311. *Indoles. Part II. The Preparation and Oxidation of the* Bz-*Nitro*-2-*methyl*-3-*ethyl*-, -2 : 3-*diphenyl*-, *and* -2-*methyl*-3-*phenyl-indoles.*

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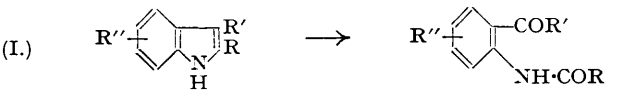
The compounds named in the title have been prepared by the Fischer indole synthesis, and their oxidation to the related propiophenones and benzophenones (I ⟶ II) has been examined. This method provides a practicable route to the nitro-2-aminobenzophenones, but not to nitro-2-aminopropiophenones. The proportions of the 4- and 6-nitroindoles formed from the *m*-nitrophenylhydrazones used have been ascertained, and are briefly discussed.

The aim of the work to be described in this series of papers is twofold : to examine the oxidative ring-fission of indole derivatives (I ⟶ II) as a source of substituted 2-aminoarylketones, and to collect data concerning the Fischer indole synthesis in its application to *m*-substituted arylhydrazones and to arylhydrazones of unsymmetrical ketones.

In Part I (*J.*, 1949, 796) we established the convenience of such oxidation of *Bz*-nitro-2 : 3-dimethylindoles (I; R = R′ = Me; R″ = NO_2) in preparing the four nitro-2-amino-



acetophenones, and showed that the cyclisation of methyl ethyl ketone *m*-nitrophenylhydrazone in hot concentrated hydrochloric acid gave a larger proportion of 6- than of 4-nitro-2 : 3-dimethylindole. The present paper describes experiments on the Fischer synthesis of indoles (I; R′ = Et or Ph; R″ = NO_2), and on the oxidation of these compounds.

Under conditions similar to those used in Part I (*loc. cit.*), methyl *n*-propyl ketone *o*- and *p*-nitrophenylhydrazones were cyclised to 7- and 5-nitro-2-methyl-3-ethylindole (as is proved below), in yields of 27% and 45% respectively based on the parent nitroanilines. The homogeneity of both products was established chromatographically. The corresponding *m*-nitrophenylhydrazone produced 33% of a mixture of isomeric indoles, m. p. 170—171° and 163—164°, in the approximate ratio 1 : 0·3, as was shown by the ready separation of the compounds on activated alumina. As with the 2 : 3-dimethylindoles, separation could not be satisfactorily accomplished by crystallisation, only a portion of the more abundant isomer being isolable by this method.

Oxidation of these indoles with chromic acid in acetic acid occurred vigorously, and as a result yields in this step were lower than in the similar oxidation of nitro-2 : 3-dimethylindoles. Recovery of 3-nitro-2-acetamidopropiophenone from 7-nitro-2-methyl-3-ethylindole was 6%, based on *o*-nitroaniline. The indoles, m. p. 170—171° and 163—164°, similarly provided 4- and 6-nitro-2-acetamidopropiophenone, giving on hydrolysis the related amines. The base from the first mentioned indole gave, by deamination, reduction, and acetylation, *p*-acetamidopropiophenone, its constitution being thus proved.

The oxidation of 5-nitro-2-methyl-3-ethylindole proved to be anomalous, providing a mediocre yield of a substance, m. p. 171—172°, different from 5-nitro-2-acetamidopropiophenone (m. p. 145—145·5°; Keneford and Simpson, *J.*, 1948, 354). The nature of this product has not yet been established, but it may be merely a polymorph of 5-nitro-2-acetamidopropiophenone since acid hydrolysis converted it into 5-nitro-2-aminopropiophenone. The present method is clearly not a practicable one by which to prepare the nitro-2-aminopropiophenones.

