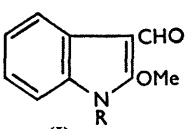
966. *Heterocyclic Compounds of Nitrogen. Part I. The Alkylation and Acylation of 3-Phenyloxindole, and the Preparation of Some Derivatives of 2-Hydroxy-3-phenylindole.*

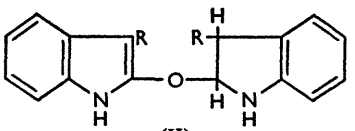
By J. Malcolm Bruce and F. K. Sutcliffe.

3-Phenyloxindole is alkylated at position 3, and acylated at position 1. 1-Substituted 3-phenyloxindoles are also alkylated at position 3, but acylation affords derivatives of 2-hydroxy-3-phenylindole, whose structures are established mainly by means of infrared and ultraviolet spectra.

Several workers [1] studied the alkylation and acylation of simple oxindoles, obtaining compounds which were formulated as derivatives of the tautomeric 2-hydroxyindole and 2-hydroxyindolenine forms, but a re-investigation of some of these reactions by Wenkert *et al.*[2,3] has shown that the products thought to be 2-alkoxyindoles are in fact 3-alkyloxindoles. The first authentic 2-alkoxyindoles (I; R = H or Me) were obtained [3] by treating the corresponding 3-hydroxymethyleneoxindoles with ethereal diazomethane, and more recently von Dobeneck and Lehnerer [4] reported the isolation of compounds believed to be (II; R = Me and $CH_2 \cdot CO_2Me$) on oxidation of ethereal solutions of skatole and methyl 3-indolylacetate respectively with ferric chloride in the presence of secondary aliphatic amines. Compounds (I; R = H and Me) are readily cleaved to the parent oxindoles by dilute alkali, but the product (II; R = Me) is stable to strong aqueous-methanolic potassium hydroxide. It is, however, converted quantitatively by dilute



(I)



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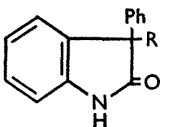


(III)

hydrochloric acid into a mixture of skatole and 3-methyloxindole. The present work has led to the isolation of the first authentic acyl derivatives of a 2-hydroxyindole.

3-Phenyloxindole (III; R = H) was most conveniently prepared by a modification of

[1] Sumpter, *Chem. Rev.*, 1945, **37**, 454; Julian, Meyer, and Printy, in Elderfield, "Heterocyclic Compounds," Wiley and Sons, New York, 1952, Vol. III, p. 126; Sumpter and Miller, in Weissberger, "The Chemistry of Heterocyclic Compounds," Interscience Publ., Inc., New York, 1954, Vol, VIII, p. 134; and references cited therein.

[2] Wenkert, Bose, and Reid, *J. Amer. Chem. Soc.*, 1953, **75**, 5514.

[3] Wenkert, Bhattacharyya, and Reid, *ibid.*, 1956, **78**, 797.

[4] Von Dobeneck and Lehnerer, *Chem. Ber.*, 1957, **90**, 161.

the procedure described by Meisenheimer and Meis.[5] In the presence of one equivalent of aqueous sodium carbonate it reacted with methyl iodide, benzyl iodide, and phenacyl bromide severally, to yield monosubstitution products which were unchanged by dilute acids or bases and readily gave monoacetates and monobenzoates. These properties suggested that the compounds were (III; R = Me, CH_2Ph, and CH_2Bz). 3-Methyl-3-phenyloxindole was synthesised by Brunner's method[6] from *N*-phenyl-*N*-α-phenylpropionylhydrazine, and was shown (mixed m. p. and ultraviolet spectrum) to be identical with the methylation product of 3-phenyloxindole. An attempt to cyclise *N*-αβ-diphenylpropionyl-*N'*-phenylhydrazine to 3-benzyl-3-phenyloxindole was unsuccessful, but the correctness of this structure for benzylated 3-phenyloxindole was established by its infrared and ultraviolet absorption spectra. The constitution (III; R = CH_2Bz) of the phenacyl derivative was confirmed by the presence of two peaks in the carbonyl region of its infrared spectrum, and the persistence of one of these in the hydrazone (III; R = CH_2·CPh:N·NH_2). 1-Methyl-3-phenyloxindole, obtained in good yield from α-bromo-*N*-methyl-α-phenylacetanilide by Julian and Pikl's modification[7] of Stollé's method,[8] similarly afforded the 3-benzyl derivative when alkylated with benzyl iodide.

1-Benzoyl-3-phenyloxindole was formed when the parent oxindole was treated with benzoic anhydride in the presence[9] of (+)-camphor-10-sulphonic acid or, more conveniently, with benzoyl chloride and aqueous sodium carbonate. The 1-acetyl derivative was obtained[10] by treating 3-phenyloxindole with acetic anhydride alone.

3-Phenyloxindole and its 1-acetyl and 1-benzoyl derivatives dissolve in aqueous sodium hydroxide with, respectively, pale yellow, bright yellow, and orange colours, which may be attributed to the corresponding enol anions. In the last two cases the colours rapidly fade as the acyl groups are hydrolysed, but more stable solutions are formed in aqueous sodium carbonate containing acetone, and addition of methyl or benzyl iodide to these affords the corresponding 1-acyl-3-alkyl-3-phenyloxindoles, identical with those obtained by appropriate acylation of (III; R = Me and CH_2Ph).

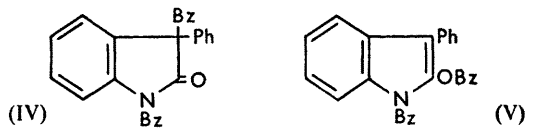
With toluene-*p*-sulphonyl chloride and sodium carbonate, 3-phenyloxindole yielded 3-phenyl-1-toluene-*p*-sulphonyloxindole, whose structure was confirmed by its infrared spectrum. Unlike the 1-acetyl or 1-benzoyl derivative this was extremely resistant to hydrolysis, but gave 3-phenyloxindole quantitatively when treated[11] with Raney nickel in ethanol.

