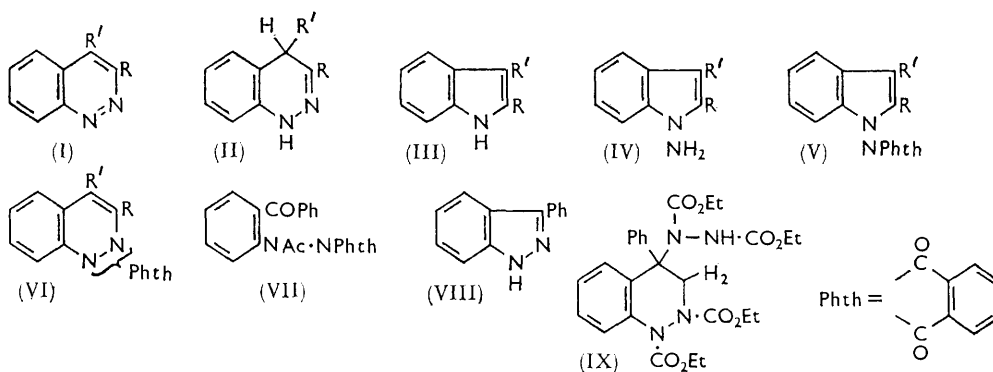


### 1009. 1-Aminoindoles: A Novel Rearrangement of 1,4-Dihydrocinnolines.

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In aqueous mineral acids at 100° 1,4-dihydrocinnolines are in equilibrium with 1-aminoindoles, the position of the equilibrium depending in the substituents. 1-Aminoindoles have also been synthesized by reduction of the 1-nitrosoindoles. The evidence suggests that 1-aminoindoles are not intermediates in the reduction of cinnolines to indoles.

CINNOLINES (I) may be reduced to dihydrocinnolines (II) or indoles (III) depending on the reagents and reaction conditions; <sup>1</sup> for example, hydrogenation in the presence of platinum or reduction with lithium aluminium hydride <sup>2</sup> usually affords the former, sodium and ethanol the latter. Reduction of the dihydrocinnoline with sodium and ethanol also gives the indole. Alder and Niklas <sup>3</sup> have suggested that 1-aminoindoles (IV) are intermediates in the reduction of dihydrocinnolines to indoles, although such compounds have not been isolated from the reduction.



We have now found that in dilute mineral acid at 100° the dihydrocinnolines (II; R = H, R' = Me, or R = H, R' = Ph, or R = Me, R' = Ph) rearrange into the corresponding 1-aminoindoles (IV). The primary amino-group was detected in the rearranged products by the ready formation of benzylidene and phthaloyl derivatives (V) which showed no N-H absorption in the infrared region. The phthaloyl derivatives showed absorption bands at 1790 and 1740  $\text{cm}^{-1}$  characteristic of a phthalimido-grouping in contrast with the phthaloyl derivatives of dihydrocinnolines (VI) which absorb at lower frequency (about 1660  $\text{cm}^{-1}$ ).<sup>4</sup> Treatment of 1-amino-3-methylindole (IV; R = H, R' = Me) with hydrogen in the presence of Raney nickel rapidly cleaved the amino-group to give 3-methylindole. Final proof of the 1-aminoindole structure was obtained by oxidation of 2-methyl-3-phenyl-1-phthalimidindole (V; R = Me, R' = Ph) with chromium trioxide to (VII) which showed absorption bands in the infrared region associated with a phthalimido-group (1785 and 1735  $\text{cm}^{-1}$ ), a ketone (1697  $\text{cm}^{-1}$ ) and an amide (1665  $\text{cm}^{-1}$ ). Hydrolysis of the oxidation product yielded 3-phenylindazole (VIII) by cyclization of the intermediate keto-hydrazine.