Clearly, nitrophenylhydrazones of methyl *n*-propyl ketone are cyclised by fuming hydrochloric acid to give only derivatives of 2-methyl-3-ethylindole, no 2-propylindoles being detected. Methyl *n*-propyl ketone phenylhydrazone is likewise converted by cuprous chloride into 2-methyl-3-ethylindole (Arbusov and Fruhauf, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 694; Arbusov and Rotarmel, *J. Gen. Chem. Russia*, 1932, **2**, 397), although Fischer (*Annalen*, 1886, **236**, 128), using zinc chloride, may have obtained a small amount of the alternative product. It does in fact seem to be generally the case that in the Fischer reaction a methylene group reacts rather than a methyl group (Buu-Hoï and Royer, *Rec. Trav. chim.*, 1947, **66**, 305), a small proportion only of the alternative product being formed as in the cyclisation of methyl ethyl ketone phenylhydrazone by nickel chloride (Korczynski, Brydowna, and Kierzek, *Gazzetta*, 1926, **56**, 903).

It is also clear that the cyclisation of methyl *n*-propyl ketone *m*-nitrophenylhydrazone is similar to that of the methyl ethyl compound (Part I, *loc. cit.*), proceeding mainly *para* to the nitro-group.

5-Nitro-2-aminobenzophenone is the only mononitro-2-aminobenzophenone so far described which contains the nitro- and amino-groups in the same ring. Its formation from 2-chloro-5-nitrobenzophenone and ammonia under pressure (Ullmann and Mallet, *Ber.*, 1898, **31**, 1694) is sluggish, and the method does not appear to be of general applicability. Oxidative fission of suitable indoles promised to be useful in this connection. Fennel and Plant (*J.*, 1932, 2872) prepared 5-nitro-2 : 3-diphenylindole from benzyl phenyl ketone *p*-nitrophenylhydrazone, and from the corresponding *m*-isomer obtained two products, m. p. 227° and 205°, which were not oriented.

We have repeated these preparations, as described in the Experimental section, and in the case of benzyl phenyl ketone *m*-nitrophenylhydrazone found, like Fennel and Plant (*loc. cit.*), that the two indoles formed were readily separated by crystallisation. Chromatography established the proportions of the compounds, m. p. 227° and 205°, in the mixture as approximately 1 : 2. On oxidation they gave 4- and 6-nitro-2-benzamidobenzophenones, respectively,

and 5-nitro-2 : 3-diphenylindole similarly gave the 5-nitro-isomer, all these ketones being formed in high yield. The structures of 4- and 6-nitro-2-benzamidobenzophenones were established by successive hydrolysis, deamination, and reduction to *p*- and *o*-aminobenzophenone, and this proof shows that the nitration products of 1-acyl-2 : 3-diphenylindoles (Fennel and Plant, *loc. cit.*) are 6-nitro-1-acyl-2 : 3-diphenylindoles. Further, if the amounts of the isomeric indoles isolated are truly indicative of the course of the cyclisation, and if the indoles, once formed, are not perhaps decomposed at differing rates by the strongly acid medium, with a consequent reversal of the true proportions, then cyclisation *ortho* to the nitro-group is preferred. That this was indeed so was proved by taking a mixture of known proportions of 4- and 6-nitro-2 : 3-diphenylindoles, submitting it to the conditions used in the Fischer synthesis, and analysing the resulting mixture. The result (see below) also proves that differing solubilities of the two indoles in the reaction medium cannot account for the ratio observed, but rather that allowance for solubilities increases the predominance of 4- over 6-nitro-2 : 3-diphenylindole.