For comparison with 3-phenyl-1-toluene-*p*-sulphonyloxindole, a synthesis of the isomeric sulphone (III; R = *p*-C_6H_4Me·SO_2) was attempted. Treatment of 3-phenyldioxindole (III; R = OH)[12] with thionyl chloride gave 3-chloro-3-phenyloxindole which, with sodium toluene-*p*-sulphinate, afforded 3-phenyl-1-toluene-*p*-sulphonyloxindole, and not the expected sulphone. With aqueous bases, the chloro-compound yielded amorphous material, but it was hydrolysed to the parent dioxindole by water, and with methanol or ethanol it gave the corresponding 3-alkoxy-3-phenyloxindole. In these properties[13] it resembles diphenylmethyl chloride, to which it is formally analogous. 3-Methoxy- and 3-ethoxy-3-phenyloxindole, like 3-phenyldioxindole, dissolve readily in aqueous 5% sodium hydroxide, and may be recovered by acidification.

Benzoylation of 3-phenyloxindole under Schotten–Baumann conditions gave a dibenzoate, which was also obtained on reaction of 1-benzoyl-3-phenyloxindole with benzoic anhydride in the presence of (+)-camphor-10-sulphonic acid. This, together with the fact that both benzoyl groups could be removed by hydrolysis (the 3-acyloxindoles are

[5] Meisenheimer and Meis, *Ber.*, 1924, **57**, 297; cf. Palazzo and Rosnati, *Gazzetta*, 1953, **83**, 211.
[6] Brunner, *Monatsh.*, 1896, **17**, 267, 479.
[7] Julian and Pikl, *J. Amer. Chem. Soc.*, 1935, **57**, 563.
[8] Stollé, *J. prakt. Chem.*, 1930, **128**, 1.
[9] Cf. Plant and Tomlinson, *J.*, 1933, 955.
[10] Brunner, *Monatsh.*, 1897, **18**, 547.
[11] Cf. Kenner and Murray, *J.*, 1949, S178.
[12] Kohn, *Monatsh.*, 1910, **31**, 747.
[13] Ward, *J.*, 1927, 2289.

readily hydrolysed [14]), suggested either structure (IV) [15] or (V). The latter was supported by cleavage of the compound to 3-phenyloxindole and benzoylhydrazine when it was treated with ethanolic hydrazine hydrate [16] and by its lack of ketonic activity,[17] and was confirmed by the infrared and ultraviolet absorption spectra. 1-Methyl-3-phenyloxindole similarly afforded 2-benzoyloxy-1-methyl-3-phenylindole. The success of these reactions is probably due to the low solubility of the products.



In the presence of aqueous sodium carbonate, 1-acetyl-3-phenyloxindole with benzoyl chloride gave a good yield of 1-acetyl-2-benzoyloxy-3-phenylindole, but 1-benzoyl-3-phenyloxindole afforded only 2% of the compound (V), and no indole was isolated on reaction with 1-methyl-3-phenyloxindole.

Both 1-acetyl- and 1-benzoyl-3-phenyloxindole afforded the corresponding 1-acyl-2-acetoxy-3-phenylindole when treated with acetic anhydride and (+)-camphor-10-sulphonic acid, but 1-methyl-3-phenyloxindole failed to yield a pure indole.

The infrared absorption maxima in the N–H and C=O stretching regions are given in Tables 1 and 2. Both 3-ethoxy-3-phenyl- and 3-phenyl-1-toluene-*p*-sulphonyl-oxindole have two peaks in the carbonyl region, although they each contain only one carbonyl group. Kellie *et al.*[18] have observed a similar effect in oxindole and some of its simpler

TABLE 1. *Absorption spectra of substituted 3-phenyloxindoles, in Nujol, in the regions 2·8—3·4 and 5·6—6·1 μ.*

Substituent	$\lambda_{max.}$ (μ) *						
None	—	3·15	3·22	—	—	5·82	—
3-Cl	—	3·18	3·25	—	—	5·81	—
3-OH	2·89	3·13	3·26 (m)	—	—	5·88	—
3-OMe	—	3·16	3·23	—	—	5·80	—
3-OEt	—	3·14	(3·23)	—	—	5·79	5·93
3-Me	—	3·18	3·27	—	—	5·87	—
3-CH_2Ph	—	3·13	3·30	—	—	5·89	—
3-CH_2Bz	—	3·13	3·22	3·28	—	5·86	5·89
3-CH_2·CPh:N·NH_2	2·87	(2·99)	3·08	(3·29)	—	5·99	—
1-Me	—	—	—	(3·31) (m)	—	5·89	—
1-Me-3-CH_2Ph	—	—	—	(3·32) (m)	—	5·86	—
1-Bz	—	—	—	—	5·68 (m)	5·90 (m)	—
1-Bz-3-OEt	—	—	—	—	5·67	5·91	—
1-Bz-3-Me	—	—	—	—	5·67	5·92	—
1-Bz-3-CH_2Ph	—	—	—	—	5·77	6·02	—
1-Ac	—	—	—	—	5·65	5·84	—
1-Ac-3-OAc	—	—	3·20 (w)	—	5·66	5·72	5·82
1-Ac-3-Me	—	—	—	—	5·68	5·83	—
1-Ac-3-CH_2Ph	—	—	—	—	5·71	5·83	—
1-Ac-3-CH_2Bz	—	3·12 (w)	—	—	5·72	5·88	5·93
1-*p*-C_6H_4Me·SO_2	—	3·08 (m)	—	—	—	5·80 (m)	5·92 (m)

* Absorption is strong unless stated otherwise. Figures in parentheses indicate shoulders.

derivatives. The 1-acyl-3-phenyloxindoles possess two peaks in the 5·6—6·0 μ region, and these may be attributed either to individual carbonyl absorption or, as suggested by Abramovitch,[19] to vibrational coupling. All the 2-acyloxy-3-phenylindoles show strong

[14] Julian, Magnani, Pikl, and Karpel, *J. Amer. Chem. Soc.*, 1948, **70**, 174.
[15] Cf. Heller and Heine, *Ber.*, 1916, **49**, 2775.
[16] Cf. Curtius and Dellschaft, *J. prakt. Chem.*, 1901, **64**, 419, and preceding papers in the series.
[17] Porter, Robinson, and Wyler, *J.*, 1941, 621.
[18] Kellie, O'Sullivan, and Sadler, *J.*, 1956, 3809.
[19] Abramovitch, *J.*, 1957, 1413.