The rearrangement of 1,4-dihydro-4-phenylcinnoline (II; R = H, R' = Ph) to the corresponding aminoindole (IV; R = H, R' = Ph) is at variance with the work of Neber

<sup>1</sup> Jacobs in Elderfield, "Heterocyclic Compounds," Wiley and Sons, New York, 1957, Vol. VI, p. 160 and references cited therein.

<sup>2</sup> Castle and Onda, *J. Org. Chem.*, 1961, **26**, 4465.

<sup>3</sup> Alder and Niklas, *Annalen*, 1954, **585**, 97.

<sup>4</sup> Besford, Allen, and Bruce, *J.*, 1963, 2867.

*et al.*<sup>5</sup> who reported that in a mixture of ethanol and concentrated hydrochloric acid at 100° the dihydrocinnoline disproportionates into 4-phenylcinnoline and 1,2,3,4-tetrahydro-4-phenylcinnoline. We have been unable to repeat this observation. Analysis of the reaction mixture by thin-layer chromatography (t.l.c.) revealed the presence of only a trace of the cinnoline which may be attributed to aerial oxidation of the dihydrocinnoline. The aminoindole was isolated in 80% yield. 1-Amino-3-phenylindole has also been prepared by Alder and Niklas<sup>3</sup> by heating the adduct (IX) between 1,1-diphenylstyrene and diethyl azodicarboxylate with hydrazine at 180°.

1-Aminoindoles have also been prepared in low yield by careful reduction of 1-nitrosoindoles. Reduction of 3-methyl-1-nitrosoindole with zinc in moist ethereal acetic acid at 0° gave the aminoindole (IV; R = H, R' = Me) in 15% yield and 1-amino-2,3-dimethylindole (IV; R = R' = Me) was obtained in 40% yield by reduction of the corresponding nitrosoindole with lithium aluminium hydride. In the latter case the optimum yield was obtained by slowly adding 1.1 mol. of lithium aluminium hydride to the nitrosoindole at 20° following the method of Poirier and Bennington.<sup>6</sup>

The amino-group in 1-amino-2-methyl-3-phenylindole (IV; R = Me, R' = Ph) proved surprisingly inert towards reducing agents the compound being recovered unchanged after treatment with lithium aluminium hydride, zinc and acetic acid, or hydrogen in the presence of platinum or Raney nickel. Reduction with ethanol and a large excess of sodium caused partial deamination (60% based on ammonia liberated). In the light of these results, the reduction of cinnolines with sodium and ethanol was re-examined,<sup>7</sup> search being made for the production of 1-aminoindoles. The reaction mixtures were analysed by t.l.c. on silica gel plates with chloroform as the developing solvent, a method which gave an excellent separation of the cinnoline, dihydrocinnoline, 1-aminoindole, and indole. Four cinnolines were reduced, 4-methyl- (I; R = H, R' = Me), 4-phenyl- (I; R = H, R' = Ph), 3,4-dimethyl- (I; R = R' = Me) and 3-methyl-4-phenylcinnoline (I; R = Me, R' = Ph). In each case the reaction mixture contained only the indole, the dihydrocinnoline, and unchanged starting material. The absence of 1-aminoindoles in the reaction mixtures, particularly in the reduction of 3-methyl-4-phenylcinnoline, militates against accepting such compounds as intermediates in the reduction.

Attempts to rearrange 1,4-dihydro-3,4-dimethylcinnoline (II; R = R' = Me) in refluxing dilute hydrochloric acid gave mainly starting material, although the small amount of material which sublimed into the condenser proved to be 1-amino-2,3-dimethylindole (IV; R = R' = CH<sub>3</sub>). On the other hand, treatment of this aminoindole under the same conditions afforded the dihydrocinnoline. Again with t.l.c. as an analytical tool, the effect of acid at 100° on the other three aminoindoles was investigated. None of the dihydrocinnoline could be detected after treatment of the 3-phenyl- or 2-methyl-3-phenyl-aminoindoles with acid but 1-amino-3-methylindole formed some material having the same  $R_F$  value as 1,4-dihydro-4-methylcinnoline. We conclude therefore that dihydrocinnolines and 1-aminoindoles are in equilibrium in acidic solutions. The following reversible steps are suggested for the course of the rearrangement. Protonation of the aminoindole followed by attack of a molecule of water at the  $\alpha$ -carbon atom would give the protonated form of the hydrazino-carbonyl compound, which may recyclize to the dihydrocinnoline or the aminoindole.