In view of these results we examined the cyclisation of benzyl methyl ketone *m*-nitrophenylhydrazone. The reaction appears to be complex. By adsorption on alumina we were able to isolate 4-nitro-3-phenyl-2-methylindole, which accounted for 60% of the cyclisation mixture, but failed to resolve the remainder of the product. Crystallisation of the cyclisation mixture likewise furnished the pure major component but was equally unsuccessful in resolving the more soluble material. Since subsequent oxidation of the major product led without difficulty to 6-nitro-2-acetamidobenzophenone, whereas the minor fraction gave only an intractable gum, it seems possible that some *Bz*-nitro-2-benzylindoles were formed, giving unstable oxidation products. This result is interesting since benzyl methyl ketone phenylhydrazone is said to give 3-phenyl-2-methylindole (though this structure does not appear to have been proved) when cyclised with zinc chloride or alcoholic hydrochloric acid (Trenkler, *Annalen*, 1888, **248**, 106). Despite the complication, however, it is clear that cyclisation *ortho* to the nitro-group is again favoured.

The significance of these results will not be clear until our knowledge of the mechanism of the Fischer synthesis becomes more certain. Since the most satisfactory mechanism proposed so far (Robinson and Robinson, *J.*, 1918, **113**, 639; see also Carlin and Fisher, *J. Amer. Chem. Soc.*, 1948, **70**, 3421) treats Fischer's reaction as a particular case of the *ortho*-benzidine rearrangement, recent views on the transition states involved in the benzidine rearrangement (see, for example, Dewar, " The Electronic Theory of Organic Chemistry," 1949, p. 233) may also be applicable. We are examining further examples of the Fischer synthesis, and also the Claisen rearrangement (Tarbell, " Organic Reactions," vol. 2, New York, 1944) which is in many ways analogous to it.

Fennel and Plant (*loc. cit.*) were unable to cyclise deoxybenzoin *o*-nitrophenylhydrazone, but we have found that benzyl methyl ketone *o*-nitrophenylhydrazone readily gives 7-nitro-3-phenyl-2-methylindole. Oxidation in the usual way converted this in good yield into 3-nitro-2-acetamidobenzophenone.

The oxidation of suitable indole derivatives is obviously a practicable method of preparing nitro-2-aminobenzophenones. The high yields promise to make these reactions suitable for studies of the mechanism of indole oxidations.

Experimental.

M. p.s are uncorrected.

Nitrophenylhydrazones.—Methyl *n*-propyl ketone *o*-, m. p. 52—53°, *m*-, m. p. 51—53°, and *p*-nitrophenylhydrazone, m. p. 111—112°, resulted in yields of 77%, 69%, and 86%, respectively, when the ketone and hydrazine were heated in equivalent quantities for 1 hour at 95°, and the product was crystallised from alcohol. By the same method, benzyl methyl ketone *o*-, m. p. 102—103° (orange needles), and *m*-nitrophenylhydrazone, m. p. 103—105°, were formed in 84% and 55% yield, respectively. The corresponding *m*- and *p*-derivatives of phenyl benzyl ketone were obtained in 74% and 93% yield by the method of Fennel and Plant (*loc. cit.*).

5- *and* 7-*Nitro*-2-*methyl*-3-*ethylindole.*—The substantially pure compounds were recovered in 45% and 27% yield (based on the parent nitroanilines) when the appropriate hydrazones were heated with 10 volumes of fuming hydrochloric acid (*d* 1·19) for 4 hours at 95°, and the products washed with concentrated hydrochloric acid. 5-*Nitro*-2-*methyl*-3-*ethylindole* separated from ethanol in brownish-orange leaflets, m. p. 191—192° (Found : C, 64·9; H, 5·8. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9%), and the 7-*nitro*-derivative formed long scarlet needles, m. p. 135—136°, from the same solvent (Found : C, 64·2; H, 6·1%). Both compounds were unresolved by passage over an alumina column.