TABLE 2. *Absorption spectra of substituted 3-phenylindoles, in Nujol, in the regions 2·8—3·0 and 5·6—6·0 μ.*

Substituent	$\lambda_{max.}$ (μ) *			Substituent	$\lambda_{max.}$ (μ) *		
None	2·93 (m)	—	—	1-Bz-2-CH_2Ph	—	—	5·90
2-Me	2·98	—	—	1-Bz-2-OAc	—	5·62	5·92
2-CH_2Ph	2·89 (m)	—	—	1-Bz-2-OBz	—	5·70	5·93
1-Me-2-CH_2Ph	—	—	—	1-Ac	—	—	5·90
1-Me-2-OBz	—	5·73	—	1-Ac-2-Me	—	—	5·91
1-Bz	—	—	5·95	1-Ac-2-OAc	—	5·62 (m)	5·86 (m)
1-Bz-2-Me	—	—	5·91	1-Ac-2-OBz	—	5·67	5·83

* See Table 1.

TABLE 3. *Absorption spectra of substituted 3-phenyloxindoles, in dioxan, in the region 220—400 mμ.*

Substituent	$\lambda_{min.}$ (mμ) *	log ε	$\lambda_{max.}$ (mμ) *	log ε	$\lambda_{min.}$ (mμ) *	log ε	$\lambda_{max.}$ (mμ) *	log ε
None	231	3·81	249	3·96	273	3·12	286	3·22
3-Cl	—	—	(255)	3·76	290	3·06	306	3·15
3-OH	238	3·70	254	3·85	280	3·11	290	3·20
3-OMe	239	3·57	255	3·84	280	3·12	294	3·24
3-OEt	240	3·77	255	3·94	282	3·01	295	3·11
3-Me	233	3·77	250	3·93	275	3·22	283	3·27
3-CH_2Ph	238	3·82	250	3·88	281	3·08	286	3·14
3-CH_2Bz	226	4·17	244	4·34	—	—	(280)	3·55
3-CH_2·CPh:N·NH_2	233	4·09	245	4·16	263	3·93	293	4·18
1-Me	236	3·75	255	4·03	—	—	(283)	3·24
1-Me-3-CH_2Ph	243	3·80	257	3·88	—	—	(288)	3·25
1-Bz	227	4·12	240	4·20	(265)	3·89	(290)	3·61
1-Bz-3-OEt	235	4·15	245	4·19	(270)	3·96	—	—
1-Bz-3-Me	229	4·13	239	4·20	(265)	3·90	(290)	3·64
1-Bz-3-CH_2Ph	231	4·18	240	4·23	—	—	(290)	3·55
1-Ac	(230)	4·09	—	—	—	—	—	—
1-Ac-3-OAc	—	—	—	—	—	—	—	—
1-Ac-3-Me	(233)	4·08	—	—	—	—	—	—
1-Ac-3-CH_2Ph	—	—	—	—	—	—	—	—
1-Ac-3-CH_2Bz	224	4·29	240	4·41	—	—	—	—
1-*p*-C_6H_4Me·SO_2	—	—	228	4·54	287	3·25	295	3·34

* Figures in parentheses indicate the approximate centre of a pronounced shoulder.

TABLE 4. *Absorption spectra of substituted 3-phenylindoles, in dioxan, in the region 220—400 mμ.*

Substituent	$\lambda_{min.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{min.}$ (mμ)	log ε	λ_{max} (mμ) *	log ε	$\lambda_{min.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
None	—	—	225	4·50	245	3·73	270	4·18	—	—	—	—
2-Me	—	—	228	4·53	247	3·75	279	4·19	—	—	—	—
2-CH_2Ph	—	—	228	4·59	249	3·89	282	4·22	—	—	—	—
1-Me-2-CH_2Ph	—	—	231	4·59	249	3·89	285	4·17	—	—	—	—
1-Me-2-OBz	—	—	232	4·66	252	4·03	275	4·25	—	—	—	—
1-Bz	—	—	227	4·53	245	4·28	258	4·34	294	3·81	310	3·96
1-Bz-2-Me	—	—	228	4·55	251	4·25	266	4·28	301	3·67	318	3·74
1-Bz-2-CH_2Ph	—	—	228	4·58	250	4·23	266	4·30	301	3·67	319	3·75
1-Bz-2-OAc	—	—	225	4·50	—	—	(255)	4·31	295	3·74	313	3·82
1-Bz-2-OBz	—	—	230	4·63	—	—	(260)	4·37	297	3·82	313	3·89
1-Ac	224	4·27	246	4·40	—	—	—	—	284	3·89	305	4·08
1-Ac-2-Me	230	4·18	246	4·33	—	—	—	—	292	3·85	303	3·91
1-Ac-2-OAc	229	4·25	245	4·00	—	—	—	—	287	3·93	301	4·00
1-Ac-2-OBz	—	—	238	4·57	—	—	—	—	291	4·02	301	4·05

* See Table 3.

or medium absorption at 5·6—5·75 μ, which is characteristic [20] of a carbonyl group in the system CO·O·C:C, and this confirms the structures assigned to the compounds.

The main features of the ultraviolet absorption spectra are shown in Tables 3 and 4. The introduction of a 1-acetyl group has a pronounced effect on the spectra of both classes of compound, and in the oxindole series causes complete suppression of the peaks in all cases except that of 3-phenacyl-3-phenyloxindole, where the persistence of a maximum may be attributed to the phenacyl group. In the 220—300 mμ region the spectra of the 2-acyloxy-3-phenylindoles are very similar to those of similarly substituted 3-phenylindole reference compounds, whose preparations are described in the Experimental section. Tailing of the absorption into the visible region accounts for the yellowish colour of several of the benzoyl derivatives.

Experimental

Solutions in organic solvents were dried with sodium sulphate. Solvents, and reagents present in excess, were removed on the water-bath, where necessary under reduced pressure (water-pump). Solids were dried *in vacuo*. Sublimation temperatures are those of the heating-bath. Sodium carbonate refers to " AnalaR " anhydrous material. Reagents were purified by conventional procedures. M. p.s are corrected.