Rearrangement of 1-aminoindoles followed by oxidation of the dihydrocinnolines<sup>2,8</sup> may, in certain instances, provide a convenient synthesis of cinnolines.

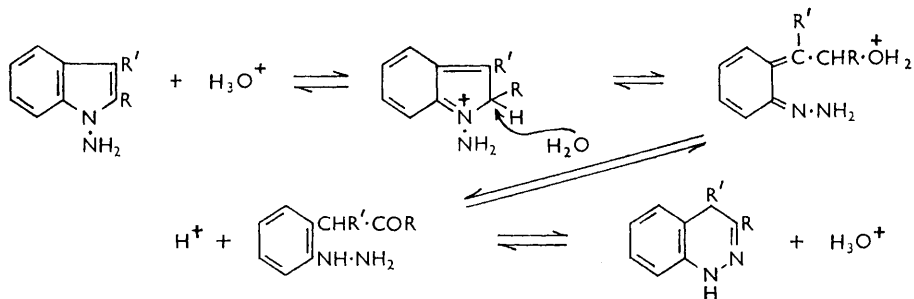
The hydrogen nuclear magnetic resonance spectra of the rearrangement products are in agreement with the formulation as 1-aminoindoles. In carbon tetrachloride solution a singlet was observed in each spectrum in the region  $\tau$  5.85—6.55. This peak occurs at a

<sup>5</sup> Neber, Knöller, Herbst, and Trissler, *Annalen*, 1929, **471**, 113.

<sup>6</sup> Poirier and Bennington, *J. Amer. Chem. Soc.*, 1952, **74**, 3192.

<sup>7</sup> Atkinson and Simpson, *J.*, 1947, 1649.

<sup>8</sup> Busch and Rast, *Ber.*, 1897, **30**, 521.



lower field than that associated with an NH<sub>2</sub> group attached to carbon, which occurs at  $\tau$  8–9, and is ascribed to the NH<sub>2</sub> group attached to the nitrogen of the pyrrole ring since phenylhydrazine also shows a band in this region ( $\tau$  6.05). Intensity measurements indicate the presence of two equivalent hydrogens attached to the nitrogen. The spectrum of dihydro-3,4-dimethylcinnoline shows a singlet at  $\tau$  2.3 and a quartet centred at  $\tau$  6.66 associated with the hydrogen atoms at positions one and four, respectively. The 3-methyl group gives a singlet at  $\tau$  7.98 and the 4-methyl group a doublet at  $\tau$  8.84. The spectrum is in harmony with the spectra of the dihydrocinnolines reported by Besford, Allen, and Bruce,<sup>4</sup> which led these workers to assign the hydrazone structure (II) to dihydrocinnolines.

#### EXPERIMENTAL

Infrared spectra were determined in potassium bromide pellets. Nuclear magnetic resonance spectra were measured at 40 Mc./sec. with a Perkin-Elmer spectrometer using tetramethylsilane as internal standard. Grade H alumina (P. Spence Ltd.) was used for column chromatography. Thin-layer chromatography was on silica gel plates with chloroform as the developing solvent. Light petroleum had b. p. 60–80° unless otherwise stated.

