621. *Indoles. Part V.* The Fischer Cyclisation of Some* meta-*Substituted Arylhydrazones.*

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New examples of the above reaction have been examined. It is concluded that substituents which, in electrophilic substitution, are *ortho-para*-directing produce a preponderance of 6- over 4-substituted indoles. The reverse is usually true of *meta*-directing groups. The similarity to the Skraup reaction and to common electrophilic substitution is pointed out.

In Parts I [1] and II [2] the paucity of information about the direction of cyclisation of *meta*-substituted arylhydrazones in the Fischer indole synthesis (I ⟶ II + III) was noted. The evidence therein described established the ratios of products (II : III) in the cyclisation of the nitro-compounds (I; $R'' = NO_2$) where $R = R' =$ Me or Ph, and $R =$ Me and $R' =$ Et or Ph. In the present paper we describe further experiments along these lines.

We used arylhydrazones only of ethyl methyl ketone and of deoxybenzoin in order that the same chain of atoms should be involved in ring-closure in each series. We hoped that the boron trifluoride etherate–acetic acid reagent [3] would be widely applicable so that the various cyclisations might have been effected under similar homogeneous conditions. The *para*-substituted arylhydrazones were first cyclised in an attempt to establish

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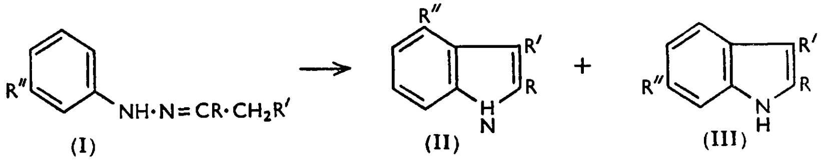
* Part IV, *J.*, 1953, 3440.

[1] Schofield and Theobald, *J.*, 1949, 796.

[2] *Idem, J.*, 1950, 1505.

[3] Snyder and Smith, *J. Amer. Chem. Soc.*, 1943, **65**, 2452.

conditions for use with the *meta*-substituted compound. However, the yield in one series only occasionally paralleled that in the other (see Experimental section).



Ethyl methyl ketone *p*-nitrophenylhydrazone was cyclised by boron trifluoride with only moderate success, but the *meta*-isomer gave a good yield of mixed indoles which were separated chromatographically. Fairly similar yields were obtained with derivatives of deoxybenzoin. Ethyl methyl ketone *p*-chlorophenylhydrazone was also satisfactorily cyclised by boron trifluoride, but from the *meta*-chloro-compound only a fair yield of 6-chloro-2 : 3-dimethylindole was obtained, together with a small quantity of what may have been a geometrical isomer of the original hydrazone (cf. Snyder and Smith [3]). Whilst deoxybenzoin *p*-chlorophenylhydrazone was very efficiently cyclised, the *meta*-chloro-compound gave only a fair yield of 4-chloro-2 : 3-diphenylindole.

High yields of indoles were obtained from ethyl methyl ketone and deoxybenzoin *p*-tolylhydrazones,[4] but in both cases the results with the *meta*-isomers were disappointing, only small yields of 2 : 3 : 6-trimethyl- and 6-methyl-2 : 3-diphenyl-indole being isolated; in each case minor yields of impure oils were obtained which very probably were the alternative isomers; this is especially likely with the cyclisation of deoxybenzoin *m*-tolylhydrazone, for since our experiments Coldham, Lewis, and Plant [5] have demonstrated the formation of both indoles from this compound. It appears from their description that 4-methyl-2 : 3-diphenylindole does not form a stable picrate, the derivative by which we attempted to characterise our product.

Attempts to cyclise ethyl methyl ketone *p*-methoxyphenylhydrazone usually gave intractable tars, but 5-methoxy-2 : 3-dimethylindole was obtained in reasonable yield by stirring *p*-methoxyphenylhydrazine hydrochloride and the ketone with dilute acetic acid.[6] The method was less successful with the *meta*-isomer, about 25% of one of the expected indoles being isolated and the presence of the other demonstrated. Similar results were obtained with deoxybenzoin derivatives.

The identification of the isomeric 4- and 6-substituted indoles formed in these experiments depended on their oxidation to derivatives of *o*-aminoacetophenone. The method failed with the methoxy-compounds, which with ozone gave tars.

The results of cyclisations of *meta*-substituted arylhydrazones examined in this series of papers, and of other relevant examples, are given in the Table annexed.

