

**1094.** *The Synthesis and Properties of 2-p-Dimethylaminophenyl-1,3,3-trimethyl-3H-indolium Salts*

By DOUGLAS F. CARSON and FREDERICK G. MANN

Two syntheses of 2-*p*-dimethylaminophenyl-2-hydroxy-1,3,3-trimethylindoline have been developed. This colourless indoline gives colourless solutions in non-polar solvents, but yellow solutions in polar solvents owing to the formation of the isomeric 2-*p*-dimethylaminophenyl-1,3,3-trimethyl-3*H*-indolium hydroxide. The indoline with one equivalent of hydrochloric acid gives the bright yellow indolium chloride, which furnishes the similar thiocyanate and perchlorate: with two equivalents of hydrochloric acid, the indoline gives the yellow hydrogen dichloride, but concentrated perchloric acid gives the colourless diperchlorate, in which both nitrogen atoms carry a positive charge and the cyanine character of the monovalent cation has been suppressed.

THE synthesis of 2-*p*-dimethylaminophenyl-1,3,3-trimethyl-3*H*-indolium salts has been investigated for two purposes:

(*a*) To study the conditions under which the salts, and particularly the hydroxide, may exist as ionic or covalent compounds, (*b*) to assess the value of the salts as dyestuffs, more particularly for synthetic fibres. The salts (I), having a cyanine structure, would undoubtedly be coloured.

The analogous pale yellow 2-*p*-dimethylaminophenyl-1-methylbenzothiazolium iodide (II) was prepared by Bogert and Taylor<sup>1</sup> by the interaction of *o*-aminophenyl disulphide and *p*-dimethylaminobenzaldehyde: to confirm its structure they also synthesised by an unambiguous route the isomeric colourless methiodide (III).

Various apparently promising syntheses of the salts (I) failed. Our most successful method utilised Brunner's oxindole synthesis,<sup>2</sup> in which *N'*-methyl-*N'*-phenylisobutyrohydrazide (IV) was heated under nitrogen with calcium oxide, giving ammonia and 1,3,3-trimethyloxindole (V) in 36% yield. This yield was increased to 44% by the use of calcium

<sup>1</sup> M. T. Bogert and W. S. Taylor, *Coll. Czech. Chem. Comm.*, 1931, **3**, 480.

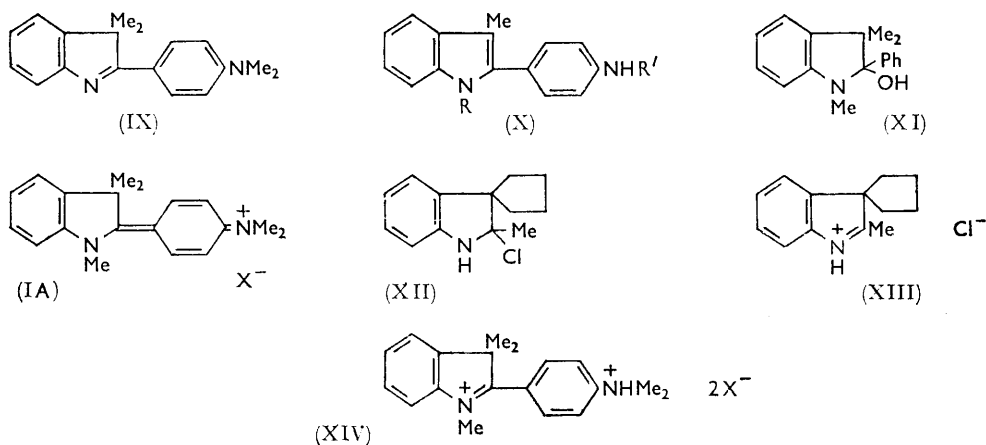
<sup>2</sup> K. Brunner, *Monatsh.*, 1896, **17**, 479.



n-propyl ketones, respectively. We have failed to carry out this reaction with isobutyryl chloride or bromide under various conditions.