*1-Amino-3-methylindole* (IV; R = H, R' = Me).—(a) *Rearrangement of 1,4-dihydro-4-methylcinnoline*. A solution of the dihydrocinnoline <sup>2</sup> (19.8 g.) in *n*-hydrochloric acid (300 ml.) was refluxed for 30 min. 1-Amino-3-methylindole hydrochloride (12.2 g.) crystallized from the cooled solution as an ill-defined hydrate, m. p. 123–125°. The *free base* crystallized from light petroleum (b. p. 40–60°) as colourless needles, m. p. 60–61°. The nuclear magnetic resonance spectrum in CCl<sub>4</sub> has a multiplet at  $\tau$  2.99 and singlets at  $\tau$  3.42, 5.85, and 7.78 (Found: C, 74.2; H, 7.1; N, 19.4. C<sub>9</sub>H<sub>10</sub>N<sub>2</sub> requires C, 73.9; H, 6.9; N, 19.2%).

(b) *Reduction of 3-methyl-1-nitrosoindole*. Zinc dust (20 g.) was added during 15 min. to a vigorously stirred solution of 3-methyl-1-nitrosoindole <sup>9</sup> (4.5 g.) in acetic acid (15 ml.) and moist ether (80 ml.), the temperature of the mixture being 0–10°. The stirring was continued for 15 min., the solution filtered and the filtrate washed with an excess of sodium bicarbonate solution. The brown oil obtained by evaporation of the ether was chromatographed on alumina (150 g.). Elution with benzene–light petroleum (1 : 4) gave 3-methylindole (0.2 g.). Elution with benzene–light petroleum (1 : 1) gave 1-amino-3-methylindole (0.91 g.) which crystallized from light petroleum (b. p. 40–60°) as colourless needles (0.67 g.), m. p. and mixed m. p. with the above rearrangement product, 61–62°. The infrared spectra of the two samples were identical (Found: C, 73.9; H, 6.9; N, 19.1%).

A solution of 1-amino-3-methylindole hydrochloride (0.18 g.) and phthalic anhydride (0.15 g.) in pyridine (2 ml.) was refluxed for 4 hr. Evaporation of the solvent and crystallization of the residue from ethanol gave 3-methyl-1-phthalimidindole (V; R = H, R' = Me) (0.16 g.), m. p. 188.5–190°,  $\nu_{\max}$  1790 and 1740 cm.<sup>-1</sup> (phthalimido-group) (Found: C, 74.1; H, 4.4; N, 9.6. C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> requires C, 73.9; H, 4.4; N, 10.1%).

A mixture of the aminoindole hydrochloride (0.36 g.) and benzaldehyde (0.3 ml.) in 50% aqueous methanol (10 ml.) was warmed on a steam-bath for 5 min. The solution was cooled to give crystals of the *benzylidene derivative* (0.42 g.), m. p. 119–121° (Found: C, 81.8; H, 6.1; N, 12.1. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub> requires C, 82.0; H, 6.0; N, 12.0%).

Hydrogenation of the aminoindole hydrochloride (0.1 g.) in ethanol (50 ml.) in the presence

<sup>9</sup> Hodson and Smith, *J.*, 1957, 3546.

of Raney nickel (0.2 g.) at 20° and atmospheric pressure for 10 min. gave 3-methylindole, m. p. and mixed m. p. with an authentic sample, 95—96°.

1-Amino-3-phenylindole (IV; R = H, R' = Ph).—A mixture of 1,4-dihydro-4-phenylcinnoline (2 g.) (prepared by the method of Besford, Allen, and Bruce<sup>4</sup>) and *n*-hydrochloric acid (40 ml.) was heated at 100° in a sealed tube under nitrogen for 3 days. The mixture was cooled, basified, and extracted with ether. Evaporation of the ether and crystallization of the residue twice from methanol gave 1-amino-3-phenylindole (0.9 g.), m. p. 101—102° (lit.,<sup>3</sup> 104°) (Found: C, 80.4; H, 5.9; N, 13.5. Calc. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>: C, 80.75; H, 5.8; N, 13.45%).