Clearly, in the Fischer indole synthesis substituents which in electrophilic aromatic substitution are strongly *ortho-para*-directing produce a ratio (II) : (III) (*i.e.*, an *o* : *p* ratio) smaller than unity. This is in line with the probable mechanism [7] of the cyclisation as an intramolecular electrophilic substitution. It would then be expected that a *meta*-directing group in an arylhydrazone (R″ in I) would direct cyclisation predominantly *ortho* to itself (⟶ II), for *meta*-directing groups have been long known to be better described as *meta-ortho*-directing.[8] Branch and Calvin [9] have given a qualitative explanation of this. It will be seen from the Table that in the Fischer synthesis the nitro- and the carboxyl-group do (with two exceptions) produce a ratio (II) : (III) greater than one.

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[4] Ockenden and Schofield, *J.*, 1953, 612.

[5] Coldham, Lewis, and Plant, *J.*, 1954, 4528.

[6] D.R.P. 574,840/1933.

[7] Carlin, *J. Amer. Chem. Soc.*, 1952, **74**, 1077.

[8] Holleman, "Die direkte Einführung von Substituenten in der Benzolkern," Leipzig, 1910; *Chem. Rev.*, 1924, I, 187; *J.*, 1949, 463; Kleene, *J. Amer. Chem. Soc.*, 1949, **71**, 2259; Kobe and Levin, *Ind. Eng. Chem.*, 1950, 352.

[9] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., New York, 1945.

The exceptions are the cyclisations of ethyl methyl ketone and methyl *n*-propyl ketone *m*-nitrophenylhydrazone with hydrochloric acid, which produce a preponderance of the 6-nitroindoles. This might be a steric phenomenon, for the deoxybenzoin derivative behaves normally. However, by cyclising (I; R = R' = Me, R'' = NO_2) with boron trifluoride the usual preponderance of the 4-nitroindole was restored, a reagent effect not previously observed. The electronic influence of R'' in (I) might generally become of secondary importance in cases where R' is a bulky alkyl group. Alternatively, the acidity of the cyclisation medium may be the important factor.[10]

Cyclisation of meta-*substituted phenylhydrazones,* (I) ⟶ (II) + (III).

Hydrazone (I)			Ratio (II) : (III)			
R	R'	R''	HCl or AcOH–HCl	BF_3–AcOH	$ZnCl_2$	Others
Me	Me	NO_2	0·6	1·3		
,,	,,	Me		Only (III)		Only (III)
,,	,,	Cl		,,	Only (III)	
Ph	Ph	NO_2	2·0	2·0		
,,	,,	Me		?	*ca.* 0·4 [f]	
,,	,,	Cl		Only (II)	Only (II)	
–$[CH_2]_4$–		NO_2				1·0 [a]
,,		CO_2H				2·7 [b]
–$[CH_2]_3$–		NO_2				3·0 [c]
CO_2H	$CH_2\cdot CO_2H$	OMe				Only (III) [d]
Ph	H	Me		Only (III)		
CO_2Et	$CH_2\cdot CO_2Et$	CO_2Et				1·5 [e]
Me	Ph	NO_2	Only (II)			
,,	Et	,,	0·3			

[a] Barclay and Campbell, *J.*, 1945, 530. [b] Moggridge and Plant, *J.*, 1937, 1125. [c] Plant and Whitaker, *J.*, 1940, 283. [d] Kermack, Perkin, and Robinson, *J.*, 1921, 1602. [e] Koelsch, *J. Org. Chem.*, 1943, **8**, 295. [f] See ref. 5.

With the data available it seems that the Fischer synthesis shows the same general characteristics as those previously observed for the Skraup reaction,[11] and, to a more limited extent, the Doebner–Miller and Conrad–Limpach cyclisation.[12] In the Skraup reaction the relatively weakly *ortho-para*-directing halogen groups produce mixtures of 5- and 7-substituted quinolines, the latter predominating. In the Fischer synthesis halogen substituents can lead to either 4- or 6-substituted indoles.

EXPERIMENTAL

Cyclisations with the boron trifluoride–ether complex were effected by refluxing the reactants for 3 hr., filtering the hot solution, washing the boron trifluoride–ammonia complex with hot acetic acid, and evaporating the filtrate.

Some of the compounds gave bad analyses, probably owing to instability.

Arylhydrazones.—Except where stated, these were obtained by heating the respective ketone and arylhydrazine together in equivalent amounts at 95° for 1 hr. The products were dried (Na_2SO_4) in ether, and after removal of the solvent were used immediately.

