g., 92%) as bright yellow needles, m. p. 265—266° (decomp.). Crystallisation from glacial acetic acid followed by two further sublimations at 220°/5 × 10^{-3} mm. raised the m. p. to 266—268° (decomp.) (Found: C, 70·7; H, 4·3; N, 12·0. $C_{14}H_{10}O_2N_2$ requires C, 70·6; H, 4·2; N, 11·8%). The solution in aqueous 5% sodium hydroxide was intensely blood-red, becoming brown in air.

3-(3 : 4-*Dihydroxyphenyl*)*indole*.—The foregoing cinnoline (1·2 g.) was reduced as described for 3-*p*-hydroxyphenylindole, and the product obtained by removal of the ethyl acetate was crystallised from benzene to give irregular plates which were then distilled (bulb-to-bulb, 200—205°/5 × 10^{-3} mm.). Crystallisation of the distillate from benzene, under nitrogen, afforded plates (0·73 g.), m. p. 126·5—127°, from which, by distillation (bulb-to-bulb, 200°/4 × 10^{-3} mm.) and recrystallisation of the distillate, the *indole* was obtained as blades, m. p. 127·5° (Found: C, 74·4; H, 4·9; N, 6·3. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The solution in aqueous 5% sodium hydroxide was intensely blue, changing rapidly to green and then slowly to brown.

4-3′-*Indolyl*-1,2-*benzoquinone*.—(*a*) Sodium iodate hydrate (0·25 g.) in ethanol–water (3 c.c., 10 c.c.) was added all at once to a solution of the foregoing indole (0·25 g.) in ethanol–water (15 c.c., 25 c.c.), and the resulting deep blue solution was left at room temperature for 20 min. Water (15 c.c.) was added and then, after 5 hr., the precipitate was collected, washed with aqueous 15% ethanol and with water, and dried. The product was shaken for 30 min. with acetone (5 c.c.), collected, and dried (P_2O_5), to give the quinone (0·20 g., 81%) as deep blue needles with a strong bronze reflex, m. p. 175—176° (Found: C, 74·5; H, 4·3; N, 6·6. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·0; N, 6·3%), $\lambda_{max.}$ (247), 286, 355, 487 mμ (log ε 4·16, 4·06, 3·71, 3·80), $\lambda_{min.}$ 270, 323, 405 mμ (log ε 3·99, 3·57, 3·31), $\nu_{max.}$ 3171, 1674(m), 1621, 1594, 1540 cm.$^{-1}$.

(*b*) Indole (0·2 g.) was treated with 1,2-benzoquinone (0·4 g.) as described by Bu'Lock and Harley-Mason,[3] but, instead of being recrystallised, the product was washed successively with aqueous 50% ethanol, water, and acetone, and dried (P_2O_5), to give the quinone (0·17 g., 45%) as deep blue needles, m. p. 176° undepressed on admixture with material prepared by method (*a*) [lit.,[3] 160° (decomp.)] (Found: C, 74·3; H, 4·3; N, 6·0%). $\lambda_{max.}$ (247), 285·5, 356, 488 mμ (log ε 4·15, 4·04, 3·71, 3·75), $\lambda_{min.}$ 271, 323, 409 mμ (log ε 4·00, 3·63, 3·45), $\nu_{max.}$ 3181, 1678, (1621), (1610), 1595, 1543 cm.$^{-1}$.

1-o-*Aminophenyl*-1-(2,3-*dimethoxyphenyl*)*ethylene*.—Veratrole (48·3 g.) in ether (100 c.c.) was added during 30 min. to a stirred solution of *n*-butyl-lithium, from *n*-butyl bromide (55 g.) and lithium (6·2 g.), in ether (200 c.c.) at 15°, and stirring was continued for 3 hr. more. The grey suspension was cooled in ice, vigorously stirred, and to it was added during 30 min. *o*-aminoacetophenone (15·8 g.) in ether (100 c.c.). Stirring was continued at room temperature for 3 hr., water (150 c.c.) was added dropwise at 0°, and the mixture was filtered. The ethereal phase was separated, washed with aqueous 10% sodium hydroxide, then with water, and dried. The solvent was removed, the residue was distilled, and the fraction with b. p. 148—155°/0·01 mm. was shaken with a mixture of concentrated sulphuric acid (16 c.c.) and water (200 c.c.) until no further material dissolved. A little insoluble oil was removed by extraction with ether, and the aqueous phase was then heated on the boiling-water bath for 2 hr., cooled, and diluted with water (150 c.c.). An excess of concentrated aqueous ammonia was added and the precipitate, isolated by extraction with ether, was distilled. Crystallisation of the fraction with b. p. 135—155°/0·01 mm. from light petroleum (250 c.c.) gave the *olefin* as hexagonal tablets [(A), 8·75 g.], m. p. 102—102·5°. The mother-liquor was filtered through alumina (100 × 30 mm.), and the eluate was concentrated to yield further solid, m. p. 101·5—102·5°, which was combined with (A) (total 9·88 g., 33%). Distillation (bulb-to-bulb, 175°/0·01 mm.) and crystallisation of the distillate from light petroleum raised the m. p. to 103·5—104° (Found: C, 75·1; H, 6·6; N, 5·2. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%).