A. Derivatives of 3-*Phenyloxindole.*

3-*Phenyloxindole.*—(*a*) Powdered (±)-mandelanilide [21] (57 g.) was added during 5 min. to vigorously stirred concentrated sulphuric acid (300 c.c.) at 20—25°, stirring was continued for 10 min., and the solution was added to crushed ice (2 kg.). After 2 hr. the precipitate was collected, washed with water, and crystallised from ethanol to give a solid which, on being sublimed at 180°/0·01 mm., afforded the oxindole (37 g., 71%) as needles, m. p. 191° undepressed on admixture with material prepared by method (*b*) or (*c*) (lit.,[5, 10, 22] 183°, 185—187°) (Found: C, 80·4; H, 5·4; N, 6·7. Calc. for $C_{14}H_{11}ON$: C, 80·4; H, 5·3; N, 6·7%).

(*b*) A mixture of 3-phenyldioxindole [12] (10 g.), stannous chloride (20 g.; " AnalaR "), acetic acid (50 c.c.), and concentrated hydrochloric acid (50 c.c.) was refluxed for 1½ hr. (addition of porous plate to prevent bumping lowers the yield), diluted with water (100 c.c.), and cooled to room temperature. The resulting microcrystalline powder (9 g., 97%) had m. p. 188—189°, which was raised to 192° by sublimation at 180°/0·01 mm. and crystallisation from ethanol.

(*c*) *N*-Phenylacetyl-*N'*-phenylhydrazine (2·25 g.) was cyclised [10] with calcium oxide (10 g.) as described below for 3-methyl-3-phenyloxindole, giving 3-phenyloxindole (80 mg., 4%), m. p. 190—191°.

α-*Bromophenylacetic Acid.*—To a stirred mixture of 48% hydrobromic acid (85 c.c.) and concentrated sulphuric acid (21 c.c.) were added successively (±)-mandelic acid (59 g.) and sulphuric acid (21 c.c.), and the solution was stirred, under reflux, at 125—130° for 3 hr., cooled, and added to water (300 c.c.). The precipitate was isolated by extraction with ether, and distilled, giving an oil, b. p. 120—121°/0·02 mm., which largely solidified and, on being crystallised from light petroleum (b. p. 60—80°), afforded the acid (62 g., 74%) as prisms, m. p. 68—69° (lit.,[23] in the range 82—84°) (Found: Br, 37·9. Calc. for $C_8H_7O_2Br$: Br, 37·2%). The amide, needles (from xylene), had m. p. 147° (lit.,[24] 144°, 146°) (Found: N, 6·5; Br, 37·6. Calc. for C_8H_8ONBr: N, 6·5; Br, 37·4%).

1-*Methyl*-3-*phenyloxindole.*—α-Bromophenylacetic acid (54 g.) was refluxed (water-bath) with thionyl chloride (45 c.c.) for 5 hr., the excess of reagent was removed, and the residue, in benzene (50 c.c.), was added during 30 min. to a cooled (ice-bath) and vigorously stirred solution of *N*-methylaniline (54 g.) in benzene (75 c.c.). The mixture was stirred at room temperature for 30 min., heated to the b. p., and cooled to 5°. The solid was removed and rinsed with cold benzene, and the filtrate was washed with 5% hydrochloric acid containing 5% of sodium

[20] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 156, and references cited therein.
[21] Bischoff and Walden, *Annalen*, 1894, **279**, 123.
[22] Marschalk, *Bull. Soc. chim. France*, 1952, 949.
[23] Alexander, *Annalen*, 1890, **258**, 70; Tillmanns, *ibid.*, p. 88; Hell and Weinzweig, *Ber.*, 1895, **28**, 2447; Darapsky, *J. prakt. Chem.*, 1917, **96**, 285.
[24] Opolski and Weinbaum, *Ber.*, 1914, **47**, 1561; Fourneau and Nicolitch, *Bull. Soc. chim. France*, 1928, **43**, 1251.

chloride, then with aqueous 5% sodium chloride, and dried. Removal of the solvent and distillation of the residue gave crude *α-bromo-N-methyl-α-phenylacetanilide* (45 g.), b. p. 171—172°/0·03 mm. with slight decomposition. A mixture of this anilide (40·5 g.) and powdered anhydrous aluminium chloride (36 g.) was stirred and cautiously warmed (water-bath) until evolution of hydrogen bromide commenced. The vigorous reaction was moderated by water-cooling, and, when it had subsided, the mixture was stirred for 30 min. in a metal-bath at 175—180°. The melt was cooled, powdered, and slowly added to crushed ice (500 g.) and water (100 c.c.), and the suspension was stirred for 30 min. Concentrated hydrochloric acid (100 c.c.) was added, stirring was continued for 30 min., and the temperature raised to 60° to coagulate the precipitate which, after being cooled to 15°, was collected, washed with water, and crystallised (charcoal) from ethanol. Sublimation of the product at 115°/0·01 mm., and crystallisation of the sublimate from light petroleum (b. p. 100—120°), afforded the *oxindole* (23·5 g.) as needles, m. p. 119·5° (Found: C, 80·5; H, 5·9; N, 6·3. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8; N, 6·3%). The oxindole was recovered [25] after being refluxed for 24 hr. with an excess of anhydrous pyridine hydrochloride.