2 : 3-*Dimethyl*-5-*nitroindole.*—Ethyl methyl ketone *p*-nitrophenylhydrazone (1·0 g.), glacial acetic acid (10 c.c.), and boron trifluoride–ether complex (0·69 g.) gave the desired material (0·46 g., 50%; m. p. 183—185°). Longer reaction times and excess of the reactant did not improve the yield.

2 : 3-*Dimethyl*-4- *and* -6-*nitroindole.*—A mixture of 4- and 6-nitro-2 : 3-dimethylindole (73%) was obtained from the *m*-nitrophenylhydrazone (10 g.), acetic acid (100 c.c.), and boron trifluoride–ether (6·9 g., 1 equiv.). A filtered solution of the crude residue (7·4 g.) in benzene

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[10] Hammond, Modic, and Hedges, *J. Amer. Chem. Soc.*, 1953, **75**, 1388.

[11] Bradford, Elliott, and Rowe, *J.*, 1947, 437.

[12] Spivey and Curd, *J.*, 1949, 2656.

(350 c.c.) was adsorbed on alumina (60 cm. × 3·5 cm.), and the adsorbate developed with benzene until separation into a lower, orange band and an upper, red band occurred. Elution with benzene gave pure red prisms of 2 : 3-dimethyl-4-nitroindole (3·76 g.; m. p. 171—173°), while washing out the upper layer with benzene–pyridine (10 : 1) gave pure 2 : 3-dimethyl-6-nitroindole (2·94 g.; m. p. 139—141°). The intermediate fraction was negliglble.

Bz-*Nitro*-2 : 3-*diphenylindoles*.—Deoxybenzoin *m*-, m. p. 155—157° (77%), and *p*-nitrophenylhydrazone, m. p. 158—160° (73%), were obtained by heating the ketone and corresponding hydrazine in equivalent amounts at 135° for ¾ hr. and recrystallising the products from alcohol.

5-*Nitro*-2 : 3-*diphenylindole*.—Deoxybenzoin *p*-nitrophenylhydrazone (1·0 g.), acetic acid (10 c.c.), and boron trifluoride–ether (0·43 g.) gave the indole (0·47 g., 50%; m. p. 198—200°). Longer reaction times and excess of the reagent did not improve the yield.

4- *and* 6-*Nitro*-2 : 3-*diphenylindole*.—A mixture of 4- and 6-nitro-2 : 3-diphenylindole (60%) was obtained from deoxybenzoin *m*-nitrophenylhydrazone (10 g.), acetic acid (100 c.c.), and the boron trifluoride reagent (4·3 g.). A filtered solution of the crude mixture (7·7 g.) in benzene (350 c.c.) was chromatographed as before. The lower orange band was eluted with benzene (3·86 g.; m. p. 198—203°), and the upper red layer washed out with acetone–benzene (1 : 1) (2·28 g., m. p. 190—200°; and 0·97 g., m. p. 140—165°). The intermediate fraction was negligible. The first fraction crystallised from benzene, giving orange plates of 4-nitro-2 : 3-diphenylindole (3·2 g.; m. p. 203—205°). The second fraction crystallised from ethanol, and gave dark brown plates of 6-nitro-2 : 3-diphenylindole (1·93 g.; m. p. 225—227°). The mother-liquors were evaporated, and the residue dissolved in benzene and readsorbed on alumina (40 × 2 cm.). Working up as before gave 4-nitro-2 : 3-diphenylindole (0·54 g.; m. p. 200—203°) and very crude 6-nitro-2 : 3-diphenylindole (0·31 g.; m. p. 140—160°).

5-*Chloro*-2 : 3-*dimethylindole*.—(*a*) Ethyl methyl ketone *p*-chlorophenylhydrazone (0·77 g.) was treated gradually with powdered anhydrous zinc chloride (1·5 g.), and the mixture was heated gently until a moderate reaction set in. After 5 min. the mixture solidified, and the product was then extracted with ether. Concentration of the dried extract and addition of light petroleum (b. p. 40—60°) gave the substantially pure indole (0·36 g., 52%; m. p. 139—141°). 5-*Chloro*-2 : 3-*dimethylindole* formed white, glistening plates, m. p. 141—142° (Found : C, 67·0; H, 5·7. $C_{10}H_{10}NCl$ requires C, 66·8; H, 5·6%), from the same solvent.