In an attempt to disproportionate 1,4-dihydro-4-phenylcinnoline under the conditions of Neber *et al.*,<sup>5</sup> the dihydrocinnoline (0.1 g.) was heated at 100° in a sealed tube under nitrogen with ethanol (2 ml.) and concentrated hydrochloric acid (8 ml.) for 18 hr. The precipitate which separated on cooling was treated with dilute alkali and extracted with ether to give 1-amino-3-phenylindole (0.08 g.), m. p. 100—101°. Basification and extraction of the acidic filtrate gave an oil which by t.l.c. analysis showed a low 4-phenylcinnoline content.

The benzylidene derivative had m. p. 108—109° (lit.,<sup>3</sup> 108°) (Found: N, 9.55. Calc. for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>: N, 9.45%).

The *phthaloyl derivative* crystallized from ethanol as pale yellow needles, m. p. 225—226°,  $\nu_{\max}$  1790, 1740 cm.<sup>-1</sup> (Found: C, 77.8; H, 4.2; N, 8.3. C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C, 78.1; H, 4.2; N, 8.3%).

1,4-Dihydro-3-methyl-4-phenylcinnoline (II; R = Me, R' = Ph).—A solution of 3-methyl-4-phenylcinnoline<sup>10</sup> (5.5 g.) and lithium aluminium hydride (2.3 g.) in ether (500 ml.) was refluxed for 3 hr. Ether-methanol-water (50 ml., 2:2:1) was added cautiously and the mixture filtered. Evaporation of the filtrate and crystallization of the residue from ethanol gave 1,4-dihydro-3-methyl-4-phenylcinnoline (3.6 g.), m. p. 134—135°. A mixture with the starting material (m. p. 134—136°) melted at about 100° (Found: C, 80.7; H, 6.7; N, 12.8. C<sub>15</sub>H<sub>14</sub>N<sub>2</sub> requires C, 81.0; H, 6.4; N, 12.6%).

1-Amino-2-methyl-3-phenylindole (IV; R = Me, R' = Ph).—1,4-Dihydro-3-methyl-4-phenylcinnoline (2.4 g.) in *n*-hydrochloric acid (125 ml.) was heated under reflux for 18 hr. The solid which separated from the cooled solution was treated with dilute caustic soda solution and extracted with ether. Evaporation of the extract and crystallization of the residue from light petroleum (b. p. 80—100°) gave 1-amino-2-methyl-3-phenylindole (1.7 g.), m. p. 111—112°. The nuclear magnetic resonance spectrum in CHCl<sub>3</sub> has a multiplet at  $\tau$  2.62, and singlets at  $\tau$  5.94 and 7.68 (Found: C, 80.9; H, 6.4; N, 12.8. C<sub>15</sub>H<sub>14</sub>N<sub>2</sub> requires C, 81.0; H, 6.4; N, 12.6%).

The *benzylidene derivative*, pale yellow needles from ethanol, had m. p. 100—101° (Found: C, 85.1; H, 5.7; N, 9.1. C<sub>22</sub>H<sub>18</sub>N<sub>2</sub> requires C, 85.1; H, 5.8; N, 9.0%).

The *phthaloyl derivative* crystallized from benzene-light petroleum as pale yellow prisms, m. p. 224—225°,  $\nu_{\max}$  1790, 1740 cm.<sup>-1</sup> (Found: C, 78.4; H, 5.0; N, 7.9. C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> requires C, 78.4; H, 4.6; N, 8.0%).

*Degradation of 2-Methyl-3-phenyl-1-phthalimidoindole to 3-Phenylindazole.*—A mixture of the phthalimido-compound (0.5 g.) and chromium trioxide (0.29 g.) in acetic acid (10 ml.) and water (2 ml.) was stirred at 20° for 4 hr. The filtered solution was diluted with water and extracted with chloroform to give 1-(2-benzoylphenyl)-2-phthaloylacetylhydrazide (VII) (0.37 g.) which crystallized from ethanol as colourless prisms, m. p. 209—211°,  $\nu_{\max}$  1785 and 1735 (phthalimido-group), 1695 (ketone), and 1665 cm.<sup>-1</sup> (amide) (Found: C, 71.7; H, 4.5; N, 7.1. C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> requires C, 71.9; H, 4.2; N, 7.3%). A solution of the oxidation product (0.13 g.) in ethanol (5 ml.) and 2*n*-hydrochloric acid (5 ml.) was refluxed for 24 hr. The solution was adjusted to pH 10 and extracted with ether to give 3-phenylindazole (46 mg.) which, after crystallization from light petroleum (b. p. 100—120°), had m. p. 113—114°, not depressed on admixture with an authentic sample, m. p. 115—116°, prepared by the method of Auwers.<sup>11</sup> The infrared spectra of the two samples were identical.