Alkylation Experiments.—The alkyl halide (0·011 mole) in acetone (15 c.c.) was added to a mixture of the powdered oxindole (0·01 mole), sodium carbonate (0·53 g.), acetone (10 c.c.), and water (10 c.c.), and the solution was stirred and refluxed for the period indicated below, cooled, and added to water (200 c.c.). The precipitate was collected, washed with water, dried, and triturated with a little cold light petroleum (b. p. 60—80°). It was then sublimed at 0·01 mm., and the sublimate was crystallised. The following *3-phenyloxindoles* were prepared by alkylation with methyl or benzyl iodide, or phenacyl bromide, of the corresponding oxindole; the reflux period, yield, and solvent used for crystallisation are indicated, in that order, in parentheses: 3-Methyl- * (6 hr., 63%, aq. MeOH), blades, m. p. 155—155·5° (Found: C, 80·6; H, 5·7; N, 6·5. Calc. for $C_{15}H_{13}ON$: C, 80·7; H, 5·8; N, 6·3%). *3-Benzyl-* (6 hr., 83%, MeOH), tablets, m. p. 158° (Found: C, 84·0; H, 5·6; N, 5·0. $C_{21}H_{17}ON$ requires C, 84·3; H, 5·7; N, 4·7%). *3-Phenacyl-* (4 hr., 62%, Bu^nOH), prisms, m. p. 203·5—204° (Found: C, 80·5; H, 5·1; N, 4·3. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2; N, 4·3%). *1-Acetyl-3-methyl-* (3 hr., 67%, EtOH), prisms, m. p. 113° (Found: C, 76·7; H, 5·6; N, 5·0. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7; N, 5·3%). *1-Acetyl-3-benzyl-* (1 hr., 93%, aq. EtOH), blades, m. p. 139° (Found: C, 81·0; H, 5·3; N, 4·4. $C_{23}H_{19}O_2N$ requires C, 80·9; H, 5·6; N, 4·1%). *1-Acetyl-3-phenacyl-* (4 hr., 62%, EtOH), needles, m. p. 163·5—164° (Found: C, 78·3; H, 5·3; N, 4·1. $C_{24}H_{19}O_3N$ requires C, 78·0; H, 5·2; N, 3·8%). *1-Benzoyl-3-benzyl-* (15 min., 89%, EtOH), tablets, m. p. 154° (Found: C, 83·5; H, 5·1; N, 3·7. $C_{28}H_{21}O_2N$ requires C, 83·4; H, 5·2; N, 3·5%). *3-Benzyl-1-methyl-* (5 hr., 96%, MeOH), prisms, m. p. 127—127·5° (Found: C, 84·3; H, 6·0; N, 4·5. $C_{22}H_{19}ON$ requires C, 84·4; H, 6·1; N, 4·5%).

N-Phenyl-N'-α-phenylpropionylhydrazine.—A mixture of α-phenylpropionic acid [26] (7·5 g.), phenylhydrazine (5·5 g.), and benzene (60 c.c.) was refluxed under an azeotropic water-separator for 18 hr., the solvent was removed, and the residue was distilled. Crystallisation of the fraction with b. p. 170—175°/0·02 mm. from light petroleum (b. p. 80—100°) gave the *hydrazine* (6 g., 50%) as stout needles, m. p. 85·5—86° (Found: C, 75·3; H, 6·5; N, 12·0. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%). The compound separated from aqueous methanol as needles, m. p. 99—100°, and a mixture of the two forms partially melted at 86°, solidified at 90°, and then had m. p. 99—100°. The latter species was converted into the form of low m. p. by crystallisation from light petroleum.

3-Methyl-3-phenyloxindole.—An intimate mixture of the foregoing hydrazine (1·2 g.) and freshly ignited calcium oxide (6 g.) was heated at 210—215° (metal-bath) in a slow stream of oxygen-free nitrogen for 4 hr., cooled, powdered, and added, below 20°, to 10% hydrochloric acid (75 c.c.). The resulting gum was isolated by extraction with ether and sublimed at 155°/0·01 mm., and the sublimate was crystallised from aqueous methanol to give a solid which, after being dried, was triturated with a little cold light petroleum (b. p. 60—80°) and sublimed, in a vertical tube, at 145°/0·01 mm. until the molten residue was no longer turbid; two bands were formed. The lower was crystallised first from benzene–light petroleum (b. p. 40—60°),

* A specimen of 3-methyl-3-phenyloxindole prepared from (±)atrolactanilide, and kindly supplied by Dr. E. F. M. Stephenson (*J.*, 1957, 1928) was identical in crystalline form, mixed m. p., and infrared spectrum with this compound. The solubility in aqueous 10% sodium hydroxide at 60° is *ca.* 0·3%.

[25] Cf. Klamann and Schaffer, *Chem. Ber.*, 1954, **87**, 1294.

[26] Hauser and Brasen, *J. Amer. Chem. Soc.*, 1956, **78**, 494.

and then from aqueous methanol, to give the oxindole (75 mg., 7%) as slender blades, m. p. 156° undepressed on admixture with material prepared by methylation of 3-phenyloxindole (Found: C, 81·0; H, 5·9; N, 6·6%).

N-αβ-*Diphenylpropionyl*-N'-*phenylhydrazine*.—αβ-Diphenylpropionyl chloride [27] (7·4 g.), in ether (50 c.c.), was added at 0—5° during 30 min. to a vigorously stirred solution of phenylhydrazine (6·5 g.) in ether (75 c.c.), and the suspension was stirred at room temperature for 1½ hr. Benzene (200 c.c.) and water (150 c.c.) were added, stirring was continued until the solid had dissolved, and the organic phase was removed, washed with water, and dried. Removal of the solvent left a residue which, on being triturated with a little cold ether and crystallised from aqueous methanol, gave the *hydrazine* (7·8 g., 82%) as needles, m. p. 139·5—140·5° (Found: C, 79·8; H, 6·4; N, 9·2. $C_{21}H_{20}ON_2$ requires C, 79·8; H, 6·3; N, 8·9%).

3-*Phenacyl*-3-*phenyloxindole Hydrazone*.—3-Phenacyl-3-phenyloxindole (3·3 g.), 99—100% hydrazine hydrate (6 c.c.), and ethanol (30 c.c.) were stirred and refluxed for 10 hr., the solvent and excess hydrazine were removed, and the residue was washed with water and boiled for 5 min. with methanol (100 c.c.). The hot suspension was filtered; the solid was rinsed with hot methanol and crystallised from butan-1-ol, to give the *hydrazone* (0·8 g., 23%) as needles, m. p. 208—209° (Found: C, 77·6; H, 5·6; N, 12·5. $C_{22}H_{19}ON_3$ requires C, 77·4; H, 5·6; N, 12·3%). The compound was readily hydrolysed to the parent ketone by dilute hydrochloric acid. An attempted preparation of 3-phenethyl-3-phenyloxindole by the Wolff–Kishner method was unsuccessful.