(*b*) The hydrazone (0·83 g.), acetic acid (85 c.c.), and boron trifluoride–ether (0·65 g.) gave a sticky product which crystallised from ether–light petroleum (charcoal), providing the indole (0·50 g., 65%; m. p. 138—140°).

6-*Chloro*-2 : 3-*dimethylindole*.—The crude product from ethyl methyl ketone *m*-chlorophenylhydrazone (1·71 g.), acetic acid (20 c.c.), and boron trifluoride–ether (1·33 g.) was passed in benzene over an alumina column (50 × 2·5 cm.). Apart from small amounts of intractable oils, only one product (0·89 g. of sticky solid) was isolated. Crystallisation of this from ether–light petroleum furnished the indole (0·52 g.; m. p. 164—166°). 6-*Chloro*-2 : 3-*dimethylindole* formed white leaflets, m. p. 166—167° (Found : C, 66·2; H, 5·7%).

Further elution of the column provided a small amount (0·10 g.) of a sticky product which on crystallisation from dilute alcohol furnished brown needles of a *substance*, m. p. 222—224° (Found : C, 61·8; H, 5·4. $C_{10}H_{13}N_2Cl$ requires C, 61·0; H, 5·3%).

On ozonisation in ethyl acetate and in acetic acid, 6-chloro-2 : 3-dimethylindole gave 43% and 47% respectively of 2-acetamido-4-chloroacetophenone, m. p. 150—152°, alone and mixed with authentic material.[13]

5-*Chloro*-2 : 3-*diphenylindole*.—The product from deoxybenzoin *p*-chlorophenylhydrazone (1·5 g.), acetic acid (15 c.c.), and boron trifluoride–ether (0·7 g.) gave the almost pure indole (1·27 g., 90%; m. p. 128—130°) when crystallised from ethanol. 5-*Chloro*-2 : 3-*diphenylindole* separated as fawn prisms, m. p. 130—131° (Found : C, 78·4; H, 4·8. $C_{20}H_{14}NCl$ requires C, 79·1; H, 4·6%), from this solvent.

4-*Chloro*-2 : 3-*diphenylindole*.—(i) The benzene solution of the crude product from deoxybenzoin *m*-chlorophenylhydrazone (2·2 g.), acetic acid (20 c.c.), and boron trifluoride–ether (1·0 g.) when passed through alumina (50 × 2·5 cm.) gave two main fractions (0·84 and 0·35 g., oily solids). Two crystallisations of each fraction from ether–light petroleum furnished the same product (0·78 g. total, 37%; m. p. 165—167°). 4-*Chloro*-2 : 3-*diphenylindole* formed

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[13] Atkinson and Simpson, *J.*, 1947, 232.

white plates, m. p. 168—170° (Found : C, 78·4; H, 4·8%). No other crystalline product could be isolated.

(ii) The hydrazone (1·0 g.) and powdered anhydrous zinc chloride (2·0 g.) were warmed gently until reaction started. After 20 min. the cool mixture was extracted with benzene. Resolution of the concentrated solution as above provided a sticky main product (0·5 g.), which on crystallisation from ether–light petroleum (b. p. 40—60°) furnished the same product (0·21 g.; m. p. 165—169°) in 22% yield.

2 : 3 : 6-*Trimethylindole*.—(*a*) The reaction solution from ethyl methyl ketone *m*-tolylhydrazone (7·0 g.), boron trifluoride–ether (6·0 g., 1·1 mol.), and acetic acid (70 c.c.) was concentrated, basified with ammonia solution, and extracted with benzene. The dried (Na_2SO_4) solution was concentrated and passed over alumina (60 × 3·5 cm.). Development with benzene showed one very light brown band which was eluted with benzene, giving an oily solid (5·0 g.). Further elution with benzene gave a small yield of a further dark oil (1·95 g.). The major product was distilled, yielding a sticky solid (4·0 g., 63%; b. p. 170—180°/9 mm.). Several crystallisations from aqueous alcohol gave plates of 2 : 3 : 6-trimethylindole, m. p. 117—118° (Found : C, 81·8; H, 8·1. Calc. for $C_{11}H_{13}N$: C, 82·9; H, 8·2%). The picrate, formed in alcohol, crystallised in dark red-brown needles (Found : C, 52·7; H, 3·9. Calc. for $C_{11}H_{13}N,C_6H_3O_7N_3$: C, 52·6; H, 4·15%), m. p. 153—155°, from aqueous methanol.