A mixture of benzoylaniline and dimethylaniline when heated with phosphorus oxychloride reacts vigorously to give the readily hydrolysed anil of *p*-dimethylaminophenyl phenyl ketone,<sup>11</sup> but isobutyrylaniline when used under these conditions was unaffected.

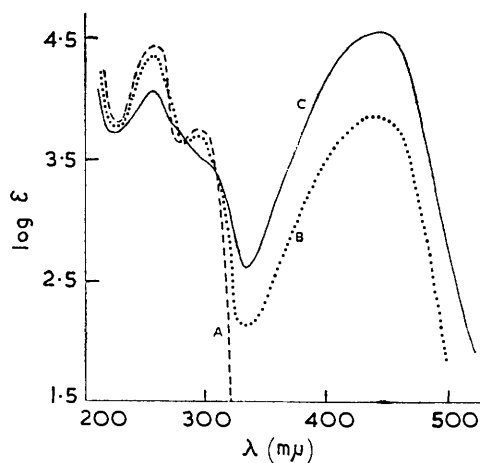
*p*-Acetamidophenyl ethyl ketone gave a phenylhydrazone which by the Fischer reaction gave 2-*p*-aminophenyl-3-methylindole (X; R = R' = H): the methylphenylhydra-



zone with ethanolic hydrogen chloride gave 2-*p*-aminophenyl-1,3-dimethylindole (X; R = Me, R' = H). These indoles and their acetyl derivatives (X; R = H or Me, R' = Ac) gave unsatisfactory products on attempted methylation or quaternisation.

2-*p*-Dimethylaminophenyl-2-hydroxy-1,3,3-trimethylindoline (VI) separates from ethanol as a colourless crystalline monohydrate, which when exposed to the air becomes

Ultraviolet absorption spectra of 2-*p*-dimethylaminophenyl-2-hydroxy-1,3,3-trimethylindoline (VI) in cyclohexane (A) and ethanol (B), and of 2-*p*-dimethylaminophenyl-1,3,3-trimethylindolenium chloride (I; X = Cl) in ethanol (C)



sticky and then forms a glass, regenerating the indoline on recrystallisation from ethanol. The indoline gives colourless solutions in non-polar solvents (cyclohexane, light petroleum, benzene, ether) and deep yellow solutions in polar solvents (methanol, ethanol). The essential difference in structure of the solute in these solvents is shown by the striking difference in their ultraviolet spectra (see Figure), the ethanolic solution having a strong band at 445 mμ, a region in which the cyclohexane solution shows no absorption. There

<sup>11</sup> *Org. Synth.*, Coll. Vol. I, 1932, p. 211.

is no doubt that the colourless compound, in the solid state and in non-polar solvents, is the true covalent indoline (VI), but that in polar solvents it exists almost wholly as the ionic indoleninium hydroxide (I; X = OH). The interconversion of the two forms must occur very readily, and both are probably present in equilibrium in solvents of intermediate polarity.

Three points can be cited in support of these structures. (a) The deep yellow ethanolic solution of the hydroxide (I; X = OH) becomes colourless when concentrated ethanolic sodium hydroxide is added and the equilibrium thus thrust back to the indoline (VI): dilution with ethanol then restores the yellow colour as ionisation to the hydroxide (I; X = OH) is re-established. (b) The hydroxide in ethanol, when treated with hydrochloric acid (1 equiv.) and taken to dryness, gives the orange-yellow crystalline chloride dihydrate (I; X = Cl), which is insoluble in cyclohexane and in light petroleum (b. p. 60–80°) but gives intensely yellow solutions in water and in ethanol. The ultraviolet absorption spectrum of this salt in ethanol (see Figure) is remarkably similar to that of the hydroxy-compound in ethanol. (c) Jenisch,<sup>9</sup> and also Leuchs *et al.*,<sup>12</sup> have prepared 2-hydroxy-1,3,3-trimethyl-2-phenylindoline (XI), a colourless compound which apparently gives only colourless solutions, and affords no evidence of ionisation. This indicates strongly that our colourless compound is the indoline (VI). The ionisation of the latter in polar solvents is promoted by resonance of the canonical ionic forms (I; X = OH) and (IA; X = OH), which cannot occur in the indoline (XI).