1-*Acetyl*-3-*phenyloxindoles*.—The oxindole was refluxed for 3 hr. with an excess of acetic anhydride, the reagent was removed, and the residue was crystallised from ethanol. The yield of 1-acetyl-3-phenyloxindole was markedly reduced by traces of impurities in the reagents, and the derivative was conveniently purified by short-path distillation at 140°/0·02 mm. before crystallisation. The following 1-*acetyl*-3-*phenyloxindoles* were prepared, the yield being indicated in parentheses: Unsubstituted (36—61%), needles, m. p. 106° (lit.,[10] 103°) (Found: C, 76·5; H, 5·3; N, 5·6; Ac, 18·0. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; N, 5·6; Ac, 17·1%). 3-Acetoxy- (76%), needles, m. p. 142° (lit.,[28] 140—141°) (Found: C, 69·9; H, 4·8; N, 4·5. Calc. for $C_{18}H_{15}O_4N$: C, 69·9; H, 4·9; N, 4·5%). For 3-methyl- (75%), 3-benzyl- (98%), and 3-phenacyl- (84%), see "Alkylation Experiments."

1-*Benzoyl*-3-*phenyloxindoles*.—(*a*) 3-Methyl-3-phenyloxindole (0·45 g.) and benzoic anhydride (0·6 g.) were heated in a metal-bath at 190—200° for 4 hr., the sublimate of benzoic acid was removed, and the residue was crystallised from ethanol, to give 1-*benzoyl*-3-*methyl*-3-*phenyloxindole* (0·46 g., 71%) as prisms, m. p. 136—136·5° (Found: C, 80·7; H, 5·1; N, 4·4. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2; N, 4·3%). The derivative is dimorphic, with a metastable form of m. p. 122·5°. The corresponding 3-benzyl compound (yield 74%) was identical with that prepared by benzylation of 1-benzoyl-3-phenyloxindole, but a metastable form, m. p. 120°, was also obtained.

(*b*) 3-Phenyloxindole (0·21 g.), benzoic anhydride (1 g.), and (+)-camphor-10-sulphonic acid (5 mg.) were heated together for 2 hr. in a metal-bath at 180—185°, the sublimate was removed, and the residue was twice crystallised from ethanol. Sublimation of the product at 170°/0·01 mm. and crystallisation of the sublimate from ethanol afforded 1-*benzoyl*-3-*phenyloxindole* (37 mg., 9%) as felted needles, m. p. 175·5° (Found: C, 80·7; H, 4·8; N, 4·8; Bz, 35·1. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8; N, 4·5; Bz, 33·6%).

(*c*) A mixture of 3-phenyloxindole (4·2 g.), sodium carbonate (5·3 g.), water (40 c.c.), and acetone (40 c.c.) was refluxed until the solids had dissolved, and to the boiling solution, vigorously stirred, was added during 1 min. benzoyl chloride (14 g.) in acetone (20 c.c.). Refluxing was continued for 15 min., the mixture was cooled and added to water (400 c.c.), and, after several hours at room temperature, the semisolid precipitate was isolated by decantation, washed with water, and extracted with cold benzene. The extract, after being dried and concentrated to 50 c.c., was stirred and diluted by the dropwise addition of light petroleum (200 c.c.; b. p. 60—80°), and the precipitate was collected, washed with light petroleum, and sublimed at 180°/0·01 mm. Crystallisation of the sublimate from ethanol gave needles (1·75 g., 28%), m. p. 175·5° undepressed on admixture with 1-benzoyl-3-phenyloxindole prepared by method (*b*).

(*d*) 1-*Benzoyl*-3-*ethoxy*-3-*phenyloxindole*, prepared in 63% yield by the Schotten–Baumann

[27] Rupe and Kerkovins, *Ber.*, 1912, **45**, 1401.
[28] Inagaki, *J. Pharm. Soc. Japan*, 1939, **59**, 5.

method, formed prisms (from ethanol), m. p. 130—130·5° (Found: C, 77·4; H, 5·3; N, 4·0. $C_{23}H_{19}O_3N$ requires C, 77·3; H, 5·3; N, 3·9%).

3-*Phenyl*-1-*toluene*-p-*sulphonyloxindole*.—(*a*) A mixture of 3-phenyloxindole (10·4 g.), toluene-*p*-sulphonyl chloride (9·6 g.), sodium carbonate (3·75 g.), water (50 c.c.), and acetone (100 c.c.) was stirred and refluxed for 40 min., and the hot suspension was filtered. The solid was washed with 50% aqueous acetone, then with methanol, and crystallised from butan-1-ol, to give the *acyloxindole* (7·5 g., 41%) as felted needles, m. p. 244·5° (decomp.) (Found: C, 69·2; H, 4·5; N, 4·0; S, 8·8. $C_{21}H_{17}O_3NS$ requires C, 69·4; H, 4·7; N, 3·9; S, 8·8%).

(*b*) 3-Chloro-3-phenyloxindole (0·59 g.) was added to a solution of sodium toluene-*p*-sulphinate (2·14 g.) in ethanol–water (15 + 5 c.c.), and the mixture was refluxed for 1 hr., and cooled. The precipitate was collected, washed with 50% aqueous ethanol, dried, and crystallised from butan-1-ol, giving needles (0·35 g., 48%), m. p. 242—243° (decomp.) undepressed on admixture with material prepared by method (*a*).

Cleavage of 3-*Phenyl*-1-*toluene*-p-*sulphonyloxindole*.—A mixture of the oxindole (0·365 g.), Raney nickel [29] (2 g.), and ethanol (20 c.c.) was stirred and refluxed for 6 hr., and filtered. The nickel residues were washed with boiling ethanol, and the combined filtrate and washings were evaporated, leaving a powder (0·209 g., 100%), m. p. 192° undepressed on admixture with 3-phenyloxindole.

3-*Chloro*-3-*phenyloxindole*.—3-Phenyldioxindole [12] (4·5 g.) was refluxed with thionyl chloride (30 c.c.) for 1½ hr., the excess of reagent was removed, and the residue was dissolved in hot benzene (10 c.c.). The solution was slowly diluted with light petroleum (100 c.c.; b. p. 40—60°) and, after several hours at room temperature, the precipitate (3·25 g., 67%) was collected, washed with light petroleum, and dried. It had m. p. 137—139° (decomp.), and was used for preparative purposes without purification. For analysis and spectra, a portion (1·5 g.) was extracted for 15 min. with boiling light petroleum (50 c.c.; b. p. 100—120°), the extract was stirred at room temperature for several hours, and the solid was collected and sublimed at 135°/0·01 mm. until the residue became light brown and began to sinter. The sublimate was washed with cold light petroleum (b. p. 60—80°) and dried, giving the *oxindole* (0·36 g.) as irregular prisms, m. p. 146·5—147·5° (decomp.) (Found: C, 69·3; H, 4·3; N, 5·6; Cl, 14·9. $C_{14}H_{10}ONCl$ requires C, 69·0; H, 4·1; N, 5·8; Cl, 14·6%).

