CCCCXXIII.—3-*Methoxy-2-phenylindole and 3-Benzoylamino-2-phenylindole.*

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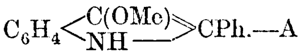
THE substances mentioned in the title have been prepared in order to show that E. Fischer's method can be extended to the synthesis of indole derivatives in which an oxygen or a nitrogen atom is directly attached to the pyrrole nucleus.

3-*Methoxy-2-phenylindole*,  $\mathrm{C_6H_4}<\begin{matrix}\mathrm{C(OMe)}\\ \mathrm{NH}\text{——}\end{matrix}>\mathrm{CPh}$.—A mixture of ω-methoxyacetophenone (10 g.) (Pratt and Robinson, J., 1923, **123**, 748; compare Malkin and Robinson, J., 1925, **127**, 372) and phenylhydrazine (10·7 g.) became warm and when the initial reaction ceased the formation of the phenylhydrazone was completed by heating on the steam-bath for 5 minutes. Acetic acid (100 c.c.) was then introduced and the yellow solution heated; it gradually became redder and at a certain stage a strong exothermic reaction occurred and the liquid boiled spontaneously. The crimson solution was then boiled for 40 minutes, cooled, and added to much water. The oil quickly crystallised; it was dried and repeatedly extracted with boiling petroleum (b. p. 80—100°), the yellowish-brown material which crystallised from the filtered solutions weighing 9·5 g. On recrystallisation from the same solvent, almost colourless prisms, m. p. 106°, were obtained (Found: C, 80·7; H, 5·8; N, 6·4. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8; N, 6·3%).

3-*Methoxy-2-phenylindole* is readily soluble in the usual organic solvents with the exception of light petroleum; it separates from aqueous alcohol in leaflets. The substance is somewhat sensitive to acids and its conversion into phenylindoxyl has not been accomplished smoothly. The action of a boiling mixture of phenol and hydrobromic acid (*d* 1·7) gave rise to products having the reactions of phenylindoxyl and of 2-phenylindolone—2-phenylindoxyl (Kalb and Bayer, *Ber.*, 1912, **45**, 2150), but these could not be fully purified.

Reduction by hydriodic acid. A mixture of methoxyphenylindole (3 g.), phenol (30 g.), and hydriodic acid (20 c.c.; *d* 1·7) was boiled for 1¼ hours. After cooling, addition of water and sodium hydroxide, isolation of the solid precipitate, and crystallisation from petroleum, 0·7 g. of the crude material was obtained. The substance was identified as 2-phenylindole and after crystallisation from alcohol had m. p. 186°, alone or mixed with a specimen prepared as described by Fischer (*Annalen*, 1886, **236**, 133).

3-*Benzoylamino-2-phenylindole*,  $\mathrm{C_6H_4}<\begin{matrix}\mathrm{C(NHBz)}\\ \mathrm{NH}\text{———}\end{matrix}>\mathrm{CPh}$.—ω-Benzoylaminoacetophenone (Robinson, J., 1909, **95**, 2167; Gabriel, *Ber.*, 1910, **43**, 134) forms a *phenylhydrazone* which crystallises from alcohol in stout, colourless needles, m. p. 153° (Found: N, 12·7. $C_{21}H_{19}ON_3$ requires N, 12·8%). The indole derivative was normally obtained without isolating this intermediate. A mixture of ω-benzoylaminoacetophenone (22 g.) with phenylhydrazine (23 g.) was heated on the steam-bath for ½ hour, and acetic acid (220 c.c.) then introduced. The orange liquid was heated over gauze; it became crimson and a vigorous reaction ensued; finally, the solution was boiled for 1 hour. The yellow, viscous mass obtained on the addition of water soon hardened and was collected, dried, and crystallised from toluene. The total yield, including a portion recovered from the mother-liquor by concentration and addition of light petroleum, amounted to 12 g. The substance crystallises from toluene in tablets, m. p. 206°. In another experiment, the dried crude product was twice extracted with a mixture of equal volumes of benzene and light petroleum; the residue crystallised from aqueous alcohol in silvery leaflets, m. p. 201·5° (Found: C, 80·8; H, 5·2; N, 8·9. $C_{21}H_{16}ON_2$ requires C, 80·8; H, 5·1; N, 9·0%). The melting point of a mixture of the tablets and leaflets was 206°. The substance is readily soluble in ethyl alcohol, acetone or acetic acid, moderately readily soluble in methyl alcohol, ethyl acetate, toluene, or xylene, less soluble in benzene or chloroform, and sparingly soluble in light petroleum.

Numerous attempts were made to hydrolyse this amide under the most varied conditions, but in no case could the process be smoothly accomplished. Benzoylaminophenylindole (0·5 g.) mixed with ethyl alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.) was heated in a sealed tube at 125—130° for 4 hours. Water was added, unchanged material removed by extraction with ether, and the aqueous layer basified; the precipitated solid, crystallised from benzene, had m. p. 171·5°. Furthermore, in an attempt to prepare a derivative of 6-carboline by intramolecular condensation, a mixture of benzoylaminophenylindole (0·5 g.) and an excess of phosphorus trichloride was boiled for 5 minutes. After treatment with water, filtration, and basification, a substance was isolated which was crystallised from benzene–petroleum. This had m. p. 174° and a mixture with the specimen, m. p. 171·5°, had m. p. 172° (Found: N, 13·5, 13·2. Calc. for $C_{14}H_{12}N_2$: N, 13·4%). Fischer and Schmitt (*Ber.*, 1888, **21**, 1074) prepared 3-amino-2-phenylindole by reducing 3-nitroso-2-phenylindole and state that it has m. p. 174°.

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