It is noteworthy that Witkop and Patrick<sup>13</sup> have isolated the colourless 2-chloro-3-spirocyclopentyl-2-methylindoline (XII) and the isomeric yellow 3-spirocyclopentyl-2-methyl-3*H*-indolium chloride (XIII): these are analogous in type to the hydroxyindoline (VI) and the hydroxide (I; X = OH); they have different absorption spectra (in an unspecified solvent) but this difference is far less than that between the spectra of the indoline (VI) in cyclohexane and in ethanol.

The dihydrated chloride (I; X = Cl), when carefully heated under reduced pressure gives the orange-red anhydrous chloride, which on exposure to air very rapidly and quantitatively reverts to dihydrate.

Aqueous solutions of the chloride, treated with aqueous perchloric acid or potassium thiocyanate, deposit the yellow crystalline perchlorate (I; X = ClO<sub>4</sub>) and thiocyanate (I; X = SCN), respectively. These three salts give a characteristic picrate (I; X = C<sub>6</sub>H<sub>2</sub>N<sub>3</sub>O<sub>7</sub>): the same picrate was obtained when the indoline (VI) was treated with picric acid, both compounds in methanolic or in dry ethereal solution. This indoline, in forming a picrate with loss of water, differs from the indoline (XI), which forms a picrate by simple union.<sup>9</sup>

The chloride, when treated with perchloric acid, both in highly concentrated aqueous or ethanolic solution, deposited the colourless perchlorate hydrogen perchlorate (XIV; X = ClO<sub>4</sub>): the loss of colour is clearly caused by the protonation of the NMe<sub>2</sub> group and the consequent suppression of the cyanine structure. When, however, ethanolic solutions of the indoline (VI) and the chloride (I; X = Cl) were respectively diluted with two and one equivalents of hydrochloric acid and evaporated under reduced pressure at room temperature, the same yellow crystalline residue, of composition C<sub>19</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>2</sub>·½H<sub>2</sub>O, was obtained. The colour of this compound shows that it cannot be the dichloride (XIV; X = Cl): in aqueous and ethanolic solution it dissociates readily to the chloride (I; X = Cl), for it has an ultraviolet absorption almost identical with that of the chloride, and gives the same picrate (I; X = C<sub>6</sub>H<sub>2</sub>N<sub>3</sub>O<sub>7</sub>). There is little doubt that this product is the hydrogen dichloride (I; X = HCl<sub>2</sub>), a salt analogous in type to the stable crystalline [Me<sub>4</sub>N<sup>+</sup>]HCl<sub>2</sub><sup>-</sup> whose structure has been studied by Waddington and his co-workers.<sup>14</sup> It is significant that the yellow

<sup>12</sup> H. Leuchs, A. Heller, and A. Hoffmann, *Ber.*, 1929, **62**, 871.

<sup>13</sup> B. Witkop and J. B. Patrick, *J. Amer. Chem. Soc.*, 1951, **73**, 1558.

<sup>14</sup> T. C. Waddington, *J.*, 1958, 1708; T. C. Waddington and F. Klanberg, *J.*, 1960, 2332; M. E. Peach and T. C. Waddington, *J.*, 1961, 1238; 1962, 600; 1963, 69.

aqueous-ethanolic solutions of the indoline (VI), the chloride (I; X = Cl), and the hydrogen dichloride (I; X = HCl<sub>2</sub>), when diluted with increasing quantities of concentrated hydrochloric acid, became steadily paler and ultimately colourless, the process being reversed on dilution with water. A high concentration of acid was thus necessary to force a positive charge on to both nitrogen atoms and thus give the colourless cation (XIV); in the presence of a small excess of hydrochloric acid, the comparative ease of formation of the HCl<sub>2</sub><sup>-</sup> anion enables the cation (I) to resist this process.

#### EXPERIMENTAL

The m. p. of certain hygroscopic compounds was determined in a sealed tube, denoted as (S.T.).