Reactions of 3-*Chloro*-3-*phenyloxindole*.—(*a*) Water (10 c.c.) at 80° was added to a solution of the oxindole (0·1 g.) in dioxan (2 c.c.), the suspension was heated on the water-bath for 15 min., and most of the solvent was removed. Sublimation of the residual solid at 190°/0·01 mm. and crystallisation of the sublimate from aqueous ethanol afforded 3-phenyldioxindole (54 mg., 50%) as needles, m. p. 213—213·5° undepressed by authentic [12] material.

(*b*) A solution of the oxindole (0·73 g.) in methanol (10 c.c.) was boiled for 2 min., diluted with water (25 c.c.) at 50°, and left overnight at room temperature. The precipitate was collected, washed with water, and sublimed at 160°/0·01 mm., and the sublimate was crystallised from aqueous methanol to give 3-*methoxy*-3-*phenyloxindole* (0·67 g., 93%), blades, m. p. 173·5° (Found: C, 75·5; H, 5·4; N, 5·9. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%).

(*c*) Experiment (*b*) was repeated, ethanol being used. 3-*Ethoxy*-3-*phenyloxindole* (88%) formed blades (from aqueous ethanol), m. p. 169—169·5° (Found: C, 75·6; H, 5·9; N, 5·5. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%).

B. Derivatives of 2-*Hydroxy*-3-*phenylindole*.

1-*Benzoyl*-2-*benzoyloxy*-3-*phenylindole*.—To a mixture of 3-phenyloxindole (8·4 g.) in acetone (100 c.c.), and sodium hydroxide (45 g.) in water (500 c.c.) at 20° was added, all at once, benzoyl chloride (20 c.c.), and the suspension was vigorously stirred for 15 min. The precipitate was collected, washed with water, and crystallised from glacial acetic acid. Sublimation of the product at 185°/0·01 mm. and crystallisation of the sublimate from ethanol–butan-1-ol (3 : 1) gave the *acyloxy-indole* (7·2 g., 43%) as very pale green hexagonal plates, m. p. 189°, which were markedly thermochromic (Found: C, 80·3; H, 4·5; N, 3·6; Bz, 48·6. $C_{28}H_{19}O_3N$ requires C, 80·6; H, 4·6; N, 3·4; Bz, 50·4%). This indole was also formed, in 4% yield, when 1-benzoyl-3-phenyloxindole (0·31 g.) was heated at 180—185° for 2 hr. with benzoic anhydride (1 g.) and (+)-camphor-10-sulphonic acid (5 mg.), and in 2% yield when it was treated with benzoyl chloride in the presence of one equivalent of sodium carbonate in aqueous acetone.

Cleavage of 1-*Benzoyl*-2-*benzoyloxy*-3-*phenylindole*.—The indole (0·83 g.) was stirred and

[29] Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013.

refluxed for 8 hr. with a mixture of 99—100% hydrazine hydrate (1·2 c.c.) and ethanol (10 c.c.), then the solvent and excess of reagent were removed, and the residue was dissolved in methanol (10 c.c.). Water (20 c.c.) was added and, after 5 hr. at room temperature, the precipitate was collected (filtrate " A "), washed with water, dried, and triturated with cold ether (2 c.c.). Sublimation of the ether-insoluble material at 180°/0·02 mm. gave 3-phenyloxindole (0·21 g., 50%), m. p. and mixed m. p. 190·5—191°. Removal of the solvent from " A " and crystallisation of the residue from benzene afforded benzoylhydrazine (0·4 g., 74%) as blades, m. p. 112·5—113° (lit.,[30] 112·5°) (Found: N, 20·5. Calc. for $C_7H_8ON_2$: N, 20·6%).

2-*Benzoyloxy*-1-*methyl*-3-*phenylindole*.—To aqueous 10% sodium hydroxide (50 c.c.) were added successively 1-methyl-3-phenyloxindole (1·1 g.) in acetone (10 c.c.), and benzoyl chloride (2 c.c.), and the suspension was vigorously stirred for 30 min. The precipitate was collected, washed with water, and crystallised from ethanol, and the product was sublimed at 160°/0·01 mm. Crystallisation of the sublimate from ethanol gave the *acyloxy-indole* (0·52 g., 32%) as very pale yellowish-green blades, m. p. 161·5° (Found: C, 80·4; H, 5·4; N, 4·5; Bz, 30·6. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2; N, 4·3; Bz, 32·1%).

1-*Acetyl*-2-*benzoyloxy*-3-*phenylindole*.—A mixture of 1-acetyl-3-phenyloxindole (2·5 g.), sodium carbonate (0·53 g.), acetone (20 c.c.), and water (10 c.c.) was rapidly heated to the b. p., and to it, with vigorous stirring, was added during 15 sec. benzoyl chloride (1·4 g.) in acetone (10 c.c.). The suspension was stirred and refluxed for 15 min., cooled, and added to water (200 c.c.). After 2 hr. the precipitate was collected, washed with water, dried, and triturated with a little light petroleum (b. p. 60—80°). Crystallisation from ethanol, sublimation at 180°/0·01 mm., and recrystallisation of the sublimate from ethanol gave the *indole* (1·98 g., 56%) as irregular rhombic plates, m. p. 184·5° (Found: C, 78·1; H, 5·0; N, 4·1; Ac + Bz, 42·4. $C_{23}H_{17}O_3N$ requires C, 77·8; H, 4·8; N, 3·9; Ac + Bz, 41·7%).