4- *and* 6-*Nitro*-2-*methyl*-3-*ethylindoles.*—Cyclisation of methyl *n*-propyl ketone *m*-nitrophenylhydrazone in a similar way gave 33% of mixed indoles. Adsorption of a filtered solution of the mixture (10 g.) in benzene (1 l.) on a column identical with that described in Part I (*loc. cit.*), and development with more benzene, led to separation into an upper crimson and a lower scarlet band. Elution of the latter (2·27 g.)

with benzene, and crystallisation from ethanol, provided 4-*nitro*-2-*methyl*-3-*ethylindole* in scarlet rectangular prisms, m. p. 163—164° (Found: C, 64·1; H, 6·0%), whilst application of benzene–pyridine (10 : 1) removed the upper band (7·48 g.) consisting of the 6-*nitro*-isomer, which separated from ethanol in brownish-orange prisms, m. p. 170—171° (Found: C, 64·9; H, 6·3%). A small intermediate fraction was not further investigated. Crystallisation of the original mixture (5 g.) from ethanol provided crude 6-nitro-2-methyl-3-ethylindole (2·07 g.), m. p. 166—168°, but the mother-liquor deposited a mixture when concentrated.

3-*Nitro*-2-*aminopropiophenone*.—7-Nitro-2-methyl-3-ethylindole (2·45 g.) in acetic acid (20 c.c.) was treated gradually with chromic anhydride (2·1 g.) in water (5 c.c.), the temperature being kept below 30°. After 2 hours the mixture was diluted with water and extracted with chloroform. Removal of the solvent after drying (Na_2CO_3) left a sticky solid (1·99 g.), crystallisation of which from alcohol gave 3-nitro-2-acetamidopropiophenone (0·60 g.), m. p. 107—108° (Found: C, 55·9; H, 5·1. Calc. for $C_{11}H_{12}O_4N_2$: C, 55·9; H, 5·1%). Hydrolysis (Keneford and Simpson, *loc. cit.*) gave 3-nitro-2-amino-propiophenone (0·37 g.), which separated from dilute ethanol in fine yellow needles, m. p. 87—88° (Found: C, 55·7; H, 5·2. Calc. for $C_9H_{10}O_3N_2$: C, 55·7; H, 5·2%).

5-*Nitro*-2-*aminopropiophenone*.—5-Nitro-2-methyl-3-ethylindole (2·4 g.) in acetic acid (20 c.c.) was treated likewise with chromic anhydride (2·04 g.) in water (5 c.c.). Worked up as above, the reaction mixture gave a sticky solid which crystallised from ethanol in pale yellow needles (0·65 g.), m. p. 165—168°. Recrystallisation from the same solvent gave the pure *product*, m. p. 171—172° (Found: C, 55·2; H, 5·3; N, 11·1. $C_{11}H_{12}O_4N_2$ requires C, 55·9; H, 5·1; N, 11·9. $C_{11}H_{14}O_4N_2$ requires C, 55·5; H, 5·9; N, 11·7. $C_{13}H_{16}O_5N_2$ requires C, 55·7; H, 5·75; N, 10·0%). This substance (0·65 g.), which depressed the m. p. of 5-nitro-2-acetamidopropiophenone (m. p. 145—145·5°; Keneford and Simpson, *loc. cit.*), was converted by boiling hydrochloric acid (5N.) into 5-nitro-2-aminopropiophenone, m. p. 130—131° (Found: C, 55·6; H, 5·3%), alone and mixed with an authentic specimen.

6-*Nitro*-2-*aminopropiophenone*.—In a similar way 4-nitro-2-methyl-3-ethylindole (0·3 g.) provided 0·6 g. of once crystallised (methanol) 6-*nitro*-2-*acetamidopropiophenone* (m. p. 154—155°), which, when pure, formed buff needles, m. p. 156—157° (Found: C, 55·7; H, 5·7%). Hydrolysis with boiling hydrochloric acid (5N.) for ½ hour, followed by basification with aqueous ammonia, gave the *amine* (0·03 g.), which crystallised from hot water in fine orange needles, m. p. 77—78° (Found: C, 56·7; H, 5·6%).