*2-p-Dimethylaminophenyl-2-hydroxy-1,3,3-trimethylindoline* (VI).—*First synthesis*: from *N'-methyl-N'-phenylisobutyrohydrazide* (IV). A mixture of *N*-methylphenylhydrazine (25 g.) and isobutyric acid (88 g., 1.4 mol.) was boiled under reflux for 3 hr. and set aside overnight. A solution of the solid product in much cyclohexane, when dried (MgSO<sub>4</sub>), concentrated, and cooled, deposited the crystalline hydrazide (20 g.), m. p. 108—109° (lit.,<sup>2</sup> 105°).

*1,3,3-Trimethylloxindole* (V). An intimate mixture of the hydrazide (IV) (25 g.) and calcium hydride (13 g.), in a 750-ml. flask fitted with a long air condenser down which nitrogen was passed, was heated rapidly until the temperature of the oil-bath reached 170°, and then more slowly. At 210° a brief but vigorous reaction occurred, producing much froth and fumes. The temperature was then kept at 220° for 20 min. The cold solid product was treated cautiously with water and then concentrated hydrochloric acid to give a clear solution, which was boiled under reflux for 1 hr. and then distilled in steam. The distillate was basified with aqueous sodium carbonate and extracted with ether. Evaporation of the extract gave a pale green oil, which crystallised from light petroleum (b. p. 60—80°), giving the oxindole (V) (10.1 g., 44%), m. p. 46.5—47.0° (lit.,<sup>2</sup> two forms, m. p. 25° (labile) and 50°,<sup>15</sup> 55—56°) (Found: C, 75.4; H, 7.7; N, 7.7. Calc. for C<sub>11</sub>H<sub>13</sub>NO: C, 75.4; H, 7.4; N, 8.0%). When the hydrazide (15 g.) and freshly ignited calcium oxide (24 g.) were used, the flask was immersed in an oil-bath at 250°, increased to 260° for 30 min. after the rapid onset of the reaction, which was so vigorous that larger quantities could not easily be used.

*The indoline* (VI). A small portion of a solution of *p*-bromodimethylaniline (40 g., 2.25 mol.) in dry tetrahydrofuran (50 ml.) was added to magnesium (5.8 g., 2.7 equiv.) under tetrahydrofuran (50 ml.), which, after the addition of an iodine crystal, was gently warmed until the reaction started. The remainder of the solution was slowly added to maintain gentle boiling, and the mixture was then stirred for 30 min. at room temperature.

The oxindole (15.6 g., 1 mol.) in the furan (50 ml.) was added dropwise to the stirred reagent, and the complete mixture was boiled under reflux for 3 hr. The product was then kept cold whilst water was cautiously added until decomposition was complete. The upper layer was decanted from the thick aqueous slurry, which was twice extracted with ether. The combined decanted extracts and upper layer were evaporated and the residual oil was distilled in steam until a clear distillate was obtained. The residual mixture contained an oil, which, after decanting the hot aqueous layer, was dissolved in hot ethanol; cooling deposited the *indoline hydrate* (VI), (21.3 g., 76% on the oxindole). A portion, twice recrystallised from ethanol, and dried *in vacuo* at room temperature, softened at *ca.* 55° with complete fusion at 70° (Found: C, 73.05; H, 8.5; N, 8.4. C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O.H<sub>2</sub>O requires C, 72.6; H, 8.3; N, 8.9%).

The use of *p*-lithiodimethylaniline gave the same product.

The colourless indoline dissolved in all organic solvents investigated: examples of the non-polar and the polar solvents giving colourless and deep yellow solutions respectively have been given. Intermediate examples were dry acetone, which gave a very faint yellow colour, and "bench" acetone in which this faint colour became deep yellow within 5—10 min.; pure (ethanol-free) chloroform gave a pale yellow solution. The indoline is almost insoluble in cold water, but when shaken with warm water dissolves sufficiently to give a yellow colour.