4-(2,3-*Dimethoxyphenyl*)*cinnoline*.—Sodium nitrite (2·45 g.) in water (40 c.c.) was added during 30 min. to a vigorously stirred solution of the foregoing olefin (8·92 g.) in 7% hydrochloric acid (125 c.c.) at 0°, and the orange solution was stirred at room temperature for 1 hr., then cooled to 0° and basified with ammonia. The precipitate was extracted with benzene, and the extract was washed with aqueous 10% sodium hydroxide, then with water, and dried. Removal of the solvent and distillation of the residue gave material, b. p. 172—175°/7 × 10^{-3} mm., which on crystallising (charcoal) from light petroleum (b. p. 100—120°) afforded the *cinnoline* (7·8 g., 81%) as pale yellow prisms, m. p. 119—120°. Sublimation at 130°/5 × 10^{-3} mm. and then recrystallisation raised the m. p. to 120·5—121° (Found: C, 72·2; H, 5·4; N, 10·4. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3; N, 10·5%).

3-(2,3-*Dimethoxyphenyl*)*indole*.—A mixture of the foregoing cinnoline (0·54 g.), amalgamated zinc wool (0·8 g.), glacial acetic acid (1 c.c.), dioxan (1 c.c.), and water (2 c.c.) was refluxed for 2½ hr., cooled, and diluted with water (5 c.c.). The precipitate was isolated by extraction with ether, washed with aqueous 10% sodium hydroxide and then with water, and distilled (bulb-to-bulb, 180°/5 × 10^{-3} mm.). Crystallisation of the distillate from light petroleum (b. p. 80—100°) gave irregular crystals contaminated by mauve material, which was removed by chromatography, in benzene, on alumina (60 × 8 mm.). Evaporation of the eluate, distillation of the residue as above, and crystallisation of the distillate from light petroleum then yielded the *indole* (0·31 g., 60%) as prismatic needles, m. p. 95—95·5° (Found: C, 76·2; H, 6·1; N, 5·7. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%).

4-(2,3-*Dihydroxyphenyl*)*cinnoline*.—A solution of 4-(2,3-dimethoxyphenyl)cinnoline (3·99 g.) in 48% hydrobromic acid (45 c.c.) was stirred and refluxed for 3 hr., then cooled to 0°, and the deep red platelets which separated were collected, suspended in water (100 c.c.), and just basified with aqueous 10% ammonia. The yellow suspension was boiled for 10 min., then cooled, and the solid was collected, washed with water, and dried. Sublimation at 235°/5 × 10^{-3} mm. then gave yellow needles (3·26 g., 91%), m. p. 272—282° (decomp.). A portion (0·6 g.) of this material was refluxed for 30 min. with ethanol (10 c.c.), and the hot suspension was filtered. The solid was washed with hot ethanol and sublimed at 235°/5 × 10^{-3} mm., and the sublimate was refluxed for 1 hr. with ethanol (10 c.c.), to give the *cinnoline* (0·5 g.) as yellow needles, m. p. 277—281° (decomp.) after becoming green at 274° (Found: C, 70·8; H, 4·3; N, 12·1. $C_{14}H_{10}O_2N_2$ requires C, 70·6; H, 4·2; N, 11·8%). The solution in aqueous 5% sodium hydroxide was deep wine red, slowly becoming brown in air.

3-(2,3-*Dihydroxyphenyl*)*indole*.—The foregoing cinnoline (1·2 g.) was reduced as described for 3-*p*-hydroxyphenylindole, and the material remaining after removal of the ethyl acetate was distilled (bulb-to-bulb, 210°/5 × 10^{-3} mm.). The glass obtained did not crystallise, and consequently the indole was purified *via* its adduct with 1,3,5-trinitrobenzene. The trinitro-compound (1·3 g.) in hot benzene (5 c.c.) was added to the distillate (1·07 g.), also in benzene (10 c.c.), and the solution was heated to the b. p., diluted with light petroleum (1·7 c.c.), and left to cool. The *adduct* (1·8 g.) separated as reddish-brown needles, m. p. 131·5—132·5° unchanged by recrystallisation (Found: C, 54·7; H, 3·5; N, 12·4. $C_{20}H_{14}O_8N_4$ requires C, 54·8; H, 3·2; N, 12·8%). Dilution of the mother-liquor with light petroleum afforded further adduct (0·15 g., total 1·95 g., 94%). This product (1·75 g.) in benzene (40 c.c.) was chromatographed on " Florisil " (250 × 20 mm.) which had been swept with nitrogen, and the column was eluted first with benzene (200 c.c.) to remove 1,3,5-trinitrobenzene, and then with ethyl acetate (130 c.c.), the first 30 c.c., containing benzene, being rejected. Removal of the ethyl acetate from the remainder of the eluate left a glass which was twice distilled (bulb-to-bulb, 220°/5 × 10^{-3} mm.), to give the *indole* (0·62 g., 69% based on adduct) as a light yellow glass, softening point *ca.* 25° (Found: C, 74·4; H, 5·0; N, 6·5. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The solution in aqueous 5% sodium hydroxide was yellow, becoming green and then red-brown in air.

Oxidation of 3-(2,3-*Dihydroxyphenyl*)*indole*.—The indole (0·25 g.) was treated with sodium iodate as described for 4-3′-indolyl-1,2-benzoquinone. The solution became green, then blue, and, after 10 sec., a brown turbidity developed. After 4 hr. the thixotropic precipitate was collected, washed with aqueous 25% ethanol, then with water, and dried (P_2O_5), to give a black powder (0·22 g.), m. p. 168—178° (Found: C, 70·9; H, 4·6; N, 5·8%).

This work was carried out during the tenure of an Imperial Chemical Industries Research Fellowship.

Department of Chemistry, University of Manchester. [*Received, February* 26*th*, 1959.]