4-*Nitro*-2-*aminopropiophenone*.—Prepared similarly from 6-nitro-2-methyl-3-ethylindole (2 g.), the *acetamido*-compound (0·37 g.; m. p. 129—131°) crystallised from ethanol in cream-coloured needles, m. p. 135—136° (Found: C, 56·2; H, 4·85%). Hydrolysis as above provided 4-*nitro*-2-*amino-propiophenone* (0·28 g.), which separated from dilute ethanol in orange-yellow leaflets, m. p. 129—130° (Found: C, 56·2; H, 5·4%).

The amine (0·35 g.) in acetic acid (2 c.c.) and sulphuric acid (1 c.c. of 30N.) was diazotised at 0° with powdered sodium nitrite (0·18 g.), and the solution was diluted with ice-water (20 c.c.) and treated with hypophosphorous acid (10 c.c. of 30%). After 24 hours at 0° the mixture was made alkaline with aqueous sodium hydroxide and extracted with ether. The dried (Na_2CO_3) extract provided crude *p*-nitro-propiophenone (0·27 g.; m. p. 85—88°), which was reduced for 1 hour at 95° with tin (0·3 g.) and concentrated hydrochloric acid (2 c.c.). Extraction of the basified mixture with ether removed the crude amine (0·18 g.), which crystallised from dilute ethanol in feathery needles (0·12 g.), m. p. 139—140° (Chattaway, *J.*, 1904, **85**, 392, gives m. p. 142°). Treatment with acetic anhydride (2 c.c.) for 1 hour at 95° gave *p*-acetamidopropiophenone (0·11 g.), m. p. 171—172° (Chattaway, *loc. cit.*, gives m. p. 175°) after crystallisation from dilute ethanol (Found: C, 69·1; H, 6·9. Calc. for $C_{11}H_{13}O_2N$: C, 69·1; H, 6·85%).

Bz-*Nitro*-2 : 3-*diphenylindoles*.—5-Nitro-, m. p. 198—200°, and a mixture of 4- and 6-nitro-2 : 3-diphenylindoles, were obtained from the appropriate hydrazones (40 g.) in 60% and 69% yields, by boiling with acetic acid and concentrated hydrochloric acid (400 c.c. of each) under reflux for 16 hours. In the former case the omission of acetic acid caused extensive hydrolysis, with the formation of tarry material.

Crystallisation of the crude mixture of 4- and 6-nitro-2 : 3-diphenylindoles (25 g.) from ethanol (750 c.c.) provided the almost pure 6-nitro-compound (5·3 g.; m. p. 225—227°). Concentration of the mother-liquor to one-third of its volume gave the impure 4-nitro-2 : 3-diphenylindole, which after crystallisation from benzene melted at 204—205° (8·4 g.).

The alcoholic filtrate (150 c.c.) from the crystallisation of the crude mixed isomers (5 g.) was evaporated to dryness after removal of the slightly impure higher-melting product (1·34 g.; m. p. 225—227°), and the residue dissolved in benzene (800 c.c.). Chromatographic separation of the contents of the solution as in previous cases, using benzene as eluent, gave first 4-nitro-2 : 3-diphenylindole (3·32 g.; m. p. 202—204°) (elution was very slow) and then, by application of acetone, 6-nitro-2 : 3-diphenylindole (0·22 g.; m. p. 227—228°), of which the total yield was therefore 1·56 g. The 4-nitro-derivative separated from benzene in clusters of orange-yellow needles, m. p. 205—206° (Found: C, 76·7; H, 4·5. Calc. for $C_{20}H_{14}O_2N_2$: C, 76·4; H, 4·5%).

A mixture of pure 4- and 6-nitro-2 : 3-diphenylindole (0·2 g. of each) was boiled under reflux for 24 hours with acetic and concentrated hydrochloric acids (10 c.c. of each), and the residue after evaporation subjected to chromatographic analysis as above. Recovery of the indoles was quantitative, with no evidence of decomposition. In a further experiment, the crystalline material (0·36 g.) from the cooled cyclisation medium was resolved chromatographically, giving 4-nitro- (0·16 g.) and 6-nitro-2 : 3-diphenylindole (0·2 g.).