*Second synthesis*: from *p*-dimethylaminophenylisopropylcarbinol (VII). Magnesium (24 g.) in the usual dry Grignard assembly was covered with ether (500 ml.), an iodine crystal added, followed by isopropyl bromide (136 g.) in ether (135 ml.) at such a rate that the ether gently

<sup>15</sup> G. Ciamician and A. Piccinini, *Ber.*, 1896, **29**, 2465; *Gazzetta*, 1897, **27**, 69.

boiled. The mixture was then boiled under reflux for 10 min., cooled in an ice-salt bath, and stirred whilst *p*-dimethylaminobenzaldehyde (69 g.) was added in 2—3-g. portions over 20 min. The final chilled mixture was stirred for 30 min., then boiled for 30 min., and cooled in ice-water whilst aqueous ammonium chloride was slowly added until hydrolysis was complete. The decanted ether layer was dried ( $\text{MgSO}_4$ ), the ether removed, and the residual oil distilled, giving the carbinol (VII) (69 g., 78%), b. p. 115—120°/0.4 mm. (Found: C, 74.4; H, 9.8; N, 7.5. Calc. for  $\text{C}_{12}\text{H}_{19}\text{NO}$ : C, 74.6; H, 9.95; N, 7.25%). There was no forerun, but an undistilled residue (ca. 15 g.) set to a glass. The infrared spectrum of the carbinol showed a sharp OH peak at 3450  $\text{cm}^{-1}$ .

In early experiments, when an ether-benzene mixture was used to increase the solubility of the aldehyde, or when the ammonium chloride was added too rapidly with insufficient cooling, distillation gave *NN*-dimethyl-*p*-2',2'-dimethylvinyl-aniline (42%), b. p. 95°/0.5 mm., a clear oil which solidified, m. p. 38—39° from methanol (Found: C, 82.3; H, 9.8; N, 8.1. Calc. for  $\text{C}_{12}\text{H}_{17}\text{N}$ : C, 82.3; H, 9.7; N, 8.0%). The infrared spectrum showed no absorption in the 3500—3200- $\text{cm}^{-1}$  region, but a sharp peak at 1620  $\text{cm}^{-1}$  indicating the C:C bond.

*p*-Dimethylaminophenyl isopropyl ketone (VIII). Freshly distilled aluminium isopropoxide (60 g.) was added to a solution of the carbinol (VII) (24 g.) in benzene (500 ml.) and pure acetone (500 ml.), which was boiled under reflux for 36 hr. Water was added to the cold product, and the organic layer decanted from the thick lower layer, which was then extracted with benzene. The combined dried extracts, on distillation, gave a forerun of unchanged carbinol, and the ketone (13 g., 55%), b. p. 135—145°/0.2 mm., which crystallised after several days, and had m. p. 47—48° from light petroleum (b. p. 60—80°) (Found: C, 75.6; H, 8.7; N, 7.4.  $\text{C}_{12}\text{H}_{17}\text{NO}$  requires C, 75.4; H, 8.95; N, 7.3%): its infrared spectrum showed sharp CO absorption at 1650  $\text{cm}^{-1}$  and none in the 3500—3200- $\text{cm}^{-1}$  region.

The indoline (VI). A solution of the ketone (VIII) (3 g.) and *N*-methylphenylhydrazine (2 g., 1.05 mol.) in ethanol (10 ml.) was rapidly added to a solution of freshly fused stannous chloride (10 g.) in ethanol (20 ml.) and concentrated hydrochloric acid (5 ml.), which was boiled under reflux for 3 hr. and the solvent removed under reduced pressure. The brown oily residue was shaken with concentrated aqueous sodium hydroxide, and twice extracted with ether. Evaporation of the ether left a yellow oil: its solution in ethanol (3—5 ml.) when scratched or seeded, deposited the indoline (VI) (0.7 g., 15%). The ethanolic mother-liquor gave the picrate (I; X =  $\text{C}_6\text{H}_2\text{N}_3\text{O}_7$ ) (1.8 g., giving total indoline yield, 38%), m. p. 145—146° from ethanol (Found: C, 59.5; H, 5.1; N, 13.9.  $\text{C}_{25}\text{H}_{25}\text{N}_5\text{O}_7$  requires C, 59.2; H, 5.0; N, 13.8%). The crystalline indoline gave the same picrate (Found: C, 59.6; H, 5.35; N, 14.05%).