The second fraction from the column was also distilled (1·5 g.; b. p. 170—180°/9 mm.) but treatment of this product with picric acid gave only amorphous black solids.

(*b*) *m*-Tolylhydrazine hydrochloride (2·86 g.), ethyl methyl ketone (1·36 g.), and 10% acetic acid (50 c.c.) were stirred rapidly at 95° for 2 hr. On cooling, the solid was collected and crystallised twice from aqueous alcohol, yielding 2 : 3 : 6-trimethylindole (0·51 g., 18%; m. p. 115—118°).

Proof of the structure of this compound has already been given.[4]

5-*Methyl*-2 : 3-*diphenylindole*.—The crude product from deoxybenzoin *p*-tolylhydrazone (5 g.), boron trifluoride–ether (2·36 g., 1·1 mol.), and acetic acid (50 c.c.) crystallised from aqueous alcohol, yielding white needles (3·85 g., 82%), m. p. 148—150°.

By heating the hydrazone (5 g.) with concentrated hydrochloric acid (50 c.c.) at 95° for 4 hr., and crystallising the product from aqueous alcohol, the same compound (3·40 g., 73%; m. p. 149—150°) was obtained. 5-Methyl-2 : 3-diphenylindole crystallised from aqueous alcohol, in which it exhibits a deep blue fluorescence, in opaque needles, m. p. 150—151° (Found : C, 90·2; H, 6·5. Calc. for $C_{21}H_{17}N$: C, 89·0; H, 6·1%).

6-*Methyl*-2 : 3-*diphenylindole*.—The hot solution from deoxybenzoin *m*-tolylhydrazone (8·0 g.), acetic acid (80 c.c.), and boron trifluoride–ether (3·8 g., 1·05 mol.) was filtered and concentrated. Last traces of acetic acid were removed *in vacuo*, giving a dark oil (7·0 g.). This, in benzene (300 c.c.), was passed over alumina (60 × 3 cm.). Development with benzene yielded two very pale green bands, the lower of which was eluted with benzene, giving a light brown oil (4·19 g.). Further, prolonged elution with benzene gave a small yield of another, dark oil (0·88 g.). The major product was distilled, yielding a yellow oil (2·3 g., 31%; b. p. 240—260°/7 mm.) which set to a yellow glass, m. p. 70—80°. With picric acid in ethanol this gave a picrate (m. p. 155—165°) which separated from alcohol in red-brown needles, m. p. 167—169° (Found : C, 63·0; H, 4·6. Calc. for $C_{21}H_{17}N,C_6H_3O_7N_3$: C, 63·3; H, 3·9%), alone and mixed with a specimen prepared as described below or with a specimen of 6-methyl-2 : 3-diphenylindole picrate.[14] The minor fraction, probably crude 4-methyl-2 : 3-diphenylindole, gave no picrate.

Treatment of the hydrazone (2·0 g.) with acetic acid (40 c.c.) and hydrochloric acid (30 c.c.) under reflux for 3 hr., with subsequent basification and ether-extraction, likewise gave an oil (1·8 g.). Purification as above gave a major product (0·9 g.) and a minor one (0·27 g.). With picric acid the former gave the picrate (0·7 g.; m. p. 162—164°) corresponding to a yield of 21% of 6-methyl-2 : 3-diphenylindole. The second fraction, as before, gave no derivative.

5-*Methoxy*-2 : 3-*dimethylindole*.—When ethyl methyl ketone *p*-methoxyphenylhydrazone (2·15 g.), boron trifluoride–ether (1·8 g.), and acetic acid (22 c.c.) were refluxed 3 hr. no ammonia–boron trifluoride complex separated. The solvent was removed and the dark sticky solid crystallised from ether–light petroleum (b. p. 40—60°). The *product* which crystallised in fawn plates, m. p. 127—128° (Found : C, 65·8; H, 6·8%), from the same solvent, was probably a boron trifluoride complex.

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[14] Ritchie, *J. Proc. Roy. Soc. New South Wales*, 1946, **80**, 33.

p-Methoxyphenylhydrazine hydrochloride (8·5 g.), ethyl methyl ketone (3·6 g.), and 10% acetic acid (70 c.c.) were stirred at 95° for 2 hr. The solid which separated on cooling was crystallised from alcohol (5·3 g., 60%; m. p. 108—110°). The reported [6] m. p. is 114—115°.