4-*Nitro*-2-*aminobenzophenone*.—A suspension of finely powdered 6-nitro-2 : 3-diphenylindole (5·3 g.) in glacial acetic acid (200 c.c.) was treated gradually with chromic anhydride (3·2 g.) in water (5 c.c.), and stirred until a clear solution was formed. After 12 hours at room temperature the mixture was diluted with an equal volume of water, and the practically pure product (4·07 g.; 70%) collected. 4-*Nitro*-2-*benzamidobenzophenone* separated from ethanol in lemon-yellow needles, m. p. 192—193° (Found: C, 68·55; H, 3·9. $C_{20}H_{14}O_4N_2$,0·33 H_2O requires C, 68·2; H, 4·2%). This compound (4·07 g.) was boiled under reflux for 4 hours with acetic and concentrated hydrochloric acids (200 c.c. of each), and the clear

solution was basified with aqueous ammonia, giving 4-*nitro*-2-*aminobenzophenone* (3·0 g.), which crystallised from dilute ethanol in small yellow needles, m. p. 172—173° (Found: C, 65·4; H, 4·2. $C_{13}H_{10}O_3N_2$ requires C, 64·5; H, 4·2%).

The amine (0·3 g.) in acetic acid (2 c.c.) and sulphuric acid (1 c.c. of 30 N.) was diazotised at 0° with powdered sodium nitrite (0·1 g.), and the diluted solution (10 c.c. of iced water) treated with hypophosphorous acid (3 c.c. of 30%). After 12 hours at 0°, the mixture was basified and extracted with ether, giving a product which on crystallisation from ethanol provided *p*-nitrobenzophenone (0·22 g.), m. p. 130—131° (Basler, *Ber.*, 1883, **16**, 2717, gives m. p. 138°). Reduction of the compound (0·1 g.) with stannous chloride (0·3 g.) and concentrated hydrochloric acid (2 c.c.) for 1 hour at 95°, gave 0·06 g. of once crystallised *p*-aminobenzophenone, m. p. 122—123° (Doebner, *Annalen*, 1881, **210**, 268, gives m. p. 124°), showing a large mixed m. p. depression with authentic *o*-aminobenzophenone (m. p. 105—106°, Hewett *et al.*, *J.*, 1948, 292).

5-*Nitro*-2-*aminobenzophenone*.—5-Nitro-2 : 3-diphenylindole (6·9 g.) was oxidised in a similar way, giving the *benzamido*-derivative (6·97 g., 91%), m. p. 196—197°. Recrystallisation from ethanol gave small colourless needles, m. p. 197—198° (Found: C, 68·2; H, 5·3. $C_{20}H_{14}O_4N_2,0{\cdot}33H_2O$ requires C, 68·2; H, 4·2%). Hydrolysis as above gave the amine (4·8 g.), m. p. 160—161° (Ullmann and Mallet, *loc. cit.*, give m. p. 161·5°).

6-*Nitro*-2-*aminobenzophenone*.—Similar treatment of 4-nitro-2 : 3-diphenylindole (7·4 g.) provided the *benzamido*-compound (8·1 g., 97%), m. p. 117—119°, which formed small colourless leaflets, m. p. 123—124°, from ethanol (Found: C, 68·9; H, 4·5. $C_{20}H_{14}O_4N_2,0{\cdot}33H_2O$ requires C, 68·2; H, 4·2%). Hydrolysis of this compound (8·1 g.) in the usual way led to 6-*nitro*-2-*aminobenzophenone*, forming yellow leaflets, m. p. 172—173°, after crystallisation from dilute ethanol (Found: C, 64·1; H, 4·2%). Deamination of this compound as before gave *o*-nitrobenzophenone, m. p. 100—102°, forming on reduction *o*-aminobenzophenone, m. p. 105—106°, alone and mixed with an authentic specimen.