This Fischer indolisation failed when zinc chloride, polyphosphoric acid, or dilute sulphuric acid were used as reagents.

2-*p*-Dimethylaminophenyl-1,3,3-trimethyl-3H-indolium Salts (I).—A solution of the indoline (VI) (3 g.) in ethanol (40 ml.) was treated with 0.20 *N*-hydrochloric acid (47.8 ml., 1 mol. of acid), and the clear yellow solution taken to dryness under reduced pressure. The orange crystalline residue was insoluble in boiling dry acetone, but dissolved readily on the addition of water (a few drops): the solution deposited the dihydrated chloride (I; X = Cl) (2.7 g.), m. p. 100—102° (Found: C, 65.8; H, 8.0; Cl, 10.4; N, 8.1.  $\text{C}_{19}\text{H}_{23}\text{ClN}_2 \cdot 2\text{H}_2\text{O}$  requires C, 65.0; H, 7.7; Cl, 10.1; N, 8.1%). The dihydrate, heated at 60°/0.1 mm., gave the very hygroscopic, orange-red anhydrous chloride, m. p. 175° (decomp.) (S.T.): on exposure to air it was converted quantitatively into the dihydrate.

The aqueous chloride, treated with aqueous potassium thiocyanate gave the yellow thiocyanate (I; X = SCN), m. p. 180—181°, from ethanol (Found: C, 71.2; H, 6.9; N, 12.7.  $\text{C}_{20}\text{H}_{23}\text{N}_3\text{S}$  requires C, 71.2; H, 6.9; N, 12.5%): aqueous sodium perchlorate similarly gave the yellow perchlorate, m. p. 149—150°, from ethanol (Found: C, 60.2; H, 5.8; N, 7.75.  $\text{C}_{19}\text{H}_{23}\text{ClN}_2\text{O}_4$  requires C, 60.2; H, 6.1; N, 7.4%). The use of more concentrated solutions of the chloride and the perchlorate gave a dark green solution which deposited the colourless crystalline perchlorate hydrogen perchlorate (XIV; X =  $\text{ClO}_4$ ), m. p. 200—210° (decomp.) (Found Cl, 14.55; N, 5.6.  $\text{C}_{19}\text{H}_{24}\text{Cl}_2\text{N}_2\text{O}_8$  requires Cl, 14.8; N, 5.85%). The compound exploded during attempted C and H analyses. The salt could not be recrystallised, for it was insoluble in non-polar solvents, and gave deep yellow solutions in polar solvents.

A solution of the indoline (VI) in hydrochloric acid (2 equivs.) was evaporated as before, and the yellow-orange crystalline residue, when dissolved in ethanol and precipitated by ether, gave the yellow hydrogen dichloride hemihydrate (I; X =  $\text{HCl}_2$ ), m. p. 180—200° (decomp.) (Found:

C, 63·6; H, 7·4; Cl, 20·3; N, 7·9.  $C_{19}H_{24}Cl_2N_2 \cdot \frac{1}{2}H_2O$  requires C, 63·4; H, 6·95; Cl, 19·7; N, 7·8%).

All the above salts gave the picrate, m. p. and mixed m. p., 145—146°.

An aqueous solution of the chloride (I; X = Cl), treated with concentrated hydrochloric acid until colourless, was evaporated at room temperature as before. The sticky residue was dissolved in ethanol, and ether added to give a white precipitate, which when collected under nitrogen became bright yellow and when then exposed to air rapidly became white. Confinement in an evacuated desiccator restored the yellow colour. This colour cycle could be repeated several times, but on prolonged drying the yellow form ceased to turn white on exposure to the air. Drying at 60°/0·1 mm. gave the hydrogen dichloride (I; X = HCl<sub>2</sub>). The white material also gave the picrate, m. p. 145—146°. The significance of these changes was not further investigated.