1-Amino-2,3-dimethylindole (IV; R = R' = Me).—A 0.96*M* solution of lithium aluminium hydride in ether (65.5 ml.) was added dropwise to a stirred solution of 2,3-dimethyl-1-nitrosindole<sup>12</sup> (10 g.) in ether (120 ml.) at 20° during 20 min. After a further 10 min., ether-methanol-water (25 ml., 2:2:1) was added, the temperature being kept below 20°. The

<sup>10</sup> Simpson, *J.*, 1946, 673.

<sup>11</sup> Auwers, *Ber.*, 1896, 29, 1265, 1269.

<sup>12</sup> Fischer, *Annalen*, 1886, 236, 131.

filtered solution was evaporated to give an oily solid which was chromatographed on alumina (300 g.). Elution with benzene–light petroleum (1 : 4) gave 2,3-dimethylindole (1.4 g.). Elution with benzene–light petroleum (1 : 1) gave 1-amino-2,3-dimethylindole which crystallized from light petroleum (b. p. 40–60°) as shining plates (3.4 g.), m. p. 73–74°. The nuclear magnetic resonance spectrum in  $\text{CCl}_4$  has a multiplet between  $\tau$  2.7 and 3.4 and singlets at  $\tau$  6.55, 7.9, and 8.0 (Found: C, 74.65; H, 7.7; N, 17.2.  $\text{C}_{10}\text{H}_{12}\text{N}_2$  requires C, 75.0; H, 7.55; N, 17.5%).

The *phthaloyl derivative* crystallized from ethanol as pale yellow prisms, m. p. 191–192° (Found: C, 74.1; H, 4.8; N, 9.4.  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$  requires C, 74.5; H, 4.9; N, 9.65%).

**3,4-Dimethylcinnoline (I; R = R' = Me).**—The Grignard reagent prepared from magnesium (27.5 g.) and methyl iodide (143 g.) in ether (300 ml.) was treated dropwise during 15 min. with a solution of *o*-aminopropiophenone<sup>13</sup> (37.5 g.) in ether (100 ml.). The mixture was refluxed for 1 hr. The complex was decomposed by the addition of water followed by saturated ammonium chloride solution containing a little ammonia. Evaporation of the ether layer gave 2-amino- $\alpha$ -ethyl- $\alpha$ -methylbenzyl alcohol as an oil (40.3 g.). This (36 g.) was dehydrated in boiling toluene (250 ml.) containing iodine (0.1 g.), the water being removed azeotropically. Evaporation of the solvent and distillation of the residue gave the butene (presumably as a mixture of isomers) (25.5 g.), b. p. 100–110°/10 mm. The butene was dissolved in 2*N*-hydrochloric acid (200 ml.), cooled to 0° and a solution of sodium nitrite (10 g.) in water (100 ml.) added dropwise with stirring until the nitrite was present in slight excess (starch-iodide paper). The mixture was set aside for 3 days, basified with caustic soda and continuously extracted with ether for 6 hr. The ether was removed and the residue crystallized from light petroleum to give 3,4-dimethylcinnoline (19.1 g.), m. p. 118–120° (Found: C, 75.8; H, 6.3; N, 17.8.  $\text{C}_{10}\text{H}_{10}\text{N}_2$  requires C, 75.9; H, 6.4; N, 17.7%).