6- *and* 4-*Methoxy*-2 : 3-*dimethylindole*.—*m*-Methoxyphenylhydrazine hydrochloride (2·1 g.), ethyl methyl ketone (0·9 g.), and 10% acetic acid (20 c.c.) were stirred rapidly at 95° for 2 hr. The solid (1·09 g.; m. p. 95—110°) which separated on cooling was crystallised twice from benzene–light petroleum (b. p. 60—80°), giving the main product (0·51 g.; m. p. 136—138°) in 25% yield. Impure 6(or 4)-*methoxy*-2 : 3-*dimethylindole* separated in white flakes, m. p. 137—138° (Found: C, 73·9; H, 7·3. $C_{11}H_{13}ON$ requires C, 75·5; H, 7·5%). The action of ozone on this compound gave a dark uncrystallisable oil. The picrate, formed in ethanol, had m. p. 131—132°.

Treatment of the crystallisation mother–liquors from the above indole with picric acid (0·6 g.) in benzene gave, on concentration, a second picrate (0·2 g.; m. p. 162—165°). Several recrystallisations from methanol provided 4(or 6)-*methoxy*-2 : 3-*dimethylindole picrate*, m. p. 162—165° (Found: C, 50·6; H, 4·2. $C_{11}H_{13}ON,C_6H_3O_7N_3$ requires C, 50·5; H, 4·0%), as small, dark brown needles.

5-*Methoxy*-2 : 3-*diphenylindole*.—As above, the reaction between deoxybenzoin *p*-methoxyphenylhydrazone (3·45 g.), boron trifluoride–ether (1·73 g.), and acetic acid (35 c.c.) produced no ammonia–boron trifluoride. The solvent was removed and the resulting dark oil (2·95 g.) was taken up in benzene. After addition of light petroleum (b. p. 60—80°), the slightly cloudy solution slowly deposited a yellow crystalline *product* (0·2 g.; m. p. 117—120°). Several crystallisations from benzene–light petroleum (b. p. 60—80°) raised the m. p. to 122—124° (Found: C, 80·3; H, 5·5%).

The same hydrazone (1·0 g.), alcohol (20 c.c.), and concentrated hydrochloric acid (20 c.c.) were refluxed for 4 hr. After most of the solvent had been removed, the solution was poured into a large volume of water which was extracted with ether, dried (Na_2SO_4), and concentrated. Crystallisation of the crude oily product twice from benzene–light petroleum (b. p. 60—80°) gave satisfactory material (0·2 g.; m. p. 150—154°, 21%). 5-*Methoxy*-2 : 3-*diphenylindole* separated from benzene–light petroleum (b. p. 60—80°), in which it showed a very intense blue fluorescence, as small crystals, m. p. 155—156° (Found: C, 83·8; H, 5·6. $C_{21}H_{17}ON$ requires C, 84·2; H, 5·7%).

m-Methoxyphenylhydrazine hydrochloride (5·0 g.), deoxybenzoin (5·5 g.), and 10% acetic acid (50 c.c.) were stirred at 95° for 3 hr. The sticky solid which separated on cooling crystallised from benzene–light petroleum (b. p. 60—80°), giving the indole (1·1 g., 13%; m. p. 155—158°).

6(or 4)-*Methoxy*-2 : 3-*diphenylindole*.—Deoxybenzoin *m*-methoxyphenylhydrazone (0·89 g.), alcohol (10 c.c.), and concentrated hydrochloric acid (10 c.c.) were refluxed for 3 hr. The solvent was removed, the solution was basified with ammonia, and the product extracted with benzene. The dried (Na_2SO_4) benzene extract was concentrated, light petroleum (b. p. 60—80°) added, and the crude indole (0·35 g.; m. p. 196—200°) collected. One more crystallisation gave satisfactory material (0·27 g., 32%; m. p. 204—207°). 6(or 4)-*Methoxy*-2 : 3-*diphenylindole*, crystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 206—207° (Found: C, 84·2; H, 5·9. $C_{21}H_{17}ON$ requires C, 84·2; H, 5·7%).

The product from a larger-scale (10 g. of hydrazone) experiment was subjected to chromatography on alumina. Only one, pale grey band could be seen and only one product isolated. Crystallisation provided the same indole, m. p. 204—207°, in the same yield. Ozonolysis again gave a tar.

The authors are indebted to Exeter University and to Imperial Chemical Industries Limited for financial aid, and to the D.S.I.R. for a maintenance grant (to D. W. O.).

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[*Received, March 6th*, 1957.]