*2-p-Dimethylaminophenyl-3,3-dimethyl-3H-indole* (IX). The ketone (VIII) readily gave a colourless *phenylhydrazone*, m. p. 92—94°, from methanol (Found: C, 77·1; H, 8·2; N, 15·2.  $C_{18}H_{23}N_3$  requires C, 76·9; H, 8·3; N, 14·9%).

A hot solution of the phenylhydrazone (2 g.) in ethanol (8 ml.) was diluted with saturated ethanolic hydrogen chloride (8 ml.), boiled for 10 min., cooled, filtered and evaporated to dryness. The residue in aqueous solution was basified with sodium hydroxide, and the gummy deposit extracted with ether. Evaporation of the extract gave the *3H-indole* (IX) (1·6 g., 85%), m. p. 116° from aqueous ethanol, or after sublimation (Found: C, 81·7; H, 7·8; N, 11·0.  $C_{18}H_{20}N_2$  requires C, 81·8; H, 7·65; N, 10·6%). The indole was also obtained when the phenylhydrazone was boiled with acetic acid: it is very soluble in most organic solvents.

*2-p-Aminophenyl-3-methylindole* (X; R = R' = H). *p*-Acetamidophenyl ethyl ketone, prepared by Kuncell's method,<sup>10</sup> was readily converted into the *phenylhydrazone*, m. p. 165—167° from ethyl acetate (Found: C, 72·7; H, 6·4; N, 15·1.  $C_{17}H_{19}N_3O$  requires C, 72·6; H, 6·8; N, 14·9%). The phenylhydrazone, when indolised as above, gave the *indole* (X; R = R' = H), m. p. 170—171° (Found: C, 81·4; H, 6·5; N, 12·6.  $C_{18}H_{14}N_2$  requires C, 81·8; H, 6·35; N, 12·6%). The hydrolysis of the acetyl group during the indolisation was confirmed by the infrared spectrum of the ketone, which showed CO absorption at 1650 and 1670  $cm^{-1}$ , that of the hydrazone which showed this only at 1650  $cm^{-1}$ , and that of the indole, in which it was absent. The indole was converted into *2-p-acetamidophenyl-3-methylindole* (X; R = H, R' = Ac), m. p. 186—188° from benzene (Found: C, 77·7; H, 5·85; N, 10·2.  $C_{17}H_{16}N_2O$  requires C, 77·3; H, 6·1; N, 10·6%).

*2-p-Aminophenyl-1,3-dimethylindole* (X; R = Me; R' = H). *p*-Acetamidophenyl ethyl ketone gave a *methylphenylhydrazone*, m. p. 146—147°, from methanol (Found: C, 73·1; H, 7·2; N, 14·7.  $C_{18}H_{21}N_3O$  requires C, 73·2; H, 7·2; N, 14·2%), which when indolised and worked up as before gave the *indole* (X; R = Me, R' = H), m. p. 131—132°, from methanol (Found: C, 81·75; H, 6·9; N, 12·1.  $C_{16}H_{16}N_2$  requires C, 81·4; H, 6·8; N, 11·9%).

*2-p-Acetamidophenyl-1,3-dimethylindole* (X; R = Me, R' = Ac). *p*-Acetamidophenyl ethyl ketone (6·75 g.) and *N*-methylphenylhydrazine (5 g., 1·1 mol.) were dissolved in turn in warm acetic acid (50 ml.) which was then boiled under reflux for 1 hr., and the reddish-black product poured into water (500 ml.). A solution of the gummy precipitate in boiling ethanol (100 ml.), to which Girard's reagent P (4 g.) and acetic acid (10 ml.) were added, was boiled for 30 min. and poured into water (750 ml.). The precipitated *indole* (X; R = Me, R' = Ac), (5·2 g., 53%) had m. p. 185—187°, from ethanol (Found: C, 77·5; H, 6·7; N, 9·9.  $C_{18}H_{18}N_2O$  requires C, 77·7; H, 6·5; N, 10·1%). The indole, when heated with methyl toluene-*p*-sulphonate under various conditions, gave no definite product.

We gratefully acknowledge the award of a Beaverbrook Overseas Scholarship (to D. F. C.) by the Beaverbrook Foundations.