**1,4-Dihydro-3,4-dimethylcinnoline (II; R = R' = Me).**—Ether (300 ml.) containing 3,4-dimethylcinnoline (8.7 g.) and lithium aluminium hydride (3.2 g.) was refluxed for 3 hr. Ether-methanol–water (150 ml., 2 : 2 : 1) was added cautiously, the mixture filtered and the material obtained by evaporation of the filtrate crystallized from light petroleum to give the *dihydrocinnoline* (7.4 g.). Recrystallization from the same solvent gave pale yellow needles, m. p. 51–52°. The nuclear magnetic resonance spectrum in  $\text{CCl}_4$  has a singlet at  $\tau$  2.3, a multiplet between  $\tau$  3.1 and 3.6, a quartet centred at  $\tau$  6.6, a singlet at  $\tau$  7.9 and a doublet centred at  $\tau$  8.85 (Found: C, 74.6; H, 7.6; N, 18.1.  $\text{C}_{10}\text{H}_{12}\text{N}_2$  requires C, 75.0; H, 7.55; N, 17.5%).

A solution of the dihydrocinnoline (0.5 g.) in 2*N*-hydrochloric acid (25 ml.) was refluxed for 18 hr. The crystalline material (20 mg.) which sublimed into the condenser had m. p. 70–72° and was shown to be 1-amino-2,3-dimethylindole (IV; R = R' = Me) by mixture m. p. and comparison of the infrared spectra. The acidic solution was made alkaline and extracted with ether to give an oil which on spectral and chromatographic evidence was mainly starting material.

**Treatment of 1-Aminoindoles with Acid.**—(a) *General conditions.* The aminoindole (10 mg.) and *N*-hydrochloric acid (5 ml.) were heated in a sealed tube at 100° for 18 hr. The solution was basified and extracted with ether. The ether solution was analysed by t.l.c. The products after treatment of 1-amino-3-phenylindole and 1-amino-2-methyl-3-phenylindole in this manner contained only unchanged aminoindole. Under the same conditions 1-amino-3-methylindole rearranged to a mixture of the aminoindole and the dihydrocinnoline.

(b) *Rearrangement of 1-amino-2,3-dimethylindole.* A solution of the aminoindole (0.5 g.) in *N*-hydrochloric acid (10 ml.) was refluxed for 18 hr., basified and extracted with ether. The solid (386 mg.) obtained by evaporation of the ether was chromatographed on alumina (25 g.). Elution with benzene gave unchanged starting material (49 mg.). Elution with benzene-ether (9 : 1) gave 1,4-dihydro-3,4-dimethylcinnoline (0.16 g.). Crystallization from light petroleum (b. p. 30–40°) gave material (100 mg.) m. p. 51–52°, not depressed on admixture with the authentic sample.

**Reduction of Cinnolines with Sodium and Ethanol.**—Sodium (1 g.) was added in small pieces during 30 min. to the cinnoline (1 g.) in boiling ethanol (30 ml.). When the sodium had dissolved water was added, the mixture extracted with ether, and the extract analysed by t.l.c., the corresponding indole, 1-aminoindole, and dihydrocinnoline being run concurrently. The compounds examined were 4-methyl-, 4-phenyl-, 3,4-dimethyl-, and 3-methyl-4-phenyl-cinnoline. Each reduction product showed the same pattern on the chromatogram indicating a mixture

<sup>13</sup> Keneford and Simpson, *J.*, 1948, 354.

of the indole, the dihydrocinnoline and the unchanged cinnoline. None of the aminoindole could be detected.

*Reduction of 1-Amino-2-methyl-3-phenylindole with Sodium and Ethanol.*—Sodium (2.7 g.) was added in small pieces during 1 hr. to the aminoindole (0.5 g.) in boiling ethanol while the apparatus was swept with nitrogen. The entrained ammonia was absorbed in standard acid. Titration of the excess acid indicated a 60% reduction of the amino-group.

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