4-Nitro-2-methyl-3-phenylindole (see below) (11·6 g.) in acetic acid (200 c.c.) was oxidised in the usual way with chromic anhydride (8·1 g.) in water (10 c.c.). Worked up as before, the once crystallised product (7·1 g.; m. p. 156—157°) on further crystallisation from alcohol gave colourless hexagonal tablets of 6-*nitro*-2-*acetamidobenzophenone*, m. p. 158—159° (Found: C, 63·2; H, 4·2. $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·3%). Hydrolysis of the compound (0·2 g.) with concentrated hydrochloric acid (2 c.c.), water (2 c.c.), and ethanol (5 c.c.), followed by treatment with aqueous ammonia, gave 6-nitro-2-aminobenzophenone (0·12 g.), identical with that described above.

Bz-*Nitro*-3-*phenyl*-2-*methylindoles*.—Methyl benzyl ketone *o*-nitrophenylhydrazone (6·3 g.) was heated under reflux for 2 hours with acetic and concentrated hydrochloric acids (63 c.c. of each), giving 7-*nitro*-3-*phenyl*-2-*methylindole* (51%), which crystallised from ethanol in small bright orange needles, m. p. 158—159° (Found: C, 71·3; H, 4·8. $C_{15}H_{12}O_2N_2$ requires C, 71·4; H, 4·8%).

Under the conditions used for the 2 : 3-diphenylindoles, benzyl methyl *m*-nitrophenylhydrazone gave 32% (based on *m*-nitroaniline) of mixed indoles. Adsorption of the mixture (5 g.) from benzene (1 l.) on alumina in the usual way led to separation into an upper orange and a lower canary-yellow band. The latter, on elution with benzene, proved to contain 4-*nitro*-3-*phenyl*-2-*methylindole* (3 g.) crystallising from ethanol in orange rhombs, m. p. 247—248° (Found: C, 70·5; H, 4·6. $C_{15}H_{12}O_2N_2$ requires C, 71·4; H, 4·8%). Application of benzene–pyridine (10 : 1) furnished the remaining material, m. p. 181—183°, which appeared to be homogeneous but showed evidence of further resolution on a fresh column. Crystallisation of the crude Fischer product (24 g.) from ethanol (800 c.c.) readily provided 4-nitro-3-phenyl-2-methylindole (11·6 g.), m. p. 243—244°, but the other much more soluble material was heterogeneous. The 4-nitro-compound was oxidised as already described, but similar treatment of the lower-melting fraction gave material which could not be crystallised.

3-*Nitro*-2-*aminobenzophenone*.—7-Nitro-3-phenyl-2-methylindole (1·5 g.) in acetic acid (50 c.c.) was treated with chromic anhydride (1·1 g.) in water (2 c.c.), and set aside overnight. The diluted solution was extracted with chloroform, and the extract washed, dried (Na_2CO_3), and concentrated. The residue (1·9 g.), when crystallised from ethanol, gave 3-*nitro*-2-*acetamidobenzophenone* (1·5 g., 89%), which formed cream-coloured plates, m. p. 174—175° (Found: C, 63·0; H, 3·9%). Hydrolysis of this compound (0·13 g.) for 1 hour at 95°, with concentrated hydrochloric acid (2 c.c.), water (2 c.c.), and alcohol (5 c.c.), followed by basification with aqueous ammonia, gave the *amine* (0·1 g.), crystallising from dilute ethanol in bright yellow leaflets, m. p. 99—100° (Found: C, 65·0; H, 4·0%).

The authors thank the Chemical Society, Imperial Chemical Industries Limited, and the Council of University College, Exeter, for financial aid, and the Department of Scientific and Industrial Research for a maintenance grant to one of them (R. S. T.).

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UNIVERSITY COLLEGE OF THE SOUTH WEST, EXETER. [*Received, March 6th*, 1950.]