2-*Acetoxy*-1-*acetyl*-3-*phenylindole*.—1-Acetyl-3-phenyloxindole (1·26 g.), (+)-camphor-10-sulphonic acid (25 mg.), and acetic anhydride (25 c.c.) were stirred and refluxed for 6 hr., then the solvent was removed; the residue crystallised from methanol (8 c.c.) as prisms (0·43 g.), m. p. 103·5—104° undepressed by starting material. The mother-liquors were evaporated, and the residue was powdered and extracted with boiling light petroleum (2 × 8 c.c.; b. p. 60—80°). Sublimation of the insoluble material at 170°/0·01 mm. and crystallisation of the sublimate from ethanol gave 3-phenyloxindole (0·43 g.) as prisms, m. p. and mixed m. p. 190·5—191°. The light petroleum extracts were combined, concentrated to 8 c.c., and cooled; the solid which separated was distilled at 0·01 mm. (heating-bath at 120°). Crystallisation of the distillate, which solidified, from light petroleum (b. p. 60—80°) afforded the *indole* (56 mg., 4%) as needles, m. p. 111·5—112° (Found: C, 73·5; H, 5·0; N, 4·8; Ac, 29·2. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·1; N, 4·8; Ac, 29·4%).

2-*Acetoxy*-1-*benzoyl*-3-*phenylindole*.—A mixture of 1-benzoyl-3-phenyloxindole (0·63 g.), (+)-camphor-10-sulphonic acid (10 mg.), and acetic anhydride (10 c.c.) was stirred and refluxed for 6 hr., the solvent was removed, and the residue was crystallised three times from ethanol (15, 10, 25 c.c.). Sublimation of the product at 145°/0·01 mm., and crystallisation of the sublimate from ethanol gave the *indole* (0·13 g., 18%) as very pale green needles, m. p. 153° (Found: C, 77·7; H, 4·7; N, 4·1; Ac + Bz, 43·0. $C_{23}H_{17}O_3N$ requires C, 77·8; H, 4·8; N, 3·9; Ac + Bz, 41·7%).

C. Substituted 3-*Phenylindoles.*

Derivatives of 3-*Phenylindole*.—(*a*) 3-Phenylindole[31] (0·58 g.), anhydrous sodium acetate (1·5 g.), and acetic anhydride (15 c.c.) were stirred and refluxed for 3 hr., the solvent was removed, and the residue was triturated with water (3 × 10 c.c.), and dried. Sublimation at 150°/0·02 mm. and crystallisation of the sublimate from ethanol gave 1-*acetyl*-3-*phenylindole* (0·58 g., 82%) as hexagonal plates, m. p. 138·5—139° (Found: C, 81·7; H, 5·6; N, 5·9. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0%).

(*b*) Benzoyl chloride (5 c.c.) was added all at once to a vigorously stirred mixture of 3-phenylindole (0·97 g.), acetone (15 c.c.), and aqueous 20% potassium hydroxide (50 c.c.), stirring was continued for 15 min., and the suspension was diluted with water (100 c.c.) and stirred for 15 min. more. The precipitate, washed with water and dried, was crystallised from butan-1-ol, and the product was sublimed at 160°/0·01 mm. Crystallisation of the sublimate from

[30] Curtius and Struve, *J. prakt. Chem.*, 1894, **50**, 295.
[31] Fischer and Schmidt, *Ber.*, 1888, **21**, 1811.

butan-1-ol afforded 1-*benzoyl*-3-*phenylindole* (1·2 g., 81%) as blades, m. p. 156·5° (Found: C, 85·0; H, 4·8; N, 4·7. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·1; N, 4·7%).

Derivatives of 2-*Methyl*-3-*phenylindole*.—(*a*) 2-Methyl-3-phenylindole (0·62 g.) [m. p. 61—61·5° (lit.,[32] 59—60°)] in ether (10 c.c.) was added during 5 min. to a stirred solution of methylmagnesium iodide (0·55 g.) in ether (5 c.c.), the mixture was refluxed for 1 hr., then cooled to 15°, and to it was added, dropwise with vigorous stirring, acetyl chloride (0·25 g.) in ether (5 c.c.). After being refluxed for 1 hr. the suspension was cooled, ammonium chloride (1 g.) in water (10 c.c.) was added, and the ethereal phase was separated, washed with water, and dried. The solvent was removed, the residue was crystallised from ethanol, and the product was sublimed at 125°/0·01 mm. Crystallisation of the sublimate from ethanol gave 1-*acetyl*-2-*methyl*-3-*phenylindole* (0·3 g., 40%) as rhombic tablets, m. p. 119° (Found: C, 81·7; H, 5·9; N, 5·4. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·0; N, 5·6%). The derivative also separated from ethanol as rods, m. p. 119° undepressed on admixture with the rhombic form. The species were spectroscopically identical.

(*b*) Experiment (*a*) was repeated, but with benzoyl chloride (0·42 g.). The crude product was crystallised from butan-1-ol and sublimed at 160°/0·02 mm. 1-*Benzoyl*-2-*methyl*-3-*phenylindole* (0·6 g., 64%) formed pale yellowish-green prisms (from butan-1-ol), m. p. 152° (Found: C, 85·2; H, 5·5; N, 4·3. $C_{22}H_{17}ON$ requires C, 84·9; H, 5·5; N, 4·5%).

1-*Benzoyl*-2-*benzyl*-3-*phenylindole*.—Ethereal 2-benzyl-3-phenylindolylmagnesium iodide, from the indole (0·85 g.) [m. p. 101·5—102° (lit.,[32] 100—101°)], was reacted with benzoyl chloride (0·42 g.) as described for the 2-methyl-compound, but the reflux period was 2 hr. The crude product was crystallised successively from ethanol and butan-1-ol, and then sublimed at 170°/0·01 mm. until the residue solidified. Crystallisation of the sublimate from butan-1-ol, resublimation at 160°/0·01 mm., and recrystallisation from butan-1-ol gave the *indole* (0·23 g., 20%) as pale greenish-yellow blades, m. p. 164·5° (Found: C, 86·7; H, 5·2; N, 3·5. $C_{28}H_{21}ON$ requires C, 86·8; H, 5·4; N, 3·6%). Attempts to prepare 1-acetyl-2-benzyl-3-phenylindole were unsuccessful.

2-*Benzyl*-1-*methyl*-3-*phenylindole*.—This was purified by sublimation at 120°/0·01 mm. Crystallisation of the sublimate from glacial acetic acid gave colourless rhombic plates, m. p. 122° (lit.,[33] straw-yellow, m. p. 129—130°) (Found: N, 4·5. Calc. for $C_{22}H_{19}N$: N, 4·7%).

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[32] Trenkler, *Annalen*, 1888, **248**, 106.
[33] Neber, Knöller, Herbst, and Trissler, *ibid.*, 1929, **